

12th Conference on Broadband Dielectric Spectroscopy and its Applications

BDS2024

Book of Abstracts



01 – 06 September 2024

Lisbon, Portugal

under the auspices of the International Dielectric Society



CONFERENCE CHAIRS:

Natália Correia (Université de Lille) & Madalena Dionísio (FCT-NOVA)

LOCAL COMMITTEE:

María Teresa Viciosa & Hermínio Diogo from (IST-Universidade de Lisboa), Andreia F. M. Santos & Maria do Carmo Lança (FCT-NOVA)

ORGANIZING ACADEMIC COMMITTEE:

Madalena Dionísio, Maria do Carmo Lança, Carlos J. Dias, Andreia F. M. Santos (FCT-NOVA)

María Teresa Viciosa, Hermínio Diogo, Joaquim Moura Ramos (IST-Universidade de Lisboa)

Sílvia Soreto, Manuel Pedro Graça, Luís Cadillon (Universidade de Aveiro)

Henrique Leonel Gomes (Universidade de Coimbra)

Natália Correia (Université de Lille)

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WELCOME TO BDS2024:

Dear Participants,

The BDS2024 Organizing Committee welcomes you warmly!

On organizing the 12th Conference on Broadband Dielectric Spectroscopy and its Applications (BDS2024), which is being held for the first time in Lisbon, Portugal, our first wish is for you to feel at home. Indeed, the typical hospitality of the Portuguese people is illustrated by the main symbol of BDS2024, the Tagus Bridge. It represents an open road between our country and all those who visit us, the link between research groups within and between countries.

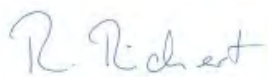
The bridge also symbolizes the link between the past, recalling the first bridge-based dielectric instruments, and the future. Since the pioneering work of theoreticians and experimentalists, probably the greatest advance in dielectric spectroscopy has been at the technological level. Today, combined methods and instruments, covering up to 18 decades of frequency, make it possible to explore a variety of time scales. In addition to molecular dynamics, charge transport and interfacial phenomena, confinement and non-linear effects, time-dependent events such as chemical reactions, molecular interconversion, phase transformations and physical ageing can be monitored by dielectric techniques. The large number of applications in the fields of science and technology, from pharmacy and biology to energy and environment, involve investigating a variety of materials, which embraces molecular and macromolecular compounds, plastic crystals, ionic liquids, (ionic) liquid crystals, eutectic systems, including emerging functional materials like self-healing/recyclable dynamic networks. All these applications and materials fall within the diverse topics of the BDS2024 conference, also covering other related techniques.

The bridge is also the common symbol of all the cities whose universities have joined their efforts to organize this BDS conference, namely Almada with the NOVA Faculty of Science and Technology on the south side of the Tagus, and Lisbon with the NOVA Rectorate and the University of Lisbon on the north side, and the cities of Aveiro (Aveiro University) and Coimbra (Coimbra University) whose bridges connect the banks of the Vouga and Mondego rivers, respectively.

Our commitment to the International Dielectric Society Board was to add new protagonists to the Invited Speakers panel, to regain links with the British community and to incentivize young people participation, and these objectives were successfully achieved.

In addition to the expected and desirable success of the lectures and scientific discussions boosting the transfer of knowledge and technological progress, may this conference also be a privileged opportunity for you to get to know one of Europe's most beautiful coastal capitals. May the geography, culture and history of Lisbon, the walks, the hills, the gardens, the river and the proximity to the sea, the flavors, colors and smells and, above all, its people, make your visit an unforgettable experience. Welcome to BDS2024!

In the end, we also hope to build a bridge between BDS2024 and BDS2026, where we can all meet again!

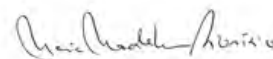


Ranko Richert
President of

The International Dielectric Society



Natália Correia



Maria Madalena Dionísio

Chairs of BDS2024

ACKNOWLEDGMENTS:

The Organizing Committee would like to thank all the sponsors and exhibitors for their support of the BDS2024 conference, including the young talks and poster prizes that motivate the participation of young researchers, one of the main goals of BDS conferences. The Organizing Committee would also like to thank the International Dielectric Society, under whose auspices the BDS conferences are organized, for its invaluable support in the person of its President, Ranko Richert, and its Secretary, Simone Napolitano. Finally, and above all, we would like to thank all the participants for their excellent contributions, which have given the BDS2024 conference an impressive scientific quality.

DEDICATION:

Several members of the Organizing Committee of the 12th Conference on Broadband Dielectric Spectroscopy and its Applications (María Teresa Viciosa, Hermínio Diogo, Natália Correia and Madalena Dionísio) dedicate BDS2024 to Professor **Joaquim J. MOURA RAMOS** (Instituto Superior Técnico, Universidade de Lisboa, Portugal) and Professor **Graham WILLIAMS** (Aberistwith and Swansea University, UK) for the excellence of their work, for making us dielectric fans, for their leadership skills and human values.

Thank you, Graham, and thank you Joaquim!



EXHIBITORS AND SPONSORS:



AWARDS:

- **Debye Prize** for Young Investigators for Excellence in Dielectric Research awarded by the **International Dielectric Society**. The prize committee was composed by the Chair, Silvina Cervený (Centro de Física de Materiales, CSIC, UPV/EHU, Spain), Zaneta Wojnarowska (University of Silesia, Poland) and Catalin Gainaru (Oak Ridge National Lab., USA).

The **winner** was **Dr. Stavros Drakopoulos** (PMI, Princeton University, USA).

- The **TWO best young** talks were awarded with two prizes by **MDPI**.

The **jury** was composed by the President, Friedrich Kremer (University of Leipzig, Germany) and Emeline Dudognon (University of Lille, France), Koji Fukao (Ritsumeikan, University, Japan), Marian Paluch (University of Silesia, Poland) and Shiwang Cheng (Michigan State, USA).

The **winners** were **Elisa Steinrücken** (TU Darmstadt, Institute for Condensed Matter Physics, Germany) and **Panagiotis Kardasis** (University of Ioannina, Greece).

- The **THREE best posters** were awarded with prizes by **i3N** (2 prizes) and **Crystals** from MDPI (1 prize); **Crystals** from MDPI also awarded the **best videoposter**.

The **jury** was composed by the President, Alexei Sokolov (University of Tennessee, USA) and Ana Šantić (Ruđer Bošković Institute, Croatia), Aurora Nogales (Instituto de Estructura de la Materia, CSIC, Spain), Jeppe Dyre (Roskilde University, Denmark) and Paulina Szymoniak (BAM, Berlin, Germany).

The **THREE best posters winners** were: **Andreia F. M. Santos** (NOVA Faculty of Science and Technology, Portugal), **Ioannis Tzourtzouklis** (University of Ioannina, Greece) and **Martin Tress** (Leipzig University, Germany); the best videoposter **winner** was: **Panagiotis Kardasis** (University of Ioannina, Greece).

- **7 honorable mentions** were awarded by **Springer** that offered printed volumes published in Springer *Advances in Dielectrics* series. The **awarded with honorable mentions** of

the **young talks** were: **Kaylie Glynn** (The Ohio State University, USA), **Kosei Kawai** (The University of Tokyo, Japan) and **Rolf Zeißler** (Institute for Condensed Matter Physics, Germany);

the **posters** were: **Achilleas Pipertzis** (Chalmers University of Technology, Sweden), **Alfred Błażytko** (University of Silesia, Poland), **Erik Thoms** (Arizona State University, USA) and **Yun Dong** (Max Planck Institute for Polymer Research, Germany).



SPECIAL ISSUES:

- **MDPI Topic** in sync with the conference entitled "Broadband Dielectric Spectroscopy Fundamentals and Applications" is now open. Participants in the 12th Conference on Broadband Dielectric Spectroscopy and its Applications (BDS2024) as well as their collaborators are invited to submit their work to this Topic.



Topic

**Broadband Dielectric Spectroscopy
Fundamentals and Applications**

Topic Editors
Dr. Natália T. Correia, Dr. Teresa Viciosa, Dr. Hermínio P. Diogo

Deadlines
Abstract Submission: 31 October 2024; Manuscript Submission: 30 April 2025

Participating Journals:       Applied Sciences, Ceramics, Crystals, Membranes, Nanomaterials, Polymers

- **Special Issue** “Advanced Research of Electroceramics for Energy Conversion, Storage and Devices” that aims to address all the relevant aspects of advanced electroceramics for energy conversion, storage and devices, attending also to the different processing and characterization techniques.



 **crystals**

Advanced Research of Electroceramics for Energy Conversion, Storage and Devices

Guest Editor Team

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University of Coimbra,
Portugal

 Dr. Luis Cadillon Costa
University of Aveiro,
Portugal

 Dr. Manuel Pedro
Fernandes Graça
University of Aveiro, Portugal

 Dr. Silvia Soreto Teixeira
University of Aveiro,
Portugal

Keywords

- electroceramics
- synthesis processes
- structural characterization
- morphological characterization
- dielectric properties
- magnetic properties
- piezoelectric properties
- energy conversion
- energy storage

SCAN ME



Welcome for submission: 20 December 2024

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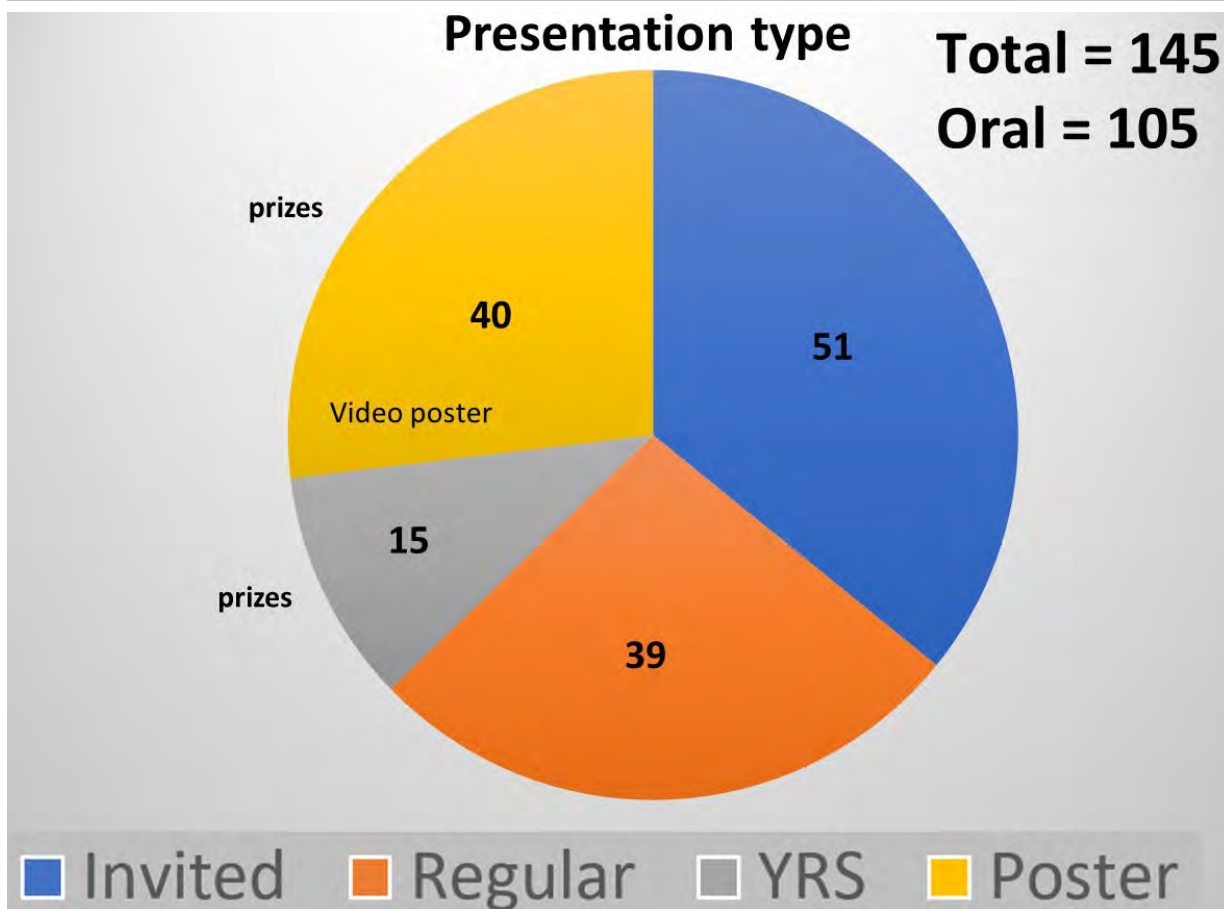
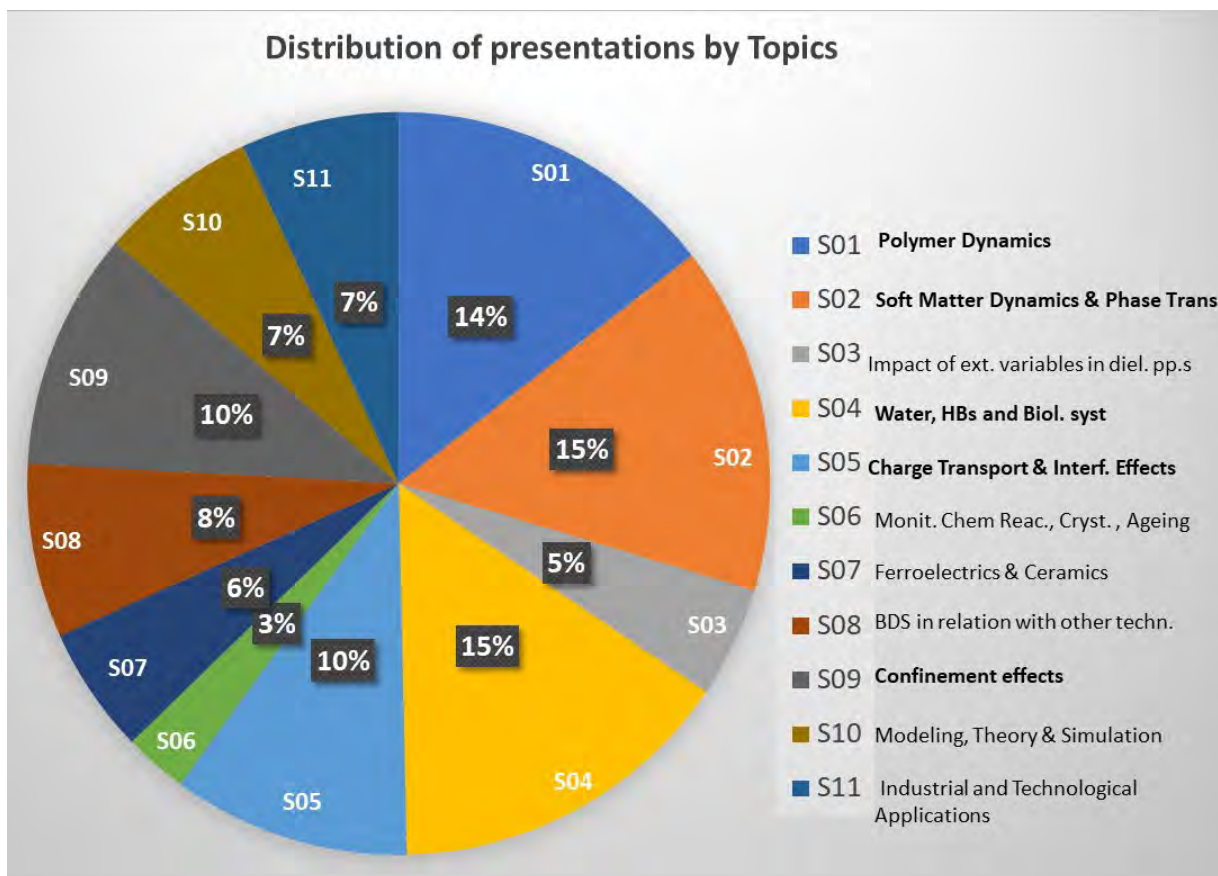
Crystals Editorial Office
MDPI AG
St. Alban-Anlage 66
4052 Basel, Switzerland

Tel: +41 61 683 77 34
Fax: +41 61 302 89 18
www.mdpi.com
crystals@mdpi.com

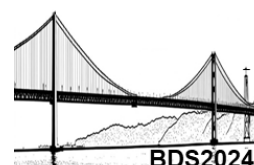
Participants in the 12th Conference on Broadband Dielectric Spectroscopy and its Applications (BDS2024) as well as their collaborators are also invited to submit their work to this Special issue.

BDS2024 BY NUMBERS:





BDS2024 BY PICTURES:



YOUNG RESEARCHER AWARD AND DEBYE PRIZE WINNERS



GROUP PHOTO



PROGRAM



TIMETABLE

ISC = Invited Speaker Communication OC = Oral Communication YRS = Young Researcher Session		20 min talk (questions included) 15 min talk (questions included) 10 min talk (questions included)	
Sunday	Monday	Tuesday	Wednesday
	Chair (A. Schönhals)	S02 Soft matter dynamics A (Chair M. Paluch)	S04- Water, H-bond, Biol A (Chair Y. Feldman)
08:30	Tutorial 1 The glass transition: linear vs non-linear perspective Daniele Cangialosi	IC13-502 Alois Loidl	IS24-504 Shinya Cerverny
08:35			Unravelling the Glass Transition of Confined Water: A Calorimetric and Dielectric study
08:40			OC19-504 Yang Yao
08:45			Water state in lipidic mesophase during phase transition
08:50			OC29-504 Hiroaki Matsura
08:55		Non linear responses in a family of oligomers: inspecting the possible influence of the length of the molecules	Slow dynamics of intracellular water measured by BDS
09:00		OC5-502 Altor Erkoreka	OC4-502 Caroline Raappert
09:05		An interpretation of the dielectric spectra of polar nematic phases	OC29-504 Hiroaki Matsura
09:10		OC14-502 Emeline Dudaupion	OC29-504 Hiroaki Matsura
09:15		Amorphous solid dispersions of Terfenolite into PVP: insights from the molecular mobility characterisation	Slow dynamics of intracellular water measured by BDS
09:20		OC6-502 Federico Caporaletti	OC29-504 Hiroaki Matsura
09:25		The slow Arrhenius process: a simple solution to multiple problems in glass relaxation	OC29-504 Hiroaki Matsura
09:30		OC7-502 Marzena Rams-Baron	OC29-504 Hiroaki Matsura
09:35		Image of the internal solid-state rotation in the dielectric response of stable molecules with polar rotors	OC29-504 Hiroaki Matsura
09:40		IC15-502 Michela Romani	OC29-504 Hiroaki Matsura
09:45		Multiple relaxations in orientationally disordered benzene derivatives with strongly restricted rotational dynamics	OC29-504 Hiroaki Matsura
09:50		OC7-502 Marzena Rams-Baron	OC29-504 Hiroaki Matsura
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19:00		OC7-502 Marzena Rams-Baron	OC29-504 Hiroaki Matsura

ORAL CONTRIBUTIONS

GENERAL INDEX – ORAL COMMUNICATIONS:

• S01 Polymer Dynamics

Invited Communications:

Alexei Sokolov

“Energy Barrier for Structural Relaxation, Molecular and Ion Transport in Polymers: a Revised Approach”

Ana R. Brás Wüschig

“Structure and Dynamics of Supramolecular poly(alkyl ether)-based Polymers: insight with DS combined with Neutron Scattering and Rheology”

Aurora Nogales

“Dielectric Spectroscopy on vitrimers based on transesterification reactions”

José Luis Gomez Ribelles

“Crystallization and dielectric properties of PVDF-ionic liquid blends”

Koji Fukao

“Slow dynamics above and below glass transition for some polymer systems”

Laurent Delbreilh

“Interest of pressure controlled dielectric spectroscopy to probe the interdependence between fragility and cooperativity for polymeric segmental relaxation”

Michael Wübbenhorst

“Glass Transition Effects in a Thermo-reversible Network”

Mustapha Raihane

“Bionanocomposites based on biodegradable polyesters and clays prepared by *in-situ* polymerization: structures, characterizations, and dielectric properties”

Paulina Szymoniak

“Vitrimer – Rethinking Epoxies Towards Recyclable and Reusable Thermosets”

Ralph H. Colby

“Anhydrous Proton Conduction in Polymers Containing Azoles and Phosphonic Acids”

Senentxu Lanceros-Mendez

“Broadband dielectric spectroscopy for advancing understanding and applicability of poly(vinylidene fluoride)/ionic liquid blends as sensor, actuators and energy storage systems”

Simone Simon Napolitano

“The dielectric response of the slow Arrhenius process (SAP)”

Regular Communications:

Jiaxin Zhao

“Chain-length-dependent relaxation dynamics in poly(methyl acrylate)”

Morgan Lecoublet

“Dielectric and viscoelastic properties of 3D-printed cellulose based bionanocomposites for electrical insulation application”

Stavros X. Drakopoulos

“Segmental Relaxation of Polystyrene Modified with Pyrene Molecules”

- **S02 Soft Matter Dynamics and Phase Transitions in Amorphous, Partially Ordered and Ordered Systems**

Invited Communications:

Alois Loidl

“Critical behavior and phase transitions in supercooled liquids and glasses”

Ana Santic

“Ionic transport in supramolecular ionic liquid gels prepared with bis(amino alcohol)oxamides as gelators”

Christiane Alba-Simionesco

“Glass Transition and Crystallisation of n-Butanol by simultaneous Dielectric Spectroscopy and Neutron Diffraction”

Emeline Dudognon

“Amorphous solid dispersions of Terfenadine into PVP: insights from the molecular mobility characterisation”

Marian Paluch

“Reorientational Dynamics of Sizable Glass-Formers - Broadband Dielectric Spectroscopy Studies”

Michela Romanini

“Multiple relaxations in orientationally disordered benzene derivatives with strongly restricted rotational dynamics”

Roberto Macovez

“Relaxation dynamics of amorphous molecular pharmaceuticals and of their binary mixtures near the eutectic composition”

Regular Communications:

Aitor Erkoreka

“An interpretation of the dielectric spectra of polar nematic phases”

Caroline Raepsaet

“Non linear responses in a family of oligomers: inspecting the possible influence of the length of the molecules”

Federico Caporaletti

“The slow Arrhenius process: a simple solution to multiple problems in glass equilibration”

Kinga Łucak

“Molecular dynamics of halogen monoalcohols at different thermodynamic conditions”

Marzena Rams-Baron

“Image of the internal solid-state rotation in the dielectric response of sizable molecules with polar rotors”

Thulasinath Raman Venkatesan

“Self-assembly in bottlebrush polymers detected using dielectric spectroscopy”

- **S03 The Impact of External Variables in Dielectric Properties**

Invited Communications:

Paul Ben Ishai

“Organic Magnetoresistance – a test bed for Dielectric-Spin interactions”

Ranko Richert

“Dielectric Spectroscopy of Vapor Deposited Films”

Shiwang Cheng

“Dynamics of monohydroxy alcohols: Rouse dynamics, chain swapping, and the Debye relaxation”

Regular Communications:

Francois Ladieu

“Optical manipulation of chromophores in a molecular glass former: from photofluidization to random pinning”

- **S04 Water, Hydrogen Bonded and Biological Systems**

Invited Communications:

Apostolos Kyritsis

“Water organization in amphiphilic block copolymers with thermoresponsive behaviour”

Henrique Leonel Gomes

“Sensing devices that use electrical double-layers and impedance spectroscopy: design strategies”

Michael Vogel

“Dynamics of Ice in Nanoconfinements and Mixtures: Combined BDS and NMR Studies”

Silvina Cerveny

“Unravelling the Glass Transition of Confined Water: A Calorimetric and Dielectric study”

Syed A. M. Tofail

“Is Nanoconfined Water Electrically ‘Dead’ or ‘Alive’”

Yasuaki Monnai

“Exploring Non-Contact Ultrasound Technology via Sub-Terahertz Photoacoustics for Human-Oriented Applications”

Yuri Feldman

“Duped or Doped? Utilizing Microwave Spectroscopy for Autologous Blood Doping Detection”

Regular Communications:

Hiroaki Matsuura

“Slow dynamics of intracellular water measured by BDS with Kramers-Kronig relations and Bruggeman–Hanai equation”

Jacob Gerasimov

“Perturbing the Dynamic Structure of Water by Ion Solvation”

Keisuke Tominaga

“Dynamics of Hydrated Soft Matters Studied by Broadband Dielectric Spectroscopy and Molecular Dynamics Simulations”

Tatiana Starciuc

“Contribution of dielectric spectroscopy used to scrutinize the protein stabilization mechanisms and the role of water”

Yang Yao

“Water state in lipidic mesophase during phase transition”

• **S05 Charge Transport and Interfacial Effects**

Invited Communications:

Bernhard Roling

“Elucidating the Transport of Electrons and Molecules in a Solid Electrolyte Interphase (SEI) close to Battery Operation Potentials using a Four-Electrode-Based Generator-Collector Setup”

Catalin Gainaru

“Achieving superionic conductivity in polymer electrolytes”

Jan Swenson

“Relaxation Dynamics and Ionic Conductivity in Structural Battery Electrolytes”

Joshua Sangoro

“Evidence of Liquid-Liquid Transitions in Ionic Liquids”

Luka Pavic

“Insight into Electrical Conduction in Phosphate-Based Glasses: The Role of Transition Metal Oxides and the Mixed Glass Former Effect”

Paula Vilarinho

“Decoding Ferroelectrics: Dielectric and Impedance Spectroscopy as Tools for Electrical Microstructure Assessment”

Regular Communications:

Achilleas Pipertzis

“Ionic and Electronic Conductivity in Structural Negative Electrode Laminas”

Aurélien Roggero

“Molecular mobility and interfacial polarization study on model two-phase epoxy-amine networks”

Martin Tress

“BDS on the nanoscale: restricted crystallization and conductivity of polymers in finite size”

Zaneta Wojnarowska

“Dynamics of Ionic Liquid-Water Mixtures at Ambient and Elevated Pressure”

- **S06 Monitoring of Chemical Reactions, Crystallization process and Physical Ageing**

Invited Communications:

Kristine Niss

“Density Scaling and Single Parameter Aging”

Raj Suryanarayanan

“Time and temperature dependence of nucleation and crystallization in amorphous pharmaceuticals”

Tiberio A. Ezquerra

“Hydrogen bonding during cold crystallization of Poly(alkylene 2,5-furanoate)s”

Regular Communications:

Jessica Mangialetto

“Modelling of the Evolving Glass Transition Temperature During Cure of Diels-Alder Thermo-reversible Networks”

- **S07 Ferroelectrics and Ceramics**

Invited Communications:

Torsten Granzow

“Structural (dis-)order, dielectric response and phase transition properties of electrocaloric ferroelectrics”

Regular Communications:

Adam Sieradzki

“Order – Disorder Phase Transitions in Hybrid Organic – Inorganic Perovskites – Insights from Broadband Dielectric Spectroscopy”

Herbert Kliem

“A feedback Model for Relaxor Ferroelectrics”

Men Guo

“Insights into the aging mechanism of ZnO ceramics from broadband dielectric spectroscopy”

- **S08 BDS in Relation to Other Spectroscopic or Scattering Techniques**

Invited Communications:

Anne-Caroline Genix

“Coupling of shear rheology with SAXS and BDS in rubber nanocomposites”

Daniele Cangialosi

“Molecular mechanisms of glass aging”

Ernst Rössler

“Glass spectrum, excess wing phenomenon, and master curves in molecular glass formers”

Thomas Blochowicz

“The spectral shape of structural relaxation in supercooled liquids: light scattering vs. dielectric spectroscopy”

Regular Communications:

Marceau Hénot

“Orientational dynamics in supercooled glycerol computed from MD simulations: self and cross contributions”

Sébastien Pruvost

“Effect of hydrogen bonds on molecular mobility in P(MMA-co-MAA)/cellulose nanofibers composites”

Silvia Arrese-Igor

“Old news: dielectric spectroscopy is a good probe to study structural relaxation of glass forming systems”

• **S09 Confinement Effects**

Invited Communications:

Andreas Schönhals

“Signature of the Adsorbed Layer on the Glass Transition of Thin Polymer Films: Broadband Dielectric Spectroscopy and Related Techniques”

George Floudas

“Nanopores as separation membranes for blends comprising polymers of different architecture and microstructure”

Regular Communications:

Anna Drzewicz

“Molecular dynamics of ultrathin films of liquid crystal obtained via organic molecular beam deposition”

Erik Thoms

“Dielectric evidence of high kinetic stability in vapour-deposited binary glasses with large T_g contrast”

Kamil Kaminski

“The influence of pore walls nanostructurization on the dynamics of low and high molecular weight systems”

Katarzyna Chat

“The influence of pressure and volume changes on the non-equilibrium segmental dynamics of polymers”

Magdalena Tarnacka

“The impact of confinement on the behavior of associating materials. The case of phenyl alcohols”

• S10 Modeling, Theory and Simulation

Invited Communications:

Carlos J. Dias

“Kramers-Kronig relations expressed as a convolution pair and its uses in Broadband Dielectric Spectroscopy”

Frédéric Affouard

“Investigation of the nature of the translational and orientational disorder in pharmaceutical cocrystals from molecular dynamics simulations and dielectric relaxation spectroscopy experiments”

Jeppe C. Dyre

“Solved and unsolved problems relating to the Random Barrier Model”

Regular Communications:

Bruno M. G. Melo

“EIS smart tool: An application software for the analysis and modeling of impedance spectroscopy data with multi-curve fitting”

Dmitry V. Matyushov

“Nonlinear dielectric spectroscopy of liquids and protein solutions”

Florian Pabst

“Dielectric Spectra from First-Principles Simulations: Water, Salty Water and Others”

Kazunori Takahashi

“Inversion of Coaxial Transmission Line Data Using Numerical Simulation”

Pierre-Michel Déjardin

“On the Kirkwood correlation factor of dense isotropic polar fluids”

Ronald P. White

“Introducing a Mechanistic Perspective on the Slow Arrhenius Process (SAP) in Glass Forming Systems”

• S11 Industrial and Technological Applications

Invited Communications:

Anatoli Serghei

“Improving electrical insulating properties by using conductive materials: the interplay between permittivity and conductivity”

Eric Dantras

“Broaden the use of dielectric spectroscopy to non-polar polymers: implementation of dipolar probes by gamma irradiation”

Geoff Smith

“Through-vial impedance spectroscopy as a process analytical technology for developing pharmaceutical freeze-drying cycles”

Regular Communications:

Cindy Galindo

“Microwave Dielectric Response of Cytoplasmic Water in Red Blood Cells Upon Glucose Uptake”

Gustavo A. Schwartz

“Using artificial neural networks to predict the dynamics of molecular glass formers”

Tina Hecksher

“Broadband mechanical spectroscopy made available for dielectric setups”

YOUNG RESEARCHER SESSION

Ioannis Tzourtzouklis

[S02] “Phase Diagram, Glassy Dynamics, & Crystallization Kinetics of the Bio-based Polyester Poly(ethylene-2,5-furanoate)”

Kaylie C. Glynn

[S02] “Decoupling viscosity and conductivity by leveraging Grotthuss diffusion in imidazole systems”

Sílvia Gavinho

[S03] “Investigation of the Effects of Cerium Oxide Addition on Bioglass 45S5”

Francesco Coin

[S04] “Water dynamics on calcium pectin-based hydrogels for application in water remediation”

Kosei Kawai

[S04] “Measurement of rotational relaxation time of water in biosystem by shortwave infrared micro spectroscopy”

Rolf Zeissler

[S04] “Identifying dipolar cross correlation contributions to the dielectric response of water”

Sandra Krüger

[S04] “Water Dynamics in Aqueous Dipeptide Solutions Studied by BDS and 2H NMR”

Vasileios Moschos

[S04] “Dynamically and Structurally Heterogeneous Ethanol/Water Mixtures”

Marianna Spyridakou

[S05] “Enhanced Ionic Conductivity in Single-Ion-Conducting Block Copolymer Electrolytes of PS-*b*-P(EO-co-GME)”

Sofia R. Mendes

[S07] “Evaluating polyantimonic acid membranes as solid-state fuel cell electrolytes”

Efrat Hochma

[S08] “Phyto- and Phyto-Second Harmonic Generation-Photodynamic Therapy of Prostate Cancer Cells”

Maxwell Sparey

[S08] “Shear Force Microwave Microscopy: Complex impedance imaging, and Single Entity Electrochemistry”

Elisa Steinrücken

[S09] “Water Dynamics in Silica Confinements with Various Surface Chemistries Studied by BDS and NMR”

Lucas Leveque

[S09] “Conductive P3HT nanotubes: structure/properties relationship and applications”

Panagiotis Kardasis

[S09] “How Do Polymers and Mixtures of Different Architecture Penetrate Nano Channels?”

POSTER CONTRIBUTIONS

Achilleas Pipertzis

[P01-S01] “Molecular Dynamics and Self-assembly in Double Hydrophilic Copolymers with Densely Grafted Macromolecular Architecture”

Diogo Gomes

[P02-S01] “Microplastics Evaluation by Electrical Spectroscopy”

Ioannis Tzourtzouklis

[P03-S01] “Molecular Dynamics and Viscoelastic Properties of the Biobased 1,4-Polymyrcene”

Marianna Spyridakou

[P04-S01] “Heterogeneous Local Environments in Mussel-Inspired Elastomers”

Mydhili Varma

[P05-S01] “Dissecting the Role of Reduced Graphene Oxide on the Dielectric Properties of PEDOT:PSS-PVA Blends”

Stavros X. Drakopoulos

[P06-S01] “Relaxation Dynamics of Hydroxypropylmethylcellulose Acetate Succinate: via Dielectric and Mechanical Methods”

Alfred Blažytko

[P07-S02] “Unusual secondary relaxation in the glass-forming molecular rotors”

Fabián Puga

[P08-S02] “Physical characterization of a carbamazepine/oxalic acid cocrystal designed by liquid-assisted grinding”

Federico Caporaletti

[P09-S02] “The slow Arrhenius process beyond thin-film geometry”

Kenneth Rojo

[P10-S02] “Comparative Analysis of the Structure, Thermodynamics, and Dynamics of Amorphous Forms of Trehalose” (Poster)

Nikolaos Fotaras

[P11-S02] “Local and global dynamics of cis-1,4-Polyfarnesene in PS-*b*-Polyfarnesene diblock copolymer as a function of phase state”

Paulina Jesionek

[P12-S02] “Variation of Activation Volume as an Indicator of the Change in Clusterization Phenomenon in Flurbiprofen Enantiomers and the Racemate”

Sara Zimny

[P13-S02] “Is There a Relationship Between Wettability and the Rates of Equilibration of Hydrogen-Bonded Oligomer PMMS under Confinement?”

Teresa Viciosa

[P14-S02] “Improving the stability of amorphous drugs by deposition on the surface of silica nanoparticles”

Michal Rajnak

[P15-S03] “Rheo-dielectric study of transformer oil-based magnetic nanofluid”

Mohamad Barzegar

[P16-S03] “High-resolution TGA combined with BDS: a new tool to investigate the effect of water on the electrical conductivity of concrete”

Kaito Sasaki

[P17-S04] “Isotopic Study on the Dynamics of High-Density-Amorphous Ice Under High Pressure”

Kang Hu

[P18-S04] “The Molecular Nature behind the Dielectric Spectra in the Gigahertz Domain”

Marianna Ambrico

[P19-S04] “Early detection of Xylella-related plant disease via Broadband Dielectric Spectroscopy”

Vasileios Moschos

[P20-S04] “Effect of Hard Confinement (in Nanopores) on the Phase State and Dynamics of 1-propanol/water mixtures”

Andreia F. M. Santos

[P21-S05] “Nanoconfined Ionic Liquid Crystals as Hybrid Materials with Improved Conductivity Properties” (Poster)

Jan Swenson

[P22-S05] “Phase Behavior, Relaxation Dynamics and Ionic Conductivity in Mixtures of Protic Ionic Liquids”

Michael Wübbenhorst

[P23-S05] “Enhanced decoupling of conductivity relaxation from structural relaxation in non-stoichiometric protic ionic liquids”

Yun Dong

[P24-S05] “Demixing of Polymerized Ionic Liquid/Ionic Liquid Mixtures by Infiltration in Nanopores”

Hyeong Yong Song

[P25-S06] “Rheo-combined Dielectric Spectroscopy to Monitor Isothermal Crystallization of Poly(butylene succinate) (PBS)”

Peng Fang

[P26-S07] “Using Dielectric-Resonance Spectroscopy to Study the Dielectric Behaviors of Polymer-Based Ferroelectrets”

Silvia Soreto Teixeira

[P27-S07] “Advanced PVDF-TiO₂ Composites for Efficient Energy Storage”

Subir Majumder

[P28-S07] “Dielectric behaviour of BFO ceramics”

Martin Tress

[P29-S08] “Thermal expansion of inter-molecular H-bonds”

Vyankat P. Pawar

[P30-S08] “Temperature Based Study of Dielectric Permittivity and Dielectric Susceptibility in the Binary Mixture of Polar Liquids”

Erik Thoms

[P31-S09] “Dielectric evidence of high kinetic stability in vapour-deposited binary glasses with large Tg contrast”

Lucas Leveque

[P32-S09] “Conductive P3HT Nanostructures: Structure/Property Relationship and Applications”

Natália T. Correia

[P33-S09] “Dynamics of a Confined Drug from Complementary Perspectives: Experiments vs MD Simulations”

Panagiotis Kardasis

[P34-S09] “Imbibition Kinetics of Poly(ethylene oxide) in Nanopores by *In Situ* Nanodielectric Spectroscopy” (Poster & Video)

Shiwang Cheng

[P35-S09] “Dynamics of polylactic acid under ultrafine nanoconfinement: the collective interface effect and the spatial gradient”

Florian Pabst

[P36-S10] “Glassy Dynamics from First-Principles Simulations”

Anatoli Serghei

[P37-S11] “Universal relationship between the electromagnetic interference shielding effectiveness of composite materials and their electrical properties”

Luís Cadillon Costa

[P38-S11] “Materials electrical characterization: from DC to microwave frequencies”

Manuel P. F. Graça

[P39-S11] “Comprehensive Electrical and Biological Analysis of Bioglass in Bulk and Pressed Powder Forms”

Youssef Elamine

[P40-S11] “Dielectric properties of honey: application in botanical origin determination”

ABSTRACTS

S01

Polymer Dynamics

Energy Barrier for Structural Relaxation, Molecular and Ion Transport in Polymers: a Revised Approach

Alexei P. Sokolov^{1,2}, Catalin Gainaru², Ivan Popov³

¹ Department of Chemistry, University of Tennessee, Knoxville, USA

² Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, USA

³ University of Tennessee – Oak Ridge Innovation Institute, Knoxville, USA

Email: * sokolov@utk.edu

Energy barriers control structural relaxations, molecular and ion transport in glasses, polymers and viscous liquids. The apparent energy barrier E_{app} is usually estimated from the slope of an Arrhenius temperature dependence:

$$\tau(T) = \tau_0 \exp\left(\frac{E_{app}}{RT}\right); \quad D(T) = D_0 \exp\left(-\frac{E_{app}}{RT}\right); \quad \sigma(T) = \sigma_0 \exp\left(-\frac{E_{app}}{RT}\right) \quad (1)$$

Many studies revealed empirical correlations between the so-obtained E_{app} and the prefactor in the eq. 1 (τ_0 , D_0 , σ_0), and this led to idea of enthalpy-entropy compensation. In this presentation we show many examples where the apparent activation energy strongly overestimates the real energy barrier E_0 . We demonstrate that linear temperature dependence of the energy barrier $E_0(T)$ will lead to a perfect Arrhenius law (eq. 1), but with $E_{app} \gg E_0(T)$ and physically unreasonable prefactor [1]. It is known that the energy barrier for many relaxations, ion and molecular transport depends on density, shear modulus and dielectric constant of the material [1-3]. Our analysis revealed that all these parameters in polymers show relatively strong temperature variations even below T_g , and this leads to the temperature dependent energy barrier $E_0(T)$ even in a glassy state (Fig. 1). Next, we show that temperature variations of the energy barrier explains well the empirical correlations between E_{app} and the prefactors τ_0 , D_0 , σ_0 (eq.1). To address this problem, we propose a different approach to estimate the temperature dependent energy barrier: use prefactors fixed at physically reasonable values. We demonstrate that this approach provides good description of many experimental data with $E_0(T)$ correlated well with temperature dependence of shear modulus and/or dielectric constant (Fig. 1) [1]. Most important, estimated in this way energy barrier appears much lower than E_{app} estimated using the traditional approach (eq. 1).

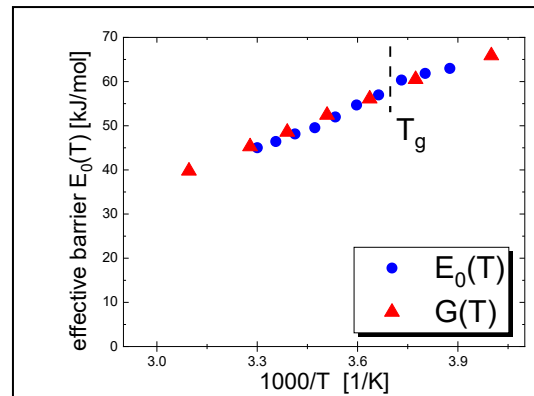


Figure 1. Temperature dependence of the estimated energy barrier for ion transport in polymerized ionic liquid with mobile TFSI ion follows well the temperature dependence of the shear modulus. Data from [1].

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Structure and Dynamics of Supramolecular Poly(alkyl ether)-based Polymers: insight with DRS, NS and Rheology

Ana Arizaga¹, Maria T. Viciosa,² Aurel Radulescu³, Orsolya Czakkel⁴, Annette M. Schmidt¹, Margarita Kruteva⁵, Wim Pyckhout-Hintzen⁵ and Ana R. Brás^{1*}

¹ University of Cologne, Cologne, Germany

² University of Lisbon, Lisbon, Portugal

³ Heinz Maier Leibnitz-Zentrum (MLZ), Forschungszentrum Jülich GmbH, Garching, Germany

⁴ Institute Laue Langevin (ILL), Grenoble, France

⁵ Forschungszentrum Jülich GmbH, Jülich, Germany

Email: *ana.eliasbras@uni-koeln.de

In this talk, a number of key results on the supramolecular association and chain structure of supramolecular polymers in the bulk and in their own oligomer chains in the melt as blend will be presented.

A combination of rheology, dielectric relaxation spectroscopy (DRS) and neutron spin echo spectroscopy (NSE) provided the association lifetimes for the supramolecular polyethylene oxide (PEO) and polypropylene oxide (PPO) (molar mass is 2000 g·mol⁻¹) carrying at the ends either the pair diaminotriazine (DAT) and thymine-1-acetic acid (THY) and mixed 50/50 [1,2]. Small angle neutron scattering (SANS) reveals that while PEO and PPO functionalized with THY/DAT self-assemble as linear chains, PEO and PPO functionalized with 2-ureido-4[1H]-pyrimidinone (UPY) as H-bonding end-groups form UPY spherical clusters, responsible for the physical crosslinks of the formed transient network [1].

In order to also obtain a molecular view by neutron scattering (NS) on the association dynamics of UPY based supramolecular polymers, it was immersed in their own deuterated (D) covalent short linear non-functionalized PEO chains (molar mass is 500 g·mol⁻¹) in the melt as blend. On contrary to the bulk structure [2], the supramolecular UPY polymer in the blend changes from compact spherical ring-like to linear conformation with decreasing supramolecular polymer mass fraction. These findings are also confirmed by the NSE analysis with the modified Rouse model for ring polymers from which the expected diffusion and segmental friction is obtained [3].

Acknowledgments

The fantastic work of the students Uxue Aguirre, Marie Dorau and Daria Sokolova. Patricia Bach and Jürgen Allgaier help on the synthesis of deuterated PEO. Michael Monkenbusch prompt help on programming and Dieter Richter for the interesting discussions. DFG for a research grant (BR5303).

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Dielectric Spectroscopy on vitrimers based on transesterification reactions

Naroa Ayensa¹, Juan Rodriguez-Hernández¹, Helmut Reinecke¹, Alejandro Sanz²,
Aurora Nogales³

¹ *Instituto de Ciencia y Tecnología de Polímeros, ICTP, CSIC. C/ Juan de la Cierva 3, Madrid 28006, Spain*

² *Departamento de Ciencias y Técnicas Fisicoquímicas, Facultad de Ciencias, UNED, 28232, Las Rozas-Madrid, Spain*

³ *Instituto de Estructura de la Materia, IEM, CSIC. C/ Serrano 121, Madrid 28006, Spain*
Email: * aurora.nogales@csic.es

The need of recyclability and circularity of polymer materials in general, and in particular in thermosettings, has boosted the development of more sustainable materials that enable the recycling, for example, by depolymerization, or reprocessing by using reversible crosslinking-decrosslinking strategies. In this context, covalent adaptative networks (CAN) have been developed, three dimensional networks with dynamic covalent bonds, that can be dynamically exchanged via reversible reactions triggered by external stimuli. A particular type of CANs are called vitrimers (also known as associative dynamic covalent adaptive networks), where the covalent bonds are not broken until a new one is formed, and in this way, the crosslinking density is constant independently of the temperature. In this work, the molecular motions occurring in a series of novel vitrimers based on transesterification reactions is studied by dielectric spectroscopy. We present here a study on the role of the ratio of crosslinker to linear monomer (crosslinking density) and the type of linear monomer, (herein limited to 2-Hydroxy acrylate), on the molecular dynamics of the vitrimer. The nature of an observed dynamic window of different properties, associated with the T_g, will be discussed.

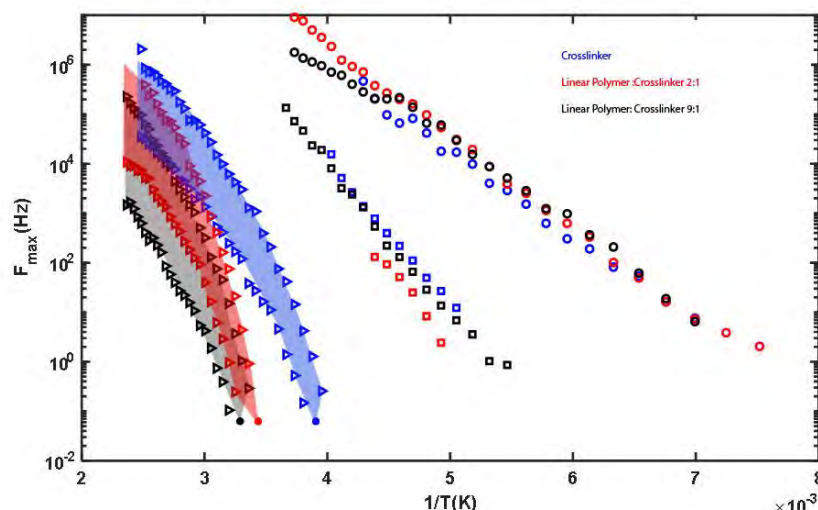


Figure 1. Relaxation map of vitrimers based on 2-Hydroxy acrylate and jeffamine crosslinker

Acknowledgments

This work has been funded by projects PID2022-138635NB-I00 from MCIN /AEI /10.13039/501100011033, TED2021-129845B-I00, PLEC2021-007793 and TED2021-130093B-C22 from European Union NextGenerationEU/PRTR funds.

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Crystallization and dielectric properties of PVDF-ionic liquid blends

José Luis Gómez Ribelles*

Center for Biomaterials and Tissue Engineering (CBIT), Universitat Politècnica de València, Spain
CIBER de Bioingeniería, Biomateriales y Nanomedicina, Instituto de Salud Carlos III
Email: jlgomez@upv.edu.es

Poly(vinylidene fluoride), PVDF, has strong permanent dipolar moments in the polymer chain which, depending on the crystalline arrangement, give the polymer a high piezoelectric coefficient. The polymer has the ability to crystallise in different phases (α , β , γ , δ , ϵ), the phases β and γ (especially β) being the electroactive phases. Nevertheless, crystallisation from the melt leads to the formation of the α phase in which the orientation of the dipoles makes the permanent dipolar moment of the whole chain zero. There are different methods of inducing the formation of crystals in the β phase. In previous work we have seen how mixing the polymer with different ionic liquids, IL, leads to a microstructure in which PVDF crystals coexist in preferentially β phase with the mixture of IL and amorphous PVDF chains and in some cases pure IL that is segregated in separate domains [1]. Studies monitoring by means of differential scanning calorimetry, DSC, and infrared spectroscopy, FTIR, the isothermal crystallisation of PVDF and IL mixtures from the liquid mixture show the evolution of the crystalline phases formed at different temperatures [1]. In this work we review experimental results from our group that show the significance of this particular microstructure on the dielectric response and ionic conductivity of these systems [2-4]. Dielectric relaxation spectrum shows the main dipolar relaxation associated to polymer segments dynamics, Maxwell-Wagner-Sillars relaxation and ionic conductivity due to the IL components. Analysing the response of mixtures with series of ILs with a common cation or with a common anion, it is shown that the behaviour of these systems depends to a large extent on the interaction between the anion or cation forming the IL with the PVDF chain segments, in addition to the size of the ions which influences their mobility.

Acknowledgments

This work has been supported by PID2022-138572OB-C41 project funded by MCIN/AEI/10.13039/501100011033/FEDER, Spain/EU. The research was also supported by CIBER – Consorcio Centro de Investigación Biomédica en Red - CB06/01/1026, Instituto de Salud Carlos III (Ministerio de Ciencia e Innovación, Spain)

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- [4] D.M.Correia, C.M.Costa, R. Sabater i Serra, J. A. Gómez Tejedor, L.Teruel Biosca, V .de Zea Bermudez, J.M.S.S.Esperança, P.M.Reis, A.Andrio Balado, J.M.Meseguer-Dueñas, S.Lanceros-Méndez, J.L.Gomez Ribelles. *Polymer* 2019, 171, 58-69 doi:10.1016/j.polymer.2019.03.032

Slow dynamics above and below glass transition for some polymer systems

Koji Fukao¹

¹ Dept. of Physics, Ritsumeikan University, Noji-Higashi 1-1-1, Kusatsu, 525-8577, Japan
Email: kfukao@se.ritsumeik.ac.jp

Recently it has been reported that there is a slower process in the liquid states above the glass transition temperature T_g which has the activation energy similar to that of the equilibration process in the glassy states [1]. The slower process is expected to be correlated with the aging dynamics in the glassy state [2]. However, the physical properties of the slower process are not yet fully elucidated. In this study, we investigated the slower process for two different types of polymeric systems to investigate the properties of the slower process and its correlation with aging dynamics more in detail.

First, we performed DRS measurements on nanocomposite of poly(2-vinylpyridine) (P2VP) and octa(phenyl) silsesquioxanes (OPS) with a variable number of hydrogen bond-donating amines (NH_2 -) [3]. In this system, we observed the slower process in addition to the alpha-process above T_g . As the number of amine groups decreases, i.e., as the intermolecular interaction between nanoparticle and P2VP decreases, the temperature dependence of the relaxation time of the slower process changes from the VFT type to the Arrhenius type. Accordingly, the fragility index decreases, and the glass transition temperature evaluated from the slower process decreases with decrease in the number of amine groups. This suggests that the dynamics of the slower process is strongly affected by the strength of the intermolecular interaction.

Secondly, we adopted poly(4-alkylstyrene) and performed the DRS measurements and volume relaxation measurements [4]. In these polymeric systems, there is also the slower process in addition to the alpha-process under the contribution from the DC conductivity above T_g . Below T_g , a volume relaxation of the glassy state can be observed through the measurements on the real part of the electric capacitance, which increases with the aging time if the volume of this polymeric system decreases due to approaching the real glassy state or the crystalline state, i.e., densification. Figure 1 shows that the relaxation time of the slower process can well be described by the Arrhenius law and the straight line for the slower process is the same as that for the volume relaxation. This suggests that the volume relaxation is not mainly controlled by the mobility due to the alpha-process but by that due to the slower process. In other words, there should be a common physical origin between the volume relaxation in the glassy state and the slower process in the liquid state.

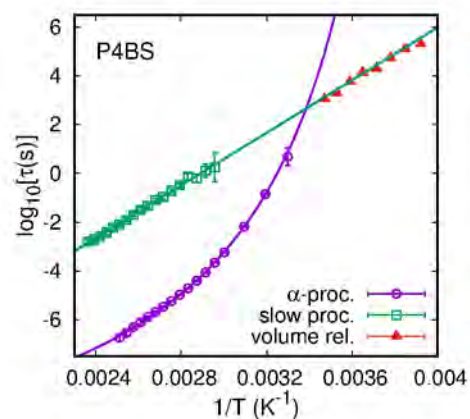


Figure 1. Temperature dependence of the relaxation times of the alpha-process, the slower process and the volume relaxation for poly(4-butylstyrene).

Acknowledgments

This work was in part supported by the Grant-in-Aid for Scientific Research (B) (Grant Nos. 23K25842) from the Japan Society for the Promotion of Science.

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Interest of pressure controlled dielectric spectroscopy to probe the interdependence between fragility and cooperativity for polymeric segmental relaxation

Jules Trubert, Liubov Matkovska, Allisson Saiter-Fourcin, Laurent Delbreilh*

Univ Rouen Normandie, INSA Rouen Normandie, CNRS, Normandie Univ, GPM UMR 6634, F-76000 Rouen, France

Email: laurent.delbreilh@univ-rouen.fr

Since the beginning of the polymer science, one of the main goal of researchers has been to understand and predict qualitatively and quantitatively the variations of the physical parameters associated with transition and relaxation phenomena. In this topic, the possible interdependences between the different relaxation parameters associated with the segmental relaxation are not yet fully understood. In a very practical way, is it possible to correlate a modification of polymer microstructure with variations of segmental parameters like glass transition temperature, dynamic fragility [1], β_{KWW} stretching parameter, cooperativity lengthscale at the glass transition...?

To try to find answers to this question, several strategies can be used. In this presentation, several experimental studies will be used to identify the interdependence between volumetric contribution of fragility and cooperativity for several polymeric systems.

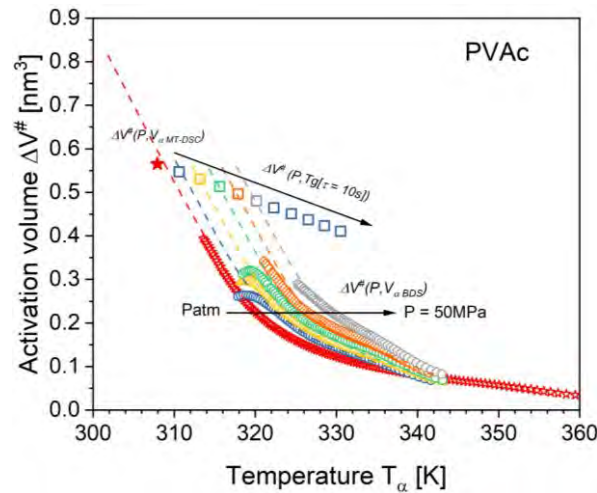


Figure 1. Activation volume $\Delta V^\#$ as a function of the temperature T_α for PVAc [from Ref 2]

The molecular mobility of three amorphous thermoplastic polymers (PVAc, PLA and PETg) has been explored by separating the isobaric fragility m_p in its thermal m_V and volumetric ($m_p - m_V$) contributions, using BDS under pressure [2]. The goal of this work was to try to understand the very high isobaric fragility of PLA comparatively to other thermoplastics with stiffer backbones. The activation volume $\Delta V^\#$ is the critical parameter allowing to calculate the volumetric contribution ($m_p - m_V$). The connection between the CRR volume V_α as defined through the Donth's Model [3], and $\Delta V^\#$ calculated from the isobaric measurement is validated, and lengthened above the glass transition thanks to the extended Donth's approach [4]. The cooperativity seems to correlate better with the volumetric contribution of m_p , than with the isobaric fragility itself.

These results have been used to investigate PVAc-EVAX sample series with uncorrelated variations of segmental relaxational parameters on one side and with structural modifications on the other side [5].

Acknowledgments

The authors thank Rouen Univ. and Normandy Region for their financial support for Liubov Matkovska's position.

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Glass Transition Effects in a Thermo-reversible Network

Michael Wübbenhorst^{1*}, Niko Van den Brande² and Jessica Mangialetto²

¹ Laboratory for Soft Matter and Biophysics, KU Leuven, Celestijnenlaan 200D, Leuven, Belgium

² Lab of Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Pleinlaan 2, Brussels, Belgium

Email: * Michael.Wuebbenhorst@kuleuven.be

Broadband dielectric spectroscopy (BDS) was applied to investigate the molecular dynamics, cure kinetics and chemical equilibria of a Diels-Alder (DA) reversible network in a systematic way. By combining specific experimental protocols, monomers of different molecular mass, and advanced fit strategies, a couple of fundamental questions were addressed:

First, we have tested three approaches to detect and to quantify effects of underlying kinetics on the dielectric spectra: i) combining isothermal measurements with stepwise heating, ii) using a randomized frequency list to create artificial data “noise”, and iii) varying the effective heating rate up to 10 K/min to separate sample kinetics from relaxation dynamics.

The glass transition temperature (T_g) was determined in two ways as a function of the state of cure, following the evolution from the monomeric mixture to a fully cured network. Using a full kinetic model, the link between T_g and the conversion was established. In all cases, a great coincidence between the thermal and the dynamic T_g was found.

Despite a total upshift of T_g by 80K upon conversion, only minor changes in the dynamic fragility and the spectral shape of the α -relaxation were found. In contrast, the ionic conductivity confirms charge transport assisted by segmental motions with partial decoupling of the α -relaxation time from ionic conductivity (fractional DSE behavior) between T_g and $T_g \times 1.2$. Surprisingly, the degree of coupling, given by the FDSE exponent S , drops until reaching the gel point (~30 min.) with no further changes upon extended cure. In contrast, a continuous increase in dc-conductivity with curing time is observed, attributed to enhanced intrinsic conductivity via improved H-bonding. Investigation of the α -relaxation strength and shape reveals subtle trends, reflecting changes in the dipole-dipole correlation and equilibrium shifts between cycloadducts.

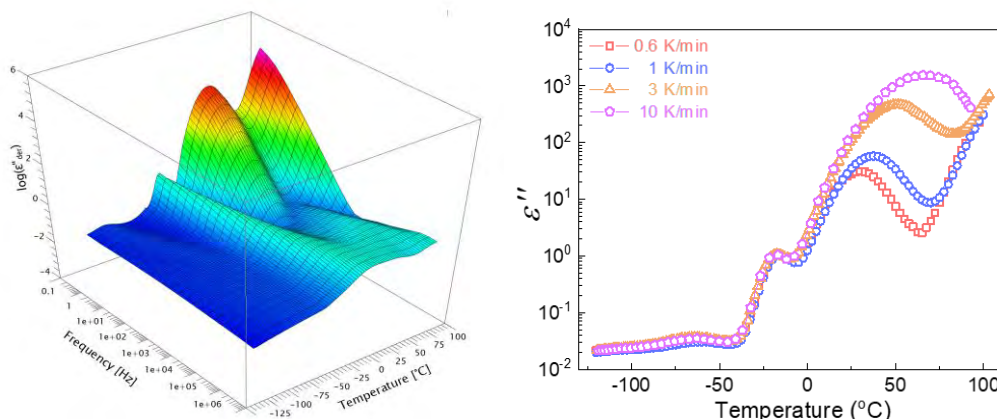


Figure 1. Left: 3D plot of the logarithmic derivative dielectric loss ϵ''_{der} of the uncured 4F230-2M230 system, Right: Loss $\epsilon''(T)$ at $f=100$ Hz for 4 different heating rates.

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Bionanocomposites based on biodegradable polyesters and clays prepared by *in-situ* polymerization: structures, characterizations, and dielectric properties

Mustapha Raihane^{1,2*} and **Mourad Arous**³

¹ IMED-Lab, Cadi Ayyad University (UCA), Faculty of Sciences and Techniques, BP549
Av. A. El Khattabi, Marrakech, Morocco

² Applied Chemistry and Engineering Research Centre of Excellence (ACER CoE), Mohammed VI Polytechnic University (UM6P), Lot 660, Hay Moulay Rachid, Ben Guérir, Morocco

³ LaMaCoP-Faculty of Sciences of Sfax-Sfax, Tunisie
Email: * m.raihane@uca.ma

We are focus on this study on nanocomposites based on poly(ϵ -caprolactone) (PCL) and poly (butylene succinate) (PBS) as a biodegradable polyesters with halloysite nanotube (HNT) and modified beidellite clays (3CTA-BDT), respectively. PCL and PBS nanocomposites were prepared by *in-situ* polymerization in the presence of different loadings of clays (1, 2 and 3 wt%). In fact, PCL nanocomposites were synthesized by ring opening polymerization of ϵ -CL and catalyzed with tetra(phenylethynyl)tin, while those of PBS were prepared by polycondensation reaction between succinic acid, butanediol in decalin solvent and utilizing chloride bismuth (BiCl_3) as catalyst [1,2]. These bionanocomposites were characterized by Scanning Electron Microscopy (SEM), X-Ray diffraction (XRD) and Differential Scanning Calorimetry (DSC). Their dielectric properties were investigated by means of broadband dielectric spectroscopy (BDS) and specially the interfacial features to further highlight the PBS or PCL and nanofillers interaction and hence the effect of added nanofiller in term of dispersion and adhesion by employing the results of the Havriliak-Negami fit particularly [3,4]. For example, for PCL/HNT, the effect of the incorporated HNT on the molecular relaxation process and interfacial polarization of PCL was studied (Figure 1). The BDS measurements revealed four significant dielectric processes α -primary relaxation attributed to glass transition, β -secondary relaxation and two interfacial polarizations due to the semi-crystalline character of PCL (IP_1) and the added HNT fillers (IP_2). According to our results, the weight ratio of HNT ranging between 3% and 5% is recommended for achieving the highest performing nanocomposite that can be used in several applications.

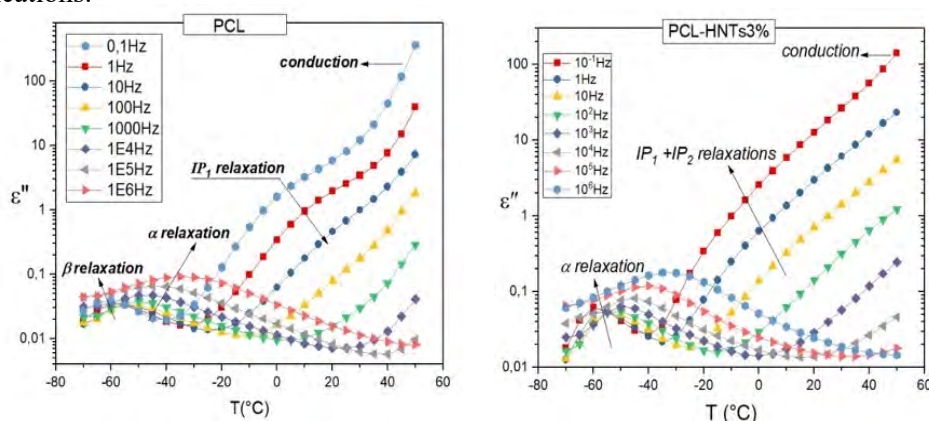


Figure 1. Behavior of the imaginary parts of the dielectric permittivity for the neat PCL (left), and PCL-HNT 3% (right) at several frequencies.

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Vitrimers – Rethinking Epoxies Towards Recyclable and Reusable Thermosets

Paulina Szymoniak¹, Andreas Schönhals¹, De-Yi Wang² and Reiner Zorn³

¹ *Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany*

² *IMDEA Materials Institute, Eric Kandel 2, 28906 Getafe, Madrid, Spain*

³ *Forschungszentrum Jülich, Jülich Centre for Neutron Science (JCNS), Wilhelm-Johnen-Straße 52428 Jülich, Germany*

Email: * Paulina.Szymoniak@bam.de

Vitrimers represent an innovative material class poised as a sustainable alternative to conventional epoxy thermosets within the framework of circular economy. Based on covalent adaptive networks (CANs), vitrimers exhibit upon external stimuli dynamic bond rearrangements, endowing the material with unprecedented properties, such as shape-memory, self-healing, and recyclability. These pioneering materials combine the robust mechanical behavior of classic lightweight thermosets with the inherent malleability of thermoplasts.

Here, the intricate interplay between the nature of CANs, i.e., microscopic structure and molecular mobility with macroscopic properties such as thermomechanical performance of newly developed vitrimers is meticulously studied. The material is based on glycerol triglycidyl ether (GTE) and vanillin-derivative hardener (VA), which represents an ideal biobased substitute for fossil-derived epoxy resins. The applied methodology comprises X-ray scattering, neutron scattering, dielectric and mechanical spectroscopy, as well as calorimetry. One interest is to understand the molecular dynamics of the CAN. Dielectric and neutron scattering investigations of the materials revealed two active processes, i.e., one related to segmental mobility, and a second process related to topology reshuffle. Further, GTE-VA is considered in the “as-prepared” and “healed” state, where the thermomechanical properties are studied as a function of recycling cycles.

Anhydrous Proton Conduction in Polymers Containing Azoles and Phosphonic Acids

Zitan Huang¹, Michelle Lehmann², Tomonori Saito², Michael A. Hickner³, and Ralph H. Colby*¹

¹*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States*

²*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States*

³*Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan 48824, United States*
Email: * rhc5@psu.edu

Developing fuel cells for automotive transportation and other applications is a critical component for achieving the goal of net zero emissions by 2050. Among the various components in a fuel cell system, the electrolyte is responsible for proton conduction, and its proton conductivity largely determines the overall performance of the fuel cell [1]. Currently, most proton conduction membranes work under aqueous conditions, as water can promote proton conduction. However, this requirement greatly limits the operational temperature range and increases the cost of a fuel cell system. Since they are both proton donors and acceptors, azole molecules can facilitate proton conduction (like water) through proton hopping, but since their boiling point is far above that of water, they can be operated at much higher temperatures.

Here we first studied proton conduction of neat 1,2,3-triazole, 1,2,4-triazole and imidazole in their liquid and crystalline solid states. Since the three are quite similar and 1,2,3-triazole has the lowest melting temperature, this molecule was blended with three different phosphonic acids, including poly(vinyl phosphonic acid), as potential candidates for high-conductivity proton conductors under anhydrous conditions. The proton conductivity and dielectric properties of these blends with no water present were examined through broadband dielectric spectroscopy over wide ranges of composition, frequency and temperature. In each blend, a maximum in proton conductivity was seen at intermediate compositions. A high proton conductivity in the range of 100 mS/cm was obtained for one of the samples at 120 °C, which proves the potential of using these systems as high temperature proton conductors under anhydrous conditions. To further understand the proton conduction mechanism in these systems, the viscosity and proton diffusion coefficients of these samples were also measured. A Walden plot proves that proton conductivity is controlled by viscosity. The protons bonded to nitrogen diffuse faster than the protons bonded to carbon, proving that proton hopping from one 1,2,3-triazole molecule to a neighboring one plays a vital role. Using Raman spectroscopy, following Watanabe [2], the fraction of 1,2,3-triazole molecules that are protonated was determined in each sample, in order to quantify the amounts of proton conduction from both vehicular motion of 1,2,3-triazole and proton hopping from one 1,2,3-triazole to the next. Lastly, a polyacrylate with 1,2,3-triazole side groups on every repeat unit was synthesized and used to study the proton conductivity of an anhydrous proton exchange membrane.

Acknowledgments

This work was supported as part of Fast and Cooperative Ion Transport in Polymer-Based Materials (FaCT), an Energy Frontier Research Center funded by the US. Department of Energy, Basic Energy Sciences.

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Broadband dielectric spectroscopy for advancing understanding and applicability of poly(vinylidene fluoride)/ionic liquid blends as sensor, actuators and energy storage systems

C.M. Costa¹, D. M. Correia² and S. Lanceros-Mendez^{1,3,4*}

¹ Physics Centre of Minho and Porto Universities (CF-UM-UP) and Laboratory of Physics for Materials and Emergent Technologies, LapMET, University of Minho, 4710-057 Braga, Portugal.

² Centre of Chemistry, University of Minho, 4710-057 Braga, Portugal

³ BCMaterials, Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940 Leioa, Spain.

⁴ IKERBASQUE, Basque Foundation for Science, Bilbao, 48009, Spain

Email: * senentxu.lanceros@bcmaterials.net

Nowdays, the combination of polymer matrix with ionic liquids (ILs) results in a variety of functional properties with strong application potential areas including sensors, actuators and energy storage systems, among other, considering the tailorability of both ILs and polymer matrix. The final functional properties of these materials are often tailored through the proper selection of anions and cations present in the ionic liquids.

Furthermore, considering that the ionic conductivity of the IL is essential for most of these applications, ionic mobility must be properly understood at diverse frequencies and temperatures. This presentation will provide an overview on the potential, processing and applications of different polymer/IL systems in relation with the increasing digitalization of society and the need of more sustainable technologies. Further, the relevance of the evaluation of ionic mobility by broadband dielectric spectroscopy (BDS) will be highlighted focusing on PVDF/IL blends, evaluating the influence of IL content [1] and different IL anions and cations [2] in the ionic conductivity behavior and dynamics of the charge carriers in the PVDF/IL blends. The observed modifications of the dielectric response of the materials, will be related to the different applications.

In particular, the IL content affects the electrical conductivity behavior of the blends from the standpoint of charge motion, ion concentration and electrode polarization effects. Also, the main relaxation process (β -relaxation) of the amorphous phase of the blend that integrates amorphous polymer chain segments and IL molecules will be discussed, the structure of the cation of the IL being less influential than the anion on the dielectric and conductivity properties of the blends.

Acknowledgments

Fundação para a Ciência e Tecnologia (FCT): UID/FIS/04650/2020, UID/QUI/0686/2020, 10.54499/2022.03931.PTDC, 2022.05932.PTDC and POCI-01-0247-FEDER-046985, 2020.02915.CEECIND (DOI: 10.54499/2020.02915.CEECIND/CP1600/CT0029) (D.M.C), and 2020.04028.CEECIND (DOI: 10.54499/2020.04028.CEECIND/CP1600/CT0018) (C.M.C.). Advanced Materials programme supported by MCIN - European Union NextGenerationEU (PRTR-C17.I1) and the IKUR Strategy of the Department of Education of the Basque Government. Funding by the Basque Government Industry Departments under the ELKARTEK programs

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The dielectric response of the slow Arrhenius process (SAP)

Simone Simon Napolitano, Federico Caporaletti, Chun Li, Erik Thoms, Kai Wang

Laboratory of Polymer and Soft Matter Dynamics, Experimental Soft Matter and Thermal Physics (EST),
Université libre de Bruxelles (ULB), Brussels 1050, Belgium
Email: * simone.napolitano@ulb.be

Experiments by dielectric spectroscopy [1–7], other experimental techniques [8], and molecular dynamics simulations [9, 10] show the presence of a relaxation mechanism slower than the structural (α -)process in the liquid state of polymers and small organic molecules. This relaxation mechanism, which we labeled SAP (the slow Arrhenius process [1]), is characterized by a temperature independent activation barrier. Because of such a property, the SAP eventually becomes faster of the (α -)process when the system reaches sufficiently low temperatures. The SAP, which we show is intimately connected to high-temperature rheological behavior [2], can efficiently drive melts and glasses toward more stable, less energetic states [1, 7]. Based on the experimental findings collected so far on more than 30 molecules polymers and small molecules, we discuss how the SAP contributes to the dielectric relaxation. We highlight the energetic and dynamic signatures [3, 10] of such a peculiar mechanism which, though insensitive to large density variations [5], can be used to probe stress at the molecular level [6].

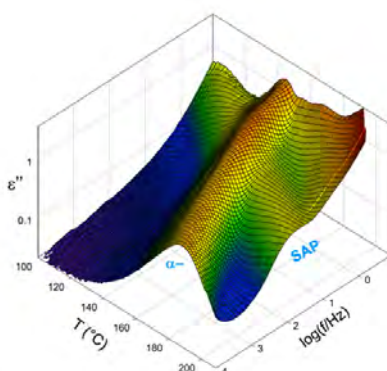


Figure 1. Dielectric relaxation of a 310 nm thick layer of poly(4-bromostyrene)

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We thank the Action de Recherche Concertée ULB under grant ARC 20061 “SADI” for financial support.

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Chain-length-dependent relaxation dynamics in poly(methyl acrylate)

Jiaxin Zhao^{1,2}, Matthew Reynolds¹, Andrew Wilson² and Johan Mattsson^{1*}

¹ School of Physics and Astronomy, University of Leeds, U.K.

² School of Chemistry, University of Leeds, U.K.

Email: * k.j.l.mattsson@leeds.ac.uk

Glassy polymers are important e.g. in construction materials (aerospace, medical implants), coatings, optical components and membranes for controlled transport of ions and gases. However, the glass-transition-related dynamics in polymers are still poorly understood due to the complexity introduced by chain connectivity and chain flexibility [1]. Here, we address this by investigating the chain-length-dependent glass transition and associated relaxation dynamics for a model polymer – poly(methyl acrylate) (PMA). We synthesize PMA using reversible addition–fragmentation chain-transfer (RAFT) polymerization, and determine the chain-length-dependent relaxation dynamics both with and without the chain transfer agent (alkyl chain end-group). Broadband dielectric spectroscopy (BDS), calorimetry and small amplitude oscillatory shear rheology were used to characterise the molecular relaxation dynamics and rheological response. We confirm the presence of three molecular relaxations: the structural α -relaxation and two secondary (β and γ) relaxations characterised by high molecular weight activation enthalpy values of ≈ 36 and 120 kJ/mol, respectively; the β -relaxation in PMA is very weak and has often been overlooked in earlier studies. The detailed T_g - M relationship for PMA was characterised both with and without the additional alkyl end-tail (which reduces T_g for short chains), and various means of describing the observed behaviour will be discussed. Moreover, we found that long-chain PMA demonstrates decoupling between ion conductivity and the α -relaxation, even though the decoupling is less dramatic than that observed in highly fragile polymers such as poly(methyl methacrylate) and polycarbonate [2].

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Dielectric and viscoelastic properties of 3D-printed cellulose based bionanocomposites for electrical insulation application

Lecoublet Morgan^{1,2*}, Ragoubi Mohamed¹, Leblanc Nathalie¹ and Koubaa Ahmed²

¹ Unité de Recherche Transformations et Agro-Ressources, UniLaSalle, Mont-Saint-Aignan, France

² Laboratoire Biomatériaux, UQAT Campus de Rouyn Noranda, Rouyn-Noranda, QC J9X 5E4, Canada

Email: * morganlouisjean.lecoublet@uqat.ca

The requirement for materials combining dielectric performances and simplicity of implementation in the microelectronics industry has oriented research towards the elaboration of polymer-based composites. Even if they have attractive properties, good processability, and desirable performance, it is increasingly necessary to replace them with bio-based alternatives. One way of promoting their integration is through the use of 3D printing process (FFF). This study aimed to develop new biomaterials containing polylactic acid (PLA) and nanocrystalline cellulose (NCC) by Fused Filament Fabrication (FFF). The influence of the 3D printing process and NCC content on thermal, viscoelastic and dielectric properties was investigated. The addition of NCC fillers played the role of a mechanical reinforcement, increasing the dynamic mechanical properties and complex viscosity of NCC-based bionanocomposites [1]. Moreover, as the used fillers had polar functions on their surfaces, their integration increased the dielectric constant (ϵ'), dielectric loss (ϵ''), as well as the electrical conductivity in alternative current (σ_{AC}) of composites. The cellulosic fillers intensively increased the crystallization rate of the materials, improving the mechanical stability of PLA in the rubbery state. Finally, the 3D printing process decreased all the measured properties, due to the combined effect of a lower crystalline content and the presence of voids induced by the 3D printing process [2]. **Figure 1** shows the influence of 3D printing on the dielectric constant. The porosity was measured at 2,5 % for the neat PLA, and between 3,1 and 5,8 % for the cellulose-based composites. These results showed the advantage provided by the FFF technology in the production of cellulose-based biocomposites with good electrical insulation properties and mechanical properties in the glassy state.

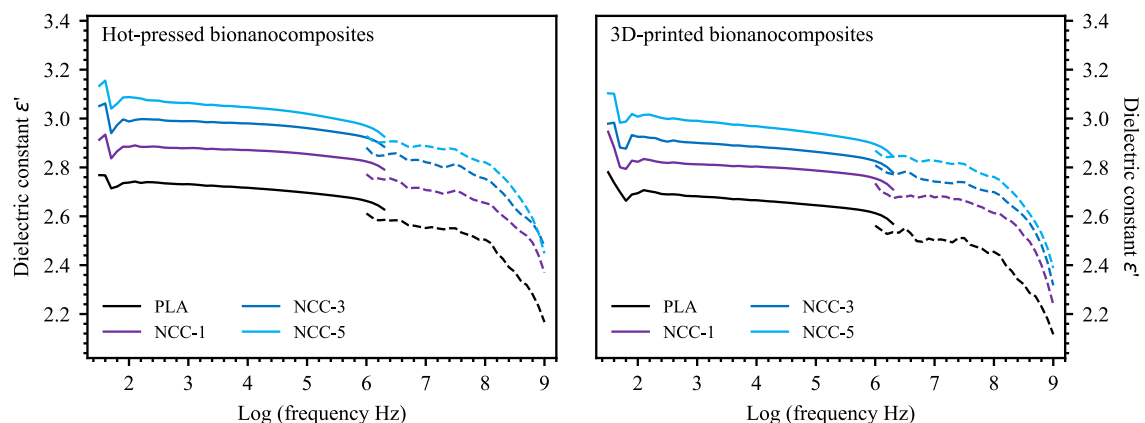


Figure 1. Dielectric constant of 3D printed and hot-pressed bionanocomposites measured at 100 Hz

Acknowledgments

This work was supported by the Région Normandie (Fr), the Canada Research Chair Program; the NSERC Discovery Grant; MITACS Globalink Program; and TABES Create Program

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Segmental Relaxation of Polystyrene Modified with Pyrene Molecules

S.X. Drakopoulos^{*1}, K. Randazzo², S. Liu¹, R.D. Priestley^{1,2}

¹Princeton Materials Institute, Princeton University, Princeton, New Jersey, 08544, United States (USA)

²Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, 08540, United States (USA)

Email: * sd5541@princeton.edu

Polystyrene (PS) samples modified with 1-pyrenebutyl methacrylate at three pyrene weight concentrations (0.8%, 1.8%, and 11.5%) were developed and compared to neat PS, through means of free-radical copolymerization. The 1-pyrenebutyl methacrylate monomers can be employed as fluorescent dyes to monitor the local chain dynamics of the interface, as studied in polymer nanocomposite systems [1]. In our work, the 1-pyrenebutyl methacrylate molecules were randomly distributed in between styrene units, with the aim of the study to be to investigate their effect on segmental dynamics. Broadband Dielectric Spectroscopy measurements were conducted employing a Phecos temperature system with an integrated dielectric cell, and an Alpha-A frequency analyzer, all provided by Novocontrol Technologies, Germany. The experiments were done in the temperature and frequency ranges of 30 – 190 °C and 10^{-1} – 10^6 Hz, respectively.

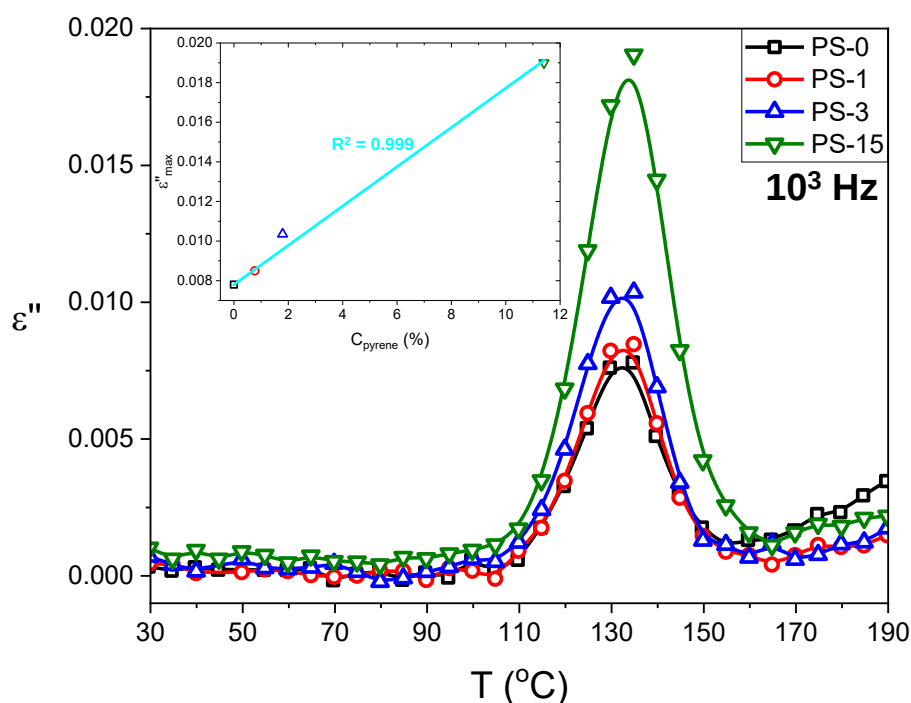


Figure 1. The imaginary part of dielectric permittivity as a function of temperature at 10^3 Hz for all samples under study. As an inset, the maximum value of ϵ'' at temperature loss peak position is plotted against pyrene concentration.

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S02

**Soft Matter Dynamics and Phase Transitions
in Amorphous, Partially Ordered and
Ordered Systems**

Critical behavior and phase transitions in supercooled liquids and glasses

Alois Loidl* and Peter Lunkenheimer

Experimental Physics V, Institute of Physics, University of Augsburg, Augsburg, Germany

Email: *alois.loidl@physik.uni-augsburg.de

Taking the relaxation dynamics of glassforming glycerol as measured by broadband dielectric spectroscopy (Fig. 1) as a prototypical example, we discuss experimental evidence for the occurrence of a sequence of critical temperatures and possible phase transitions in the temperature regime from melting till deep into the glassy state, well below the kinetic glass-transition temperature. We report on critical scaling in the transition region from the microscopic peak to structural relaxation, described by mode coupling theory [1]. In this regime the susceptibility is described by a transient behavior between rattling motion (microscopic peak) and cage decay (α -relaxation) at ~ 10 – 100 GHz. Critical behavior of this process is suppressed by thermally activated hopping processes and, on decreasing temperature, the relaxation dynamics follows a distinct super-Arrhenius behavior where cooperativity plays the dominant role [2,3]. As probed by non-linear dielectric spectroscopy [4,5], this regime is characterized by an increasing correlation length scale of cooperatively reorienting clusters. However, before any critical divergence of length scales can be reached, kinetic freezing processes at the canonical glass transition hide a possible 2nd order phase transition between the supercooled liquid and the ideal glass, expected close to the Kauzmann or Vogel-Fulcher temperature. The possibility of an underlying phase transition in the glassy freezing process is supported by the observation of a striking fragility dependence of the Prigogine-Defay ratio. For high fragilities, it comes close to unity as predicted for continuous phase transitions [6]. Finally, we provide some experimental evidence for the occurrence of a Gardner transition well below the glass temperature, characterized by a further roughening or fractionalization of the potential energy surface [7].

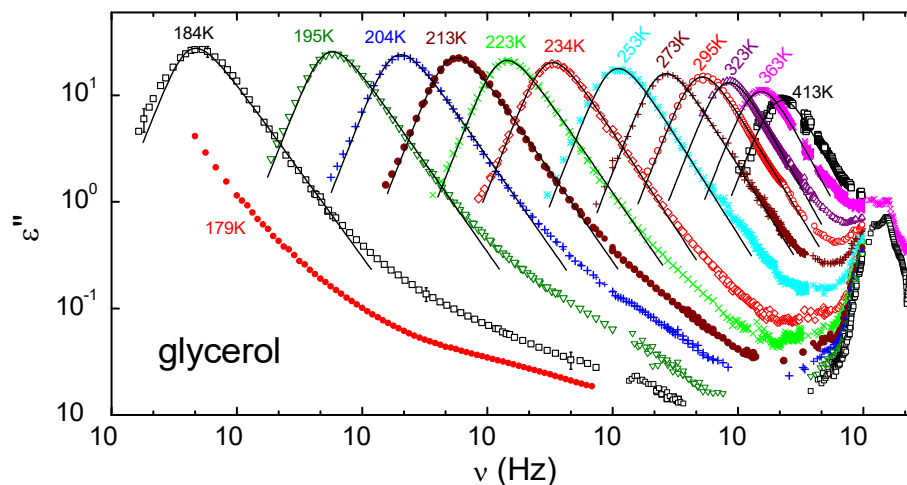


Figure 1. Broadband dielectric spectra of the dielectric loss of glycerol including ageing, THz and FIR data, covering more than 18 decades of frequency [2].

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Ionic transport in supramolecular ionic liquid gels prepared with bis(amino alcohol)oxamides as gelators

**Ana Šantić^{1*}, Marc Brinkkötter², Tomislav Portada¹, Cornelia Cramer²
and Monika Schönhoff²**

¹*Ruđer Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia*

²*Institute of Physical Chemistry, University of Münster, Corrensstraße 28/30, 48149 Münster, Germany*

Email: * asantic@irb.hr

Supramolecular ionogels prepared by the gelation of ionic liquids (ILs) using low-molecular-weight (LMW) gelators are becoming increasingly important as they exhibit a unique combination of properties that make them a superior alternative to traditional polymeric ionogels. In these materials, all physical properties of the parent IL (*i.e.* negligible vapour pressure, nonflammability, good electrochemical and thermal stability, high ionic conductivity) are kept preserved and additionally enriched with a solid-like consistency, self-healing capability and thermoreversible gelation property controlled by their sol-gel transition temperature.

In this contribution, we report a series of novel ionogels of ILs containing imidazolium/pyrrolidinium cations and tetrafluoroborate/bis(trifluoromethylsulfonyl)imide anions prepared using (*S,S*)-bis(amino alcohol)oxamides as LMW gelators. All supramolecular ionogels retain high ionic conductivity and ion diffusion coefficients of their parent IL, even for high gelator concentrations. Interestingly, at low temperatures, an enhancement of the ionic conductivity was observed for ionogels of imidazolium-based ILs with (i) tetrafluoroborate and (ii) bis(trifluoromethylsulfonyl)imide anions. While in the former case the positive effect of gelation on the ionic transport can be attributed to specific interactions between ionic species and gelator molecules [1] in the latter case it can be related to the inhibited crystallization of IL [2]. In contrast to ionic conductivity, the mechanical properties of ionogels show a wide variation depending on the gelator's structure and concentration, indicating that the ionic transport is completely decoupled from the mechanical relaxation.

Acknowledgments

This work was supported by the Croatian-German bilateral projects (MZOS-DAAD) “Development of novel supramolecular ionogels for advanced electrolytes” and “Preparation and characterisation of novel hybrid double-network ionogels with high ionic conductivity and mechanical strength”.

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Glass Transition and Crystallisation of n-Butanol by simultaneous Dielectric Spectroscopy and Neutron Diffraction

Christiane Alba-Simionesco^{1*}, Florence Porcher^{1,2}, Mikkel H. Jensen^{1,3}, Kristine Niss³, Tina Hecksher³

¹ *Laboratoire Léon Brillouin, CEA Saclay, CNRS, Univ Paris-Saclay, France*

² *European Spallation Source, Lund, Sweden*

³ *"Glass & Time"-center, Roskilde University, Denmark*

Email: * Christiane.alba-simionesco@cea.fr

The aim of this work is to better understand the connection between the structural and dynamical changes that occur in the mono-alcohol n-butanol during crystallization. We use a specialized cell designed at the LLB that allows for simultaneous dielectric spectroscopy and neutron diffraction experiments. N-butanol, a monoalcohol, is an ideal candidate for both techniques, addressing two hotly debated aspects: - the dominant dielectric relaxation process occurring in monoalcohols [1], - the putative existence of a liquid-liquid phase transition (LLT) in a simple molecular liquid [2]. We investigate the dynamics and structure of n-butanol at equilibrium, from near its boiling temperature down to its glass transition temperature (T_g), with a particular focus on crystal formation. By combining these two techniques in the supercooled liquid regime, we monitor changes in the Debye peak through dielectric spectroscopy concurrently with structural changes and Bragg peaks appearance, close to T_g or near the melting temperature (T_m). This approach allows us to differentiate between crystal nucleation and growth kinetics during crystal formation. We also discuss various interpretations from the literature, including the proposed amorphous-to-amorphous liquid-liquid transition, a transition to a liquid-crystal state, or the effects of random pinning sites on the dynamics of supercooled liquids.

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Amorphous solid dispersions of Terfenadine into PVP: insights from the molecular mobility characterisation

Emeline Dudognon^{1*}, Jeanne-Annick Bama¹ and Frédéric Affouard¹

¹ Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France

Email: * emeline.dudognon@univ-lille.fr

Active Pharmaceutical Ingredient (API) are generally developed in the crystalline state for obvious long-term stability reasons. However, due to their increasing complexity, molecules under development show poor bio-availability properties resulting from a low solubility in water. To overcome this hurdle, there is a growing interest for several years in the development of amorphous solid dispersions (ASD) in which the amorphous API is dispersed in a polymeric excipient. Indeed, on the one hand, the glassy state of the API shows an enhanced bio-availability compared to the crystalline phase due to its much higher Gibbs free energy. On the other hand, the polymeric matrix hinders the re-crystallisation of the API and promote its dissolution. However, in spite of numerous studies, parameters that control the stability of these ASD are still misunderstood, especially the role played by the molecular mobility (wide amplitude or more localised motions). The aim of the presented research work is to characterise by Dielectric Relaxation Spectroscopy (DRS) the molecular mobility of mixtures of an API, Terfenadine [1], dispersed into a polymer, Polyvinylpyrrolidone PVP K12, to gain insights into the link between dynamics and thermal stability of these ASD.

Co-milling at room temperature of Terfenadine (TFD) and PVP allows to formulate ASD in all the concentration range and the molecular mobility of blends with different TFD contents are deeply characterised by DRS. Results show that a slowing down of the main dynamics occurs as the content of PVP increases, which underlines its anti-plasticisation effect. Moreover, a modification of the shape of the α relaxation is evidenced with the development of a low-frequency component for TFD contents higher than 70 %_{w/w}, which highlights a heterogeneity of the main dynamics. The features (VTF parameters) of both components being those of an α relaxation, this heterogeneity of the dynamics reveals a structural heterogeneity with the coexistence of two amorphous phases of different compositions, each characterised by its own dynamics. These results underline the sensitivity of DRS to probe such structural heterogeneities contrary to thermodynamic techniques (DSC or heat capacity spectroscopy in the glass transition temperature range) according which the blends appear as homogeneous (single glass transition, or single relaxation).

Besides, this dynamic heterogeneity is observed whatever the ASD formulation process (by co-milling or quench from the melt). However, for high TFD contents, only ASD obtained by milling, re-crystallise on heating because of TFD crystalline nuclei remaining from the milling process. We took the opportunity of such behaviour to study in more details the main dynamics and the evolution of its heterogeneity under phase demixing/re-crystallisation of those blends. For different TFD contents, successive recordings at some chosen temperatures showed a complex evolution that can be rationalised by the confrontation with the phase and state diagrams of TFD and PVP blends established by DSC.

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Reorientational Dynamics of Sizable Glass-Formers - Broadband Dielectric Spectroscopy Studies

Marian Paluch^{1*}, Alfred Błażytko² and Marzena Rams-Baron¹

¹ *Institute of Physics, University of Silesia in Katowice, SMCEBI, 75 Pulku Piechoty 1A, 41–500
Chorzów, Poland*

Email: * marian.paluch@us.edu.pl

The overarching objective of our work was to investigate the molecular dynamics of sizable glass-formers formed by partially rigid molecular cores linked to small polar rotors and consequently shed more light on the picture of the reorientation of anisotropic systems with significant moment of inertia [1], [2], [3]. The rich and highly diverse relaxation pattern revealed by dielectric spectroscopy measurements was governed by the location of a dipole moment, its ability to rotate freely, and the degree of coupling to the motion of the entire sizable system. One of the critical aspects of our studies was to check the effect of molecular anisotropy on molecular rotation in the context of the Debye-Stokes-Einstein (DSE) relation. As a result, we pointed out that the DSE relation breakdown depends on the component of anisotropic rotation, which contributes to the dielectric response of a given system. Specifically, the DSE relation was valid throughout the supercooled regime for investigated glass-formers with dipole moment perpendicular to the long molecular axis. On the contrary, a departure from the DSE predictions was observed in the intermediate supercooled regime for glass-formers with dipole moments parallel to the long molecular axis, where only short-axes contributions were relevant in dielectric response.

Acknowledgments

This research was funded as a whole by the National Science Centre, Poland. Project No. 2021/41/B/ST5/00992.

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Multiple relaxations in orientationally disordered benzene-derivatives with strongly restricted rotational dynamics

M. Romanini*, J. F. Gebbia, R. Macovez, L. C. Pardo, M. Barrio, J. Ll. Tamarit

Grup de Caracterització de Materials, Department of Physics & Barcelona Research
Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain
Email: * michela.romanini@upc.edu

Contrary to canonical (structural) glasses, the vitrification process in glasses obtained from orientationally disordered (OD) solids made of rigid molecules involves exclusively rotational motions. These orientational glasses (OGs) are considered as "low-dimensional" systems because, unlike structural glasses where all molecular degrees of freedom are disordered (including orientational, translational, and possibly conformational), in OGs made of rigid molecules, their centres of mass display positional order and only orientational degrees of freedom exhibit disorder. Their only partial disorder makes OD solids ideal playgrounds to investigate fundamental aspects of glass transition and glass dynamics. We present dielectric spectroscopy findings on OD solids with even fewer degrees of freedom, corresponding specifically to ratcheting motions between a limited set of orientations compatible with the crystal structure. Despite the seemingly reduced complexity in terms of degrees of freedom, the dynamics prove to be more intricate than anticipated. Our results on two quasi-planar benzene derivatives, pentachloronitrobenzene^{1,2} and tetrachloro-methyl xylene, which adopt a stacked structure of parallel planes in which the molecules can occupy one of six possible orientations defined by rotation around a fixed axis orthogonal to the planes, indicate the presence of multiple relaxations in both cases. To discern whether these relaxations stem from "caging effects" similar to those leading to Johari-Goldstein secondary relaxations in structural glass formers, or from the intrinsic anisotropy of OD solids, resulting in multiple rotational energy barriers, here we expand our investigation to other benzene derivatives within the same family.

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Relaxation dynamics of amorphous molecular pharmaceuticals and of their binary mixtures near the eutectic composition

Roberto Macovez,* Wahi Noor, Sofia Valenti, Michela Romanini and Josep Lluís Tamarit

Grup de Caracterització de Materials, Department of Physics & Barcelona Research Center in Multiscale Science and Engineering, Universitat Politècnica de Catalunya, Barcelona, Spain)
Email: * roberto.macovez@upc.edu

A major concern of the pharmaceutical industry is the fact that many active pharmaceutical ingredients (APIs) and drug candidates display low oral bioavailability because by their poor aqueous solubility. A physical means to improve dissolution rate is amorphization, but this must be accompanied by kinetic stabilization of the amorphous phase to avoid recrystallization. In many formulations, multiple APIs are present, and in all of them the API is mixed with excipients whose purposes are diverse. Amorphous mixtures have in general higher kinetic stability than pure amorphous compounds thanks to the physical barrier required for phase separation of a mixed sample; for example, it was recently shown [1] that amorphous binary mixtures often display the highest kinetic stability near the eutectic composition [2, 3]. It is therefore interesting to probe the relaxation dynamics and kinetic stability of amorphous pharmaceutical mixtures to assess their viability for amorphous formulations.

In this contribution, we present results on two binary mixtures of compatible APIs, namely, the anxiolytic diazepam-nordazepam pair [4, 5], and the antifungal clotrimazol-bifonazole pair. In both cases, we determine by means of differential scanning calorimetry the equilibrium eutectic phase diagram and variation of glass transition temperature with composition (**Figure 1**), and study the dielectric relaxation response of the mixtures and their crystallization tendency compared with the pure amorphous compounds. Comparison of the secondary relaxations of similar compounds (containing identical functional moieties) indicates that the relaxation time and activation energy of conformational relaxations are similar in molecules containing the same rigid sidegroup capable of reorienting with respect to the rest of the molecule [6].

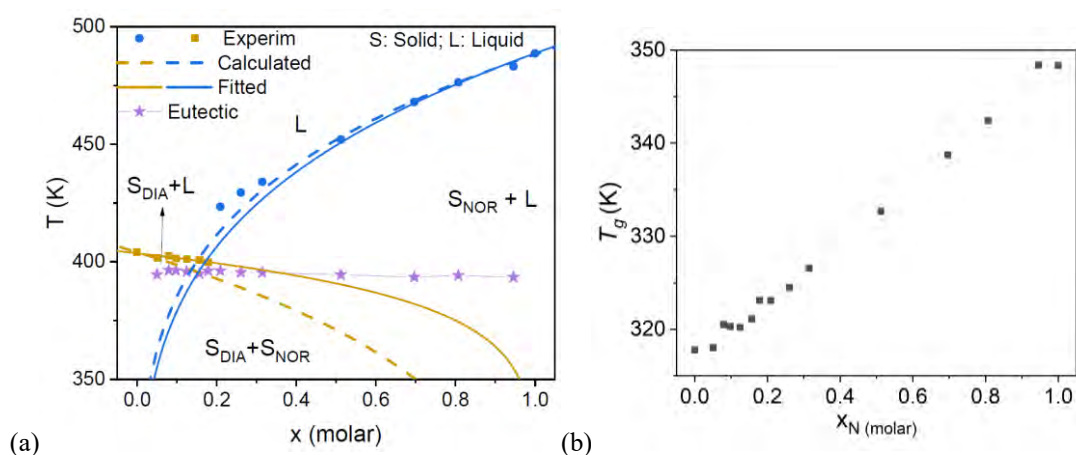


Figure 1. Equilibrium eutectic phase diagram and T_g of the diazepam-nordazepam binary system [4]

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An interpretation of the dielectric spectra of polar nematic phases

Aitor Erkoreka^{1*}, Josu Martinez-Perdiguero¹, Alenka Mertelj², Nerea Sebastián², Richard J. Mandle^{3,4}, Mingjun Huang^{5,6} and Satoshi Aya^{5,6}

¹ Department of Physics, Faculty of Science and Technology, University of the Basque Country
UPV/EHU, Bilbao, Spain

² Jozef Stefan Institute, Ljubljana, Slovenia

³ School of Physics and Astronomy, University of Leeds, Leeds, UK

⁴ School of Chemistry, University of Leeds, Leeds, UK

⁵ South China Advanced Institute for Soft Matter Science and Technology (AISMT), School of Molecular Science and Engineering, South China University of Technology, Guangzhou, China

⁶ Guangdong Provincial Key Laboratory of Functional and Intelligent Hybrid Materials and Devices, South China University of Technology, Guangzhou, China

Email: * aitor.erkorekap@ehu.eus

Ferroelectricity has long been known to occur in liquid crystalline materials, specifically in chiral smectic and columnar phases. In recent years, however, the so-called ferroelectric nematic (N_F) phase has been discovered, in which the molecules lack any positional order and constitutes a true 3D ferroelectric fluid [1]. This groundbreaking discovery has attracted considerable interest, and a zoo of new polar liquid crystalline phases has emerged. Among these is an antiferroelectric splay-modulated nematic phase (termed as N_S or SmZ_A) which appears as a prelude to the N_F phase in some compounds [2]. Measurements of the static dielectric permittivity in the N_F phase give values ranging between 10^3 and 10^5 , while complex relaxation processes are observed in broadband dielectric spectra in the entire phase sequence [3, 4]. In order to fully understand the properties of these polar nematic phases and gain insights into their molecular dynamics, a careful analysis of these data is required.

In this contribution, we present the results of a thorough and systematic set of broadband dielectric spectroscopy measurements for two different compounds, and we propose an interpretation for the observed relaxation modes in terms of collective and non-collective processes, as well as the value of the dielectric constant in the N_F phase.

Acknowledgments

A.E. and J.M.-P. acknowledge funding from the Basque Government Project IT1458-22. A.E. thanks the Department of Education of the Basque Government for a predoctoral fellowship (grant number PRE_2023_2_0113). A.M. and N.S. acknowledge financial support from the Slovenian Research and Innovation Agency (ARIS) (grant numbers P1-0192 and J1-50004). R.J.M. thanks UKRI for funding via a Future Leaders Fellowship (grant no. MR/W006391/1). M.H. and S.A. acknowledge the National Key Research and Development Program of China (Grant No. 2022YFA1405000) and the Recruitment Program of Guangdong (Grant No. 2016ZT06C322).

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Non linear responses in a family of oligomers: inspecting the possible influence of the length of the molecules

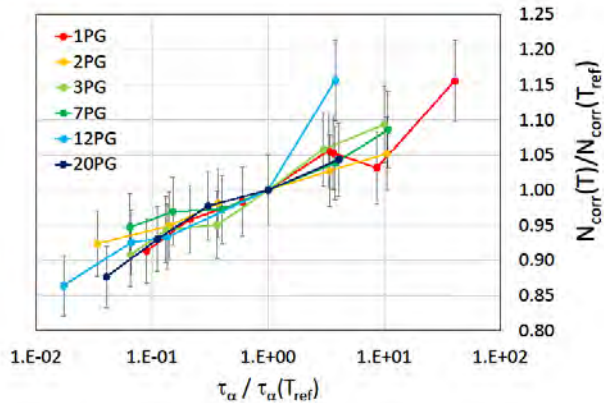
Caroline Raepsaet^{1*}, Christiane Alba-Simionesco², Cécile Wiertel-Gasquet¹ and François Ladieu¹

¹ SPEC, CEA, CNRS, Université Paris-Saclay, 91191 Gif-sur-Yvette, France

² LLB, CEA, CNRS, Université Paris-Saclay, 91191 Gif-sur-Yvette, France

Email: * caroline.raepsaet@cea.fr

The glass transition has already been the subject of numerous studies in past decades [1, 2]. However, the understanding of this phenomenon is far from complete. It seems now well established that supercooled liquids can be pictured, at a given temperature, as a patchwork of regions presenting a wide dispersion of relaxation times. These regions called dynamic heterogeneities (DH) have a typical size of a few nanometers, which increases upon cooling. At variance with the large existing body of studies devoted to molecular systems [3], we focus in this work on a family of oligomers, namely N-Propylene Glycol (OH-[C₃H₆-O]_N-H) where we systematically vary N from 1 to 20. Thus our experimental range goes from a simple molecule (N=1) to oligomer chains which spatial extension should be of the order of that of DH's around the glassy transition temperature T_g. Our linear and nonlinear dielectric experiments yield the following results: first, we find that the static linear susceptibility χ_s is proportional to 1/N, as if the only contribution to the linear response was that of the two ending -OH groups without any significant contribution of the chemical units in between. Second, the 3rd order susceptibilities, $\chi_3^{(3)}$, follow Bouchaud-Biroli predictions [4]: $|\chi_3^{(3)}(f/f_\alpha)|$ presents a hump for all values of N. Since the maximum value of the reduced quantity of $\chi_3^{(3)}$ is proportional to the average number N_{corr}(T) of correlated particles in the DH's, we demonstrate that the variation of N_{corr} as a function of the



α -relaxation time over 4 decades is not influenced by N (refer to Figure 1), even for our longest oligomers whose extension is comparable to that of DH's. We shall discuss our results by comparing them to some of the existing models of literature, e.g. by using the fact that the density of OH bonds varies a lot in our family of oligomers. We will demonstrate that these studies could be expanded to test elastic models, such as the shoving model [5], of the glass transition.

Figure 1. For all the measured oligomers N-PG, (N=1, 2, 3, 7, 12, 20), we draw from the maximum over frequency of $|\chi_3^{(3)}|$ the evolution of the mean number of correlated elements N_{corr} in a dynamic heterogeneity as a function of the relaxation time τ_α . Both N_{corr} and τ_α are normalized by their values at a reference temperature T_{ref}, corresponding to $\tau_\alpha \sim 20$ ms

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The slow Arrhenius process: a simple solution to multiple problems in glass equilibration

Federico Caporaletti¹, Martín Eduardo Villanueva², Harald Bock,³ Biao Zuo⁴, and Simone Napolitano¹

1)Laboratory of Polymer and Soft Matter Dynamics, Université libre de Bruxelles (ULB), Brussels, Belgium

2)Experimental Soft Matter and Thermal Physics, Université libre de Bruxelles, Brussels, Belgium

3)Centre de Recherche Paul Pascal-CNRS & Université de Bordeaux, 33600 Pessac, France

4) Laboratory of Surface & Interface Science
of Polymer Materials of Zhejiang Province, Zhejiang Sci-Tech University, Hangzhou, China

Email: * federico.caporaletti@ulb.be

Equilibration, the set of molecular rearrangements leading to lower energetic states, is commonly associated to the structural α -relaxation, a microscopic relaxation process whose timescale dramatically slows down on approaching the glassy state. Growing evidence shows, however, that equilibration can occur also through an alternative channel provided by the slow Arrhenius process (SAP) [1], a molecular relaxation mechanism previously observed only in polymers.

Here, we show that the SAP is present also in molecular glasses [2] (see Fig. 1). We verify that, especially at temperatures where the α -relaxation is too slow, the SAP can provide an efficient pathway for free-energy reduction. We demonstrate that the SAP is responsible for common equilibration processes in molecular glasses, as surface crystallization, orientational ordering and physical aging. Our arguments are supported by a simple model, derived from solid principles of nonequilibrium statistical physics, that allows us to identify, without any arbitrary parameter, the molecular timescale of the slow Arrhenius process responsible for the equilibration kinetics [3]. These results reinforce the universal character of the SAP and highlight its connection with orientational ordering and surface mobility.

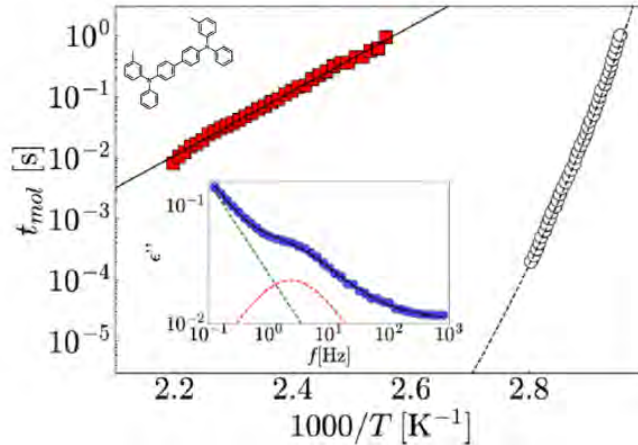


Figure 1. Relaxation map of TPD (film thickness 30 nm). The white symbols indicate the characteristic timescale of the α -relaxation, while the red squares indicate the SAP. The insets show the imaginary component of the complex dielectric permittivity (blue circles) of TPD at 421 K. The red and green dashed lines, respectively, show the contributions of conductivity and molecular relaxation to the spectrum, while the black solid line provides their sum

Acknowledgments

F.C. is a Chargé de Recherche of the Fonds de la recherche scientifique-FNRS. We acknowledge financial support from Action de Recherche Concertée ULB under grant ARC 20061 “SADI”.

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Molecular dynamics of halogen monoalcohols at different thermodynamic conditions

Kinga Łucak^{*}, Anna Z. Szeremeta, Joanna Grelska, Karolina Jurkiewicz, Sebastian Pawlus

*A. Chelkowski Institute of Physics, University of Silesia in Katowice, 75 Pułku
Piechoty 1, 41-500 Chorzów, Poland*

** kinga.lucak@us.edu.pl*

Monoalcohols represent a significant research area due to their ability to form various supramolecular structures and their manifestation in the dielectric spectra. However, so far, the properties of these alcohols are studied mainly as a function of the hydroxyl group's position and the side groups' size [1].

In this presentation, we analyze the molecular dynamics of another family of monoalcohols with halogen atoms (chlorine, bromine, iodine) at different thermodynamic conditions using broadband dielectric spectroscopy (BDS), Fourier transforms infrared (FTIR) spectroscopy and molecular

dynamics (MD) simulations. We aim to understand how halogen atoms of Cl, Br, and I affect molecular association processes and how changes in thermodynamic conditions, including pressure, modify the architecture of supramolecular structures. BDS was used to assess the effect of the halogen atom on the properties of the Debye process. MD simulations and FTIR spectroscopy have been used to investigate whether there are other dipole-dipole, halogen-halogen interactions that compete with classical H-bonds. We have shown that the position of the hydroxyl group and the presence of halogen atoms significantly modify the relaxation dynamics, including structural relaxation, affecting molecular orientation and intermolecular interactions [2]. Furthermore, studies have shown that pressure modifies the behavior of monoalcohols, affecting the stability and architecture of the supramolecular structure.

In summary, our study of a new group of monoalcohols with a halogen atom has contributed to a better understanding of the self-organization processes in alcohols with a single -OH group.

Acknowledgments

The research was financed with financial support from the National Science Centre, Poland within the OPUS Project No. UMO-2019/35/B/ST3/02670, which K. Ł., J.G., K.J., K. K., and S.P. would like to acknowledge.

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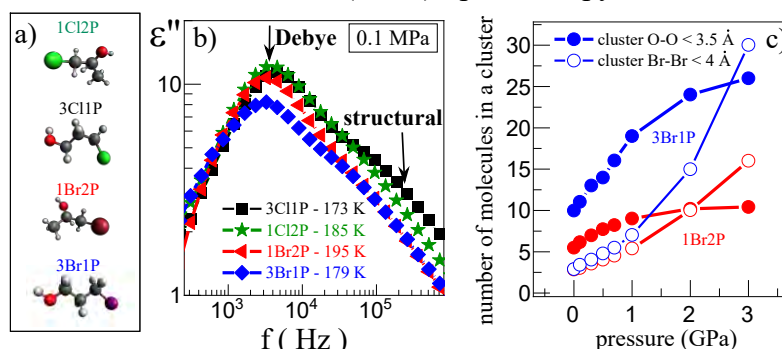


Figure 1. The chemical structures of the studied alcohols (a). Comparison dielectric loss spectra at ambient pressure for studied alcohols characterized by the same relaxation times (b). The evolution of the average number of molecules in hydrogen-bonded and halogen clusters with pressure (c).

Image of the internal solid-state rotation in the dielectric response of sizable molecules with polar rotors

Marzena Rams-Baron*, Alfred Błażytko, Maria Książek, Joachim Kusz, Marian Paluch

*August Chelkowski Institute of Physics, University of Silesia in Katowice, 75 Pulku Piechoty 1,
41- 500 Chorzow, Poland*

Email: * marzena.rams-baron@us.edu.pl

Since the discovery of the first artificial light-driven molecular system in 1999 [1], significant advancements have been made in developing molecular rotary machines, leading, among others, to a wide range of dynamic crystalline materials. This progress has dramatically heightened interest in studying the rotor's solid-state dynamics and made dielectric spectroscopy a valuable tool for polar rotors investigation. The structural design of dynamic crystals (also called amphidynamic crystals) involves using components forming a crystal lattice linked to dynamic units that undergo fast rotations in the crystalline interior (rotors). Given the relative novelty of the topic, the image of such internal rotor dynamics in dielectric research is still evolving and not yet fully established. Due to the possibility of conducting experiments across a broad spectrum of temperatures and frequencies, dielectric studies on molecular rotors enable the observation of phenomena that were previously inaccessible through other techniques, thereby opening new research pathways for the dielectric community.

In our studies, we used dielectric spectroscopy to study the dynamics of variously substituted fluorophenyl rotors in sizable molecules. We demonstrated that variations in fluorine atom position within the rotating unit notably affected the rotational behavior observed in crystals and probed using the BDS method. We take advantage of a recently reported new class of glass-forming molecules with a nonpolar sizable core and a small polar unit with high rotational freedom [2] whose dynamics are preserved in a crystalline state. Thus, the rotor dynamics could be investigated in glassy and crystalline environments. We found out that only by modifying the environment around the rotating unit we observed notable variations in spectral parameters. Our results show that internal rotation, like a probe, can sample the immediate surroundings with high sensitivity to molecular-level changes that impact the rotation parameters. [3] In crystals, we identified two patterns of the dielectric response; each pattern has a “fingerprint” of the potential asymmetry and reflects the impact of the rotor's surroundings and the character of involved rotor-stator interactions. Our observations, supported by an analysis based on an asymmetric double well-potential model, show how observed spectral differences encoded some molecular-level information important for rotor performance. It is essential to develop our intuition for the effective evaluation of rotor properties using the dielectric method.

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Self-assembly in bottlebrush polymers detected using dielectric spectroscopy

Thulasinath Raman Venkatesan¹, Yeerlan Adeli^{1,2}, Frank A. Nüesch^{1,2}, and Dorina M. Opris^{1,3*}

¹ Laboratory for Functional Polymers, EMPA, Überlandstrasse 129, 8600 Dübendorf, Switzerland

² Institute of Chemical Sciences and Engineering, EPFL, 1015 Lausanne, Switzerland

³ Department of Materials, ETH Zurich, 8093 Zurich, Switzerland

Email: * Dorina.opris@empa.ch

Bottlebrush (BB) polymers consist of repeating units with long side chains. At low mechanical strains, the backbone can be stretched relatively easily and at higher strains, when it is stretched to its contour length, the polymer shows strain stiffening [1]. This behavior leads to a high dielectric breakdown strength and high strain at break, making them suitable for dielectric applications such as sensors and transducers. In this work, a BB random copolymer was synthesized consisting of a polynorbornene backbone that carries poly(dimethylsiloxane) (PDMS) chains and nitrile groups in an almost 1 to 1 ratio and in a random sequence (Figure 1a) [2]. The BB polymer forms free-standing films with excellent elastic behavior inspite the lack of chemical crosslinks. Dynamic Mechanical Analysis revealed a low temperature peak at -120 °C, characteristic of a glass transition in PDMS chains, and traces of a second transition above -40 °C. Hence, dielectric spectroscopy was used to study these transitions in detail, which confirmed them both to be glass transitions (Figure 1b) —uncharacteristic of a random copolymer. This, along with the observation of a strong Maxwell-Wagner interface polarization, suggested self-segregation of the PDMS and the polymer backbone, whose aggregation is facilitated by the presence of the nitrile group. This hypothesis was confirmed using small-angle X-ray scattering. All these results concluded that the polynorbornene backbone aggregates to hard domains and the non-polar PDMS to soft domains, responsible for the observed thermoplastic elastomer behavior.

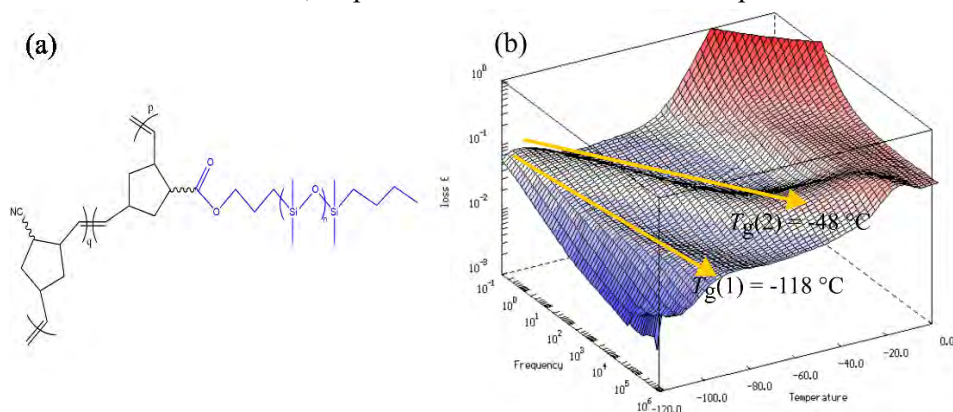


Figure 1. (a) Chemical structure of the bottlebrush polymer. (b) 3D dielectric loss plot of the bottlebrush polymer as a function of frequency and temperature.

Acknowledgments

We gratefully acknowledge the European Research Council (ERC) for financial support under the European Union's Horizon 2020 research and innovation programme (grant agreement No 101001182). We thank Prof. M. Wübbenhorst (KU Leuven, Belgium) for providing DCALC software used for the analysis of dielectric spectroscopy results.

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S03

**The Impact of External Variables in
Dielectric Properties**

Organic Magnetoresistance – a test bed for Dielectric-Spin interactions

Paul Ben Ishai¹, Amos Bardea² and Roshlin Kiruba¹

¹ Department of Physics, Ariel University, Ariel, Israel

² Department of Electrical engineering, Holon Institute of Technology, Holon, Israel

Email: * paulbi@ariel.ac.il

Organic magnetoresistance (OMAR) refers to the change of resistance in an organic material by the application of a magnetic field[1]. It has recently become a ‘hot’ topic for its ability to show organic spintronics at room temperature and for use as magnetic RAM devices[2], [3]. OMAR materials typically consist of a conducting polymer laced with ferromagnetic particles and sandwiched between electrodes. We demonstrate such a composite made from Poly-pyrrole/ polydimethylsiloxane (PPy/PDMS) matrix with nickel nanoparticle. Using a simple home- made time domain impedance spectrometer and a current pulser we demonstrate spin interaction at room temperature in the impedance spectra of the composite. The sample is in series with a 50 Ω resistor under a constant voltage of 3V (see the figure 1(b)). A pulsed magnetic field (time duration ~ 1 ms and amplitude approximately 0.2 Tesla) causes an increase in the impedance and the periodic signature of a spin interaction (see figure 1 (a)). The origin of this behaviour can be traced to the polaron conduction mechanism of delocalized π -electrons along the PPy polymer backbone and the spin they carry. A semiclassical theory is presented for the observed behaviour.

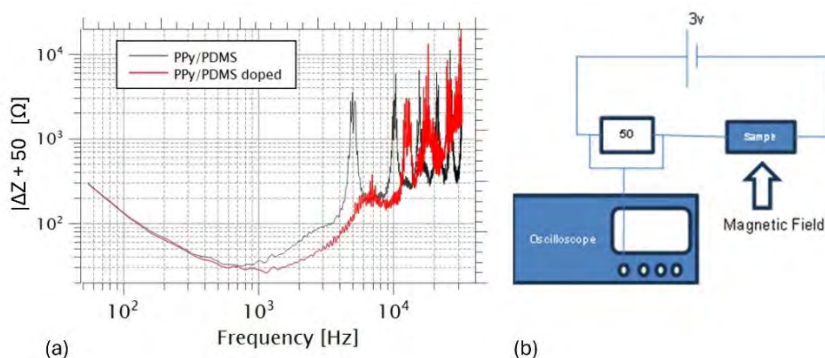


Figure 1. (a) The impedance spectra of PDMS/PPy layer when exposed to a time varying magnetic field. Periodic oscillations in the spectra point towards spin interaction with the magnetic field. The schematic of the time domain setup (b) used to make the measurements.

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Dielectric Spectroscopy of Vapor Deposited Films

Ranko Richert*

School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, USA

Email: * ranko@asu.edu

Physical vapor deposition of molecular glass-formers can lead to exceptional material properties if deposited onto a substrate temperature around $0.85T_g$ at a rate not exceeding 1 nm/s, where T_g is the glass transition temperature of the bulk material. Such glasses (amorphous solids) can display high density and kinetic stability as well as low energy and entropy states. It is estimated that it may take millions of years of aging a glass obtained by cooling the melt to achieve comparable properties. The typical explanation for such glasses approaching the very low fictive temperature of an 'ideal glass' rests on the combination of a low temperature and a highly mobile surface layer that allows molecules to find low energy states prior to becoming buried by subsequent deposition [1].

Using substrates equipped with interdigitated electrodes and employing a high resolution dielectric measurement system, the deposition of such glasses can be monitored *in-situ*, as well as the aging of the sample for long times after deposition had stopped.

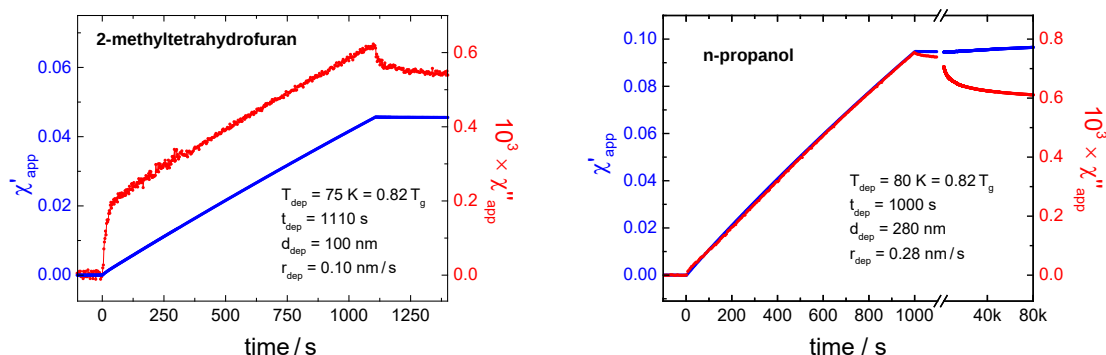


Figure 1. Susceptibilities, χ'_{app} and χ''_{app} at $\nu = 1$ kHz, versus time of a 2-methyltetrahydrofuran (MTHF, left) and an *n*-propanol (NPOH, right) film during deposition at a substrate temperature $T_{dep} = 0.82T_g$. Note the initial rapid increase of χ''_{app} seen for MTHF is absent in the case of NPOH.

Figure 1 shows dielectric deposition curves for two materials: MTHF [2] and NPOH [3], where the real part of susceptibility, χ' , rises linearly in both cases due to a constant deposition rate. MTHF displays a fast initial rise of the loss, χ'' , an indication of a mobile surface layer, while NPOH shows no such feature. This correlates with MTHF but not NPOH achieving a kinetically highly stable state, in strong support of kinetic stability being mediated by surface mobility.

Acknowledgments

This work was supported by the National Science Foundation under Grant No. CHE- 2153944.

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Dynamics of monohydroxy alcohols: Rouse dynamics, chain swapping, and the Debye relaxation

Shiwang Cheng^{1*}, Shalin Patil¹ and Shinian Cheng²

¹ Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI, United States of America

² Department of Chemistry, University of Wisconsin Madison, Madison, WI, United States of America
Email: * chengsh9@msu.edu

Monohydroxy alcohols (MAs) exhibit an intriguing strong dielectric dispersion, the Debye relaxation, at time scales much longer than their structural relaxation, whose origin remains active discussion. Through a combination of rheology and dielectric, we have unraveled new features of the dynamics of MAs from their structural relaxation to the Debye time [1,2]. In particular, our observations showed the following: (i) an interesting relationship between the structural relaxation time, τ_α , and the Debye time, τ_D , with τ_D^2/τ_α following an Arrhenius temperature dependence; (ii) the presence of an intermediate relaxation processes with characteristic time τ_m between τ_α and τ_D of MAs that are both dielectric and rheology active; (iii) τ_m agrees excellently with the hydrogen bonding exchange time of MAs from NMR measurements. These observations lead to a novel theoretical understanding of the dynamics of MAs across different time scales, i.e., the living polymer model (Figure 1). We will discuss these findings and the details of the theoretical development in the presentation.

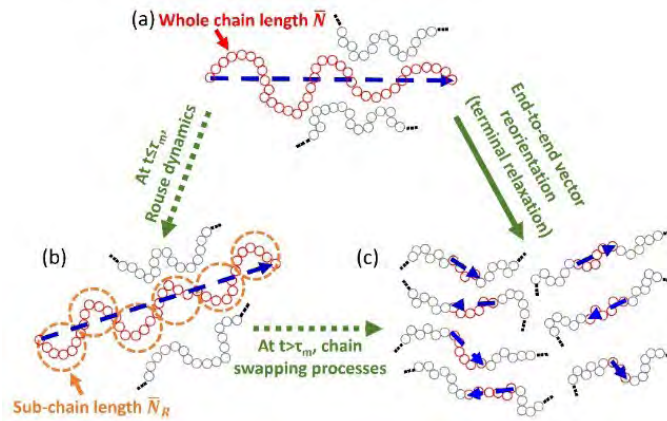


Figure 1. Relaxation mechanism of MAs with chain structures, where the grey and red circles represent individual alcohol molecules. The chains with red and grey circles are the test and surrounding chains. The dashed blue arrow represent the end-to-end dipole of the test chain or sub-chain. (a) A representative test chain with length $\bar{N}$ and end-to-end vector at $t = 0$. (b) At $t \leq \tau_m$, chain breakage has not yet taken place and Rouse dynamics dominate. (c) At $t > \tau_m$, chain breakage must happen. Chain-swapping leads to fragmentation of the original chain (the red circles) and facilitates chain end-to-end reorientation. (Figure adopted from Ref. 2)

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This work was supported by Michigan State University Discretionary Funding Initiative (MSU-DFI).

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Optical manipulation of chromophores in a molecular glass former: from photofluidization to random pinning

Eden Dzik^{1,2}, Paul Datin^{1,2}, Christophe Fajolles², Jean-Pierre Dognon², Cécile Wiertel-Gasquet¹, David Carrière², and Francois Ladieu^{1*}

¹ CEA, CNRS, SPEC, SPHYNX, Université Paris-Saclay, 91191 Gif-sur-Yvette, France

² CEA, CNRS, NIMBE, LIONS, Université Paris-Saclay, 91191 Gif-sur-Yvette, France

Email: * francois.ladieu@cea.fr

Despite decades of research, the nature of glasses is poorly understood [1]. To get new insights, we have built a new setup [2] where a small fraction of chromophores is dispersed in a transparent glass former and where both the optical absorption A , its anisotropy δA , as well as the dielectric susceptibility χ can be measured simultaneously (see Fig. 1) at a well controlled temperature T , around the glass transition temperature $T_g = 363\text{K}$. Both the chromophores and the organic glass former are chemically similar, apart from the azobenzene group responsible for the strong optical absorption of the chromophores. Starting from equilibrium at a given T and angular frequency ω , we observe dielectric variations $\delta\chi(\omega, T)$ when switching on the pumping LED(s), which are strongly coupled to that of A . We show [2] that $\delta\chi(\omega, T)$ is not due to spurious effects (e.g. the small heating induced by pump light absorption). Close to T_g , we demonstrate that $\delta\chi(\omega, T)$ comes from a light-induced reduction of the molecular relaxation time τ_α , which is divided by a factor $K_{\text{diel}}(T) > 1$. We show that K_{diel} is made of two antagonist effects: the strongest one is that light accelerates glassy dynamics (photofluidization) by a factor $K_\phi > 1$. This is predicted in [3] where the reduction of the free energy barriers due to isomerizations is computed. Extracting K_ϕ from the flux dependence of τ_c (see Fig. 1), we show that, systematically, $K_\phi > K_{\text{diel}}$. Because K_ϕ/K_{diel} increases with the fraction x_{or} of oriented chromophores, we interpret $K_{\text{pin}} = K_\phi/K_{\text{diel}}$ as the signature of a random pinning effect where pinning a small fraction of molecules strongly slows down glassy dynamics [4]. As the effect of random pinning on glassy dynamics is a distinctive feature of theories where glass formation is driven by a thermodynamic critical point, its observation, already attempted in [5], is of great interest for understanding the nature of glasses.

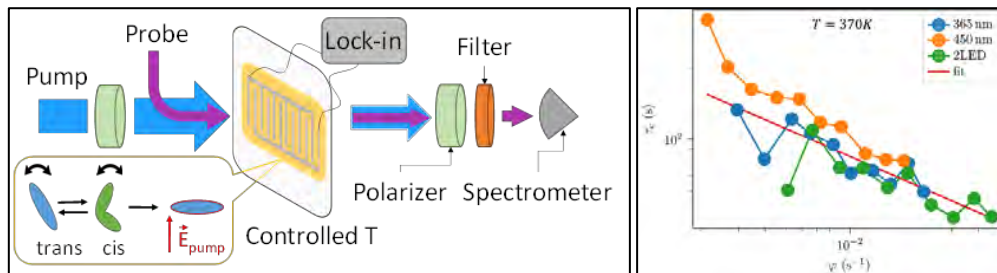


Figure 1. Left: schematic diagram of our setup. The azo-doped glass former is deposited in the yellow zone, on top of two interdigitated transparent electrodes. This allows to simultaneously record the dielectric spectrum and the optical absorption properties, using a probe LED at a wavelength different from that of the pumping LED(s). Because of the isomerization cycles $\text{trans} \rightarrow \text{cis} \rightarrow \text{trans}$ (pictured in the lower left part), a fraction x_{or} of the chromophores gets oriented along the polarization of the pump, yielding an anisotropic absorption δA . Right: Characteristic relaxation time τ_c of δA after switching off the pumps. Its dependence in the rate of isomerizations reveals the photofluidization of the glassy system.

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S04

Water, Hydrogen Bonded and Biological Systems

Water organization in amphiphilic block copolymers with thermoresponsive behaviour

A. Kyritsis^{1*}, S. Kripotou^{1,2}, A. Miasnikova³, A. Laschewsky^{3,4}, C. M. Papadakis⁵

¹ National Technical University of Athens, Zografou Campus, 15780 Athens, Greece

² University of West Attica, 12244, Athens, Greece

³ Universität Potsdam, Karl-Liebknecht-Straße 24-25, 14476 Potsdam-Golm, Germany

⁴ Fraunhofer Institut für Angewandte Polymerforschung, 14476 Potsdam-Golm, Germany

⁵ Technical University of Munich, James-Frank-Straße 1, 85748 Garching, Germany

Email: * akyrits@central.ntua.gr

Stimuli responsive polymers represent a special class of soft materials that have attracted strong attention due to their numerous applications. In the case of the thermoresponsive polymers, the key point for its thermoresponsive behavior in aqueous solutions is its amphiphilic character. The balance between the attractive and the repulsive interactions, that coexist between the polymeric segments and the water molecules, at each temperature determines the state of the mixture: one phase of homogeneous mixture or a two-phase system [1]. In this work we study the impact of those interactions in the water organization within thermoresponsive diblock and triblock copolymers consisting of poly(methoxy diethylenglycol acrylate) (PMDEGA) and polystyrene (PS) blocks [2], in a broad range of polymer/water compositions.

Differential Scanning Calorimetry (DSC) and Broadband Dielectric Spectroscopy (BDS) techniques were employed for the investigation of the role of water to the two characteristic transitions: glass to liquid, at subzero temperatures, and LCST-type coil to globule transition in the thermoresponsive copolymers. The plasticization action of water is systematically studied at varied water concentrations in the copolymers. Furthermore, the employed experimental techniques allow for the determination of the non-freezable and the crystalline water fraction at each hydration level. In addition, BDS has been widely used in the investigation of the hydration properties of materials [3], while it has proven very powerful for the investigation of the features of the various hydrogen bonding networks adopted by the interfacial water molecules [4].

The results of this study are discussed in terms of hydrogen bonding, hydrophobic interactions, ordered (ice-like) and disordered state of interfacial water. Interestingly, our results provide evidence that the water phase separation process during water crystallization at subzero temperatures (ice formation) exhibits similarities with the water detaching process during the thermoresponsive phase transition.

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Sensing devices that use electrical double-layers and impedance spectroscopy: design strategies

Henrique Leonel Gomes

Instituto de Telecomunicações e Departamento de Engenharia Electrotécnica e de Computadores, Universidade de Coimbra, 3030-290 Coimbra
Email: hgomes@uc.pt

In modern sensing technologies, diverse devices like metal-insulator-semiconductor (MIS) structures and transistor-like devices use emerging semiconductors, including organic-based semiconductors and 2D materials. These semiconducting materials establish interfaces with wet or liquid substances, including skin, complex liquids, living cells, food, etc. These interfaces, known as electrical-double-layers (EDLs), are highly charged and behave like capacitors. Minute changes in the impedance of these interfaces can be detected through small signal-impedance measurements. However, probing these capacitive layers using impedance techniques is challenging. Small changes in the AC impedance can only be detected if the device structure is properly optimized. This device design strategy includes careful consideration of the device geometry, dimensions, and electrical properties of the materials used.

This contribution focuses on designing strategies for creating reliable devices capable of probing capacitive EDLs for sensing purposes. The design of these devices involves modeling of the device structure using equivalent circuit networks. This contribution also includes a series of recipes for device optimization. Additionally, it provides examples of applications in environmental sensing and bioelectronics.

Acknowledgments

We acknowledge support from the Portuguese Foundation for Science and Technology (FCT/MCTES), The project 2022.06979.PTDC and institutional projects UIDB/EEA/50008/2020 (Instituto de Telecomunicações, IT), UIDB/04326/2020 (DOI:10.54499/UIDB/04326/2020),

Dynamics of Ice in Confinements and Mixtures: Combined BDS and NMR Studies

Michael Vogel*, Sandra Krüger and Elisa Steinrücken

Institute for Condensed Matter Physics, TU Darmstadt, Germany

Email: * michael.vogel@pkm.tu-darmstadt.de

BDS and NMR studies provided valuable information about the defect-coupled and preparation-dependent dynamics of hexagonal bulk ice [1-3]. We combine these methods to investigate molecular reorientations in ice phases that form in nano-sized confinements and in water-rich mixtures. Because water crystallizes as stacking disordered ice comprising cubic layers interlaced with hexagonal ones under such circumstances [4], one may expect more complex dynamics than in phase-pure bulk ices. Here, we focus on stacking disordered ice in mesoporous silica with different pore diameters and in mixtures of water with various alcohols and peptides.

For all these confinements and mixtures, we find good agreement of BDS and ¹H and ²H NMR results, see Fig. 1. BDS and NMR susceptibility peaks of ice are broad in such environments [5,6], consistent with stacking disorder, and the temperature dependence is described by an Arrhenius law with $E_a \approx 0.41$ eV, in agreement with data for ice in other confinements and mixtures [7,8]. Despite a common activation energy, the correlation times are shorter in mixtures and narrower confinements [5,6] than in wider ones [7], most probably due to different defect concentrations.

In confinements, ice coexists with unfreezable water at $T < T_m$. The temperature dependence is higher for water than ice in the whole range of coexistence, including the low-temperature region, where reorientation dynamics of interfacial water is commonly characterized by an activation energy of $E_a \approx 0.50$ eV, see Fig. 1. 2D ²H NMR spectra reveal that the coexisting ice and water phases exchange molecules on a time scale of milliseconds at ~ 220 K [9]. Thus, the ice-water equilibrium is highly dynamic, i.e., stack disordered ice crystallites steadily form and disintegrate.

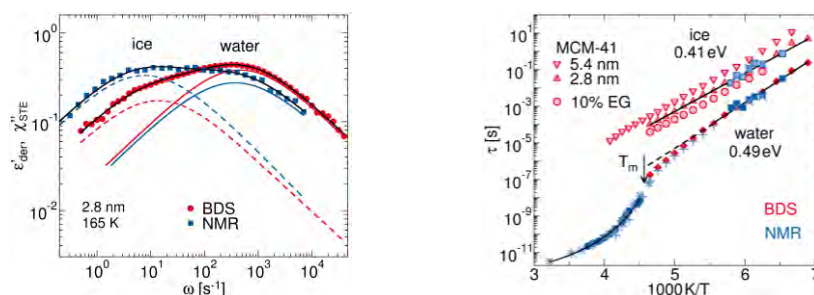


Figure 1. Results for H₂O and D₂O in MCM-41 pores with diameters of 2.8 and 5.4 nm and in a mixture with 10 mol% ethylene glycol: (left) BDS and NMR susceptibilities for 2.8 nm pores at 165K. The lines are fits with a superposition of two Cole-Cole functions, reflecting the coexisting ice and water phases. (right) BDS and NMR correlation times of water and ice. $T_m = 219$ K in 2.8 nm pores is indicated [6].

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Unravelling the Glass Transition of Confined Water: A Calorimetric and Dielectric study

Silvina Cervený^{1,2*}

¹ Centro de Física de Materiales (CSIC, UPV/EHU)-Materials Physics Center (MPC), Paseo Manuel de Lardizabal 5, San Sebastián 20018, Spain.

² Donostia International Physics Center (DIPC), San Sebastián 20018, Spain

Email: *silvina.cervený@ehu.es

The current understanding of the glass transition temperature (T_g) of confined and bulk water is highly debated in the recent literature, and determining it remains a significant challenge. In this talk, we present a calorimetric study in the model system of confined water [1], MCM-41, identifying three different contributions which can be associated with a glass transition [2]. Using annealing experiments, it is demonstrated that only one represents a glass transition, and water confined in MCM-41 undergoes a T_g at ~170 K for a confinement size of 2.1 nm. The other two relevant calorimetric features, detected at 120 and 210 K, are linked to a "shadow glass transition" and interfacial effects, respectively. Moreover, we can access the dynamics of confined water by using dielectric spectroscopy and calorimetric step response in the linear regime. We will show how the features observed in the dynamics of confined water can be correlated to its calorimetric response.

Acknowledgments

We thank the groups of Michael Vogel (Darmstadt, Germany), Daniele Cangialosi (San Sebastian, Spain) and Yuri Feldman (Jerusalem, Israel). Funded by MCIN/ AEI /10.13039/501100011033 is also acknowledge.

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Is Nanoconfined Water Electrically ‘Dead’ or ‘Alive’?

Syed A. M. Tofail

Department of Physics, and Bernal Institute, University of Limerick, Ireland

Email: Tofail.Syed@ul.ie

Around 10-25% of water in a biological cell is confined within wires’ of interconnected hydrogen-bonded water that may support proton translocation into and through ion channels. Geologically confined water, on the other hand, affects the Earth’s mantle rheology, lithosphere–asthenosphere boundary, and water reservoir in the mantle transition zone. Interfacial water confined within a narrow cavity (e.g., less than 2 nm) has been considered as ‘glassy’ or electrically ‘dead’. To the contrary, we observe 3D ordering of confined water leading to a pseudo-tetrahedral configuration, multiple glass transitions and significant electrical activity, including an unprecedented, and somewhat paradoxical, local dewetting of the hydrophilic sites of the nanocavities at ambient temperature. This ‘free’ and relatively fast ‘liquid’ water-like movement of previously thought to be ‘bound’ water contained within these nanocavities makes us to belief that water is ‘alive’ and kicking even within nanoconfinements.

Exploring Non-Contact Ultrasound Technology via Sub-Terahertz Photoacoustics for Human-Oriented Applications

Yasuaki Monnai^{*}

¹Research Center for Advanced Science and Technology, The University of Tokyo,
3-5-1 Komaba, Meguro-ku Tokyo, Japan
Email: *monnai@star.rcast.u-tokyo.ac.jp

Non-contact ultrasound generation based on the photoacoustic effect using short optical pulses has been widely used for biomedical and industrial applications. However, generating and detecting photoacoustic signals in water or aqueous samples requires careful choice of the excitation wavelength. We have recently demonstrated that continuous-wave (CW) ultrasound can be generated in aqueous samples with CW sub-terahertz waves modulated at acoustic frequencies [1]. The sub-terahertz waves exhibit a significant water absorption coefficient akin to peak near-infrared wavelengths while offering transmittance through diverse materials. This facilitates the generation of broadband ultrasound in a variety of media.

Leveraging recent advances in high-frequency electronics, we present the development of a compact experimental system for modulated sub-terahertz irradiation with a potential for further miniaturization. We then present proof-of-concept applications of the effect as a means of acoustic communication and sensing connecting between wet and dry medium, e.g. underwater drones or implantable devices, in which conventional wireless communication faces difficulties [2]. We also introduce other human-oriented sensing projects based on terahertz technology [3].

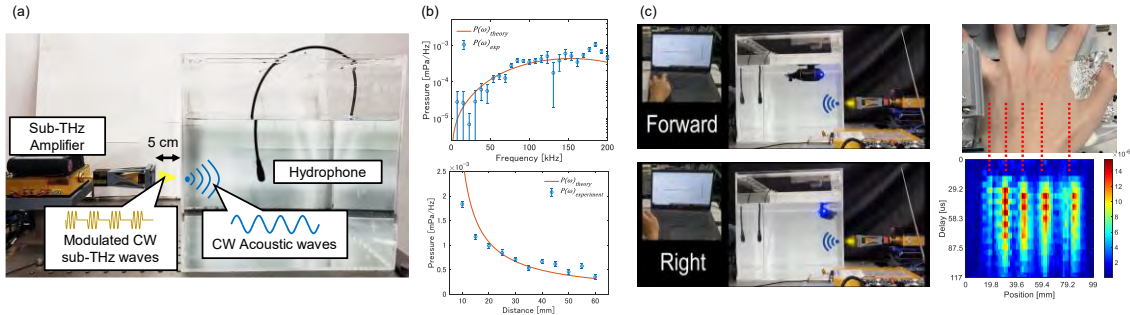


Figure 1. (a) Experimental setup for generating acoustic signals with sub-terahertz irradiation. (b) Frequency characteristics of the generated ultrasound (top) and its spatial decay at 92 kHz (bottom). (c) Demonstration of underwater communication (left) and anatomical imaging of human hands (right).

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Duped or Doped? Utilizing Microwave Spectroscopy for Autologous Blood Doping Detection

Yuri Feldman^{1*}, Gregory Barshtein², Leonid Livshits³, Cindy Galindo¹ and Paul Ben Ishai⁴

¹ Institute of Applied Physics, The Hebrew University of Jerusalem, Israel

² The Faculty of Medicine, The Hebrew University of Jerusalem, Israel

³ Institute of Veterinary Physiology, Vetsuisse Faculty, University of Zürich, Zurich, Switzerland.

⁴Department of Physics, Ariel University, Israel

Email: * yurif@mail.huji.ac.il

Microwave dielectric spectroscopy (MDS) has shown promise in detecting autologous blood doping (ABD), a form of cheating in sports where athletes enhance performance by reinfusing their own stored blood. A cohort study involving volunteers demonstrated that MDS effectively detects alterations in blood composition induced by blood donation and auto-transfusion, a hallmark of ABD. ABD involves withdrawing blood weeks before a competition, storing it, and then reinfusing it shortly before the event, resulting in a rapid performance enhancement. While challenging to distinguish from the effects of altitude training, ABD remains prevalent due to its difficulty in detection [1-4].

Various approaches, including the Athletes Biological Passport (ABP) and the Abnormal Blood Profile Score (ABPS), aim to indirectly detect ABD through longitudinal monitoring of blood parameters [4-6]. However, these methods lack specificity and may yield false positives due to the influence of other factors on hematological parameters.

MDS offers a direct method for ABD detection by monitoring minor variations in cellular water dynamics associated with the age-dependent changes in red blood cells (RBCs). The induced production of new RBCs after blood collection and the pre-competitive auto-transfusion of stored RBCs alter the cellular hydration state, which can be effectively detected by MDS. Therefore, we propose that MDS holds promise as an effective and robust tool for detecting ABD.

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Slow dynamics of intracellular water measured by BDS with Kramers-Kronig relations and Bruggeman–Hanai equation

Hiroaki Matsuura^{1*}, Kosei Kawai¹, and Ryo Shirakashi¹

¹ Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro, Tokyo, Japan

Email: * matsumura@iis.u-tokyo.ac.jp

The picosecond orientational dynamics of intracellular water was measured by broadband dielectric spectroscopy (BDS). In the dielectric spectroscopy of aqueous systems containing ions, such as cell suspensions, the dielectric loss spectrum is affected by the contribution of the direct current (DC) conductivity σ , which significantly overlaps the dielectric relaxations related to the slow dynamics of water molecules distributing in sub-GHz frequency range. In this study, the dielectric loss without this contribution (Ohmic loss) was obtained by the Kramers–Kronig (KK) transform of the experimentally obtained dielectric dispersion [1].

Using this technique, Jurkat cells (human T lymphocyte cells) suspended in aqueous sucrose solutions were examined at 25 °C with a frequency range up to 43.5 GHz [2]. The Bruggeman–Hanai equation was employed to obtain a cellular dielectric spectrum without extracellular contributions from the measured complex permittivity of the cell suspensions. By analyzing the γ process around 10^{10} Hz based on the Debye relaxation function, two types of water (bulk-like water and hydration water with slower molecular dynamics) were observed. An increase in the fraction of intracellular slower water was observed in the dehydrated cells (Figure 1).

Also, the relaxation time of intracellular water determined by the hydrogen bond strength calculated by shortwave FT-IR spectrum [3-5] will be discussed.

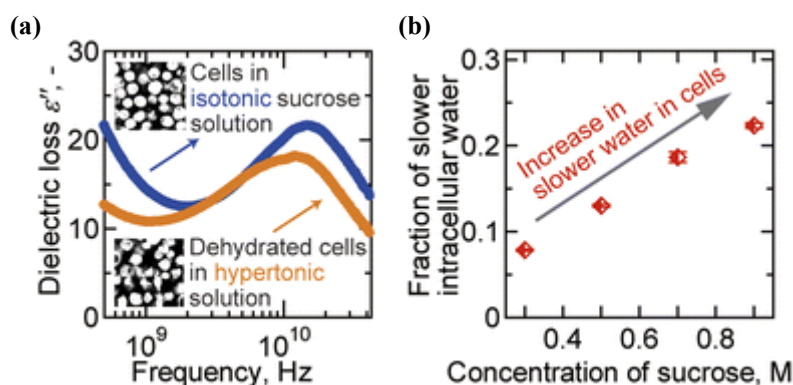


Figure 1. (a) The dielectric loss of Jurkat cells suspended in aqueous sucrose solution. (b) The fraction of slower intracellular water. [2]

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This work was supported by Japan Society for the Promotion of Science (JSPS) KAKENHI Grant Number JP22K14190.

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Perturbing the Dynamic Structure of Water by Ion Solvation

Jacob Gerasimov^{1,2}, Adnan Haj Yehya², Michael Gerasimov², Aharon Friedman² and Paul Ben Ishai^{1*}

¹ Department of Physics, Ariel University, Ariel 4070000, Israel

² Department of Electrical and Electronics Engineering, Ariel University, Ariel 4070000, Israel.

Email: * paulbi@ariel.ac.il

Solvation dynamics in aqueous solutions involve water molecules constantly interchanging between bulk water and the hydration shell. Dynamic H-bonded networks of water molecules are interspersed with perturbed regions around the solvated ions. This is evident in the IR spectra of the solutions, in particular the band associated with the OH stretching modes. Multiple gaussians are required to fit the data and these are assigned to populations of fully coordinated or to partially coordinated water molecules. The effect of ionic concentration on the fitting parameters, offers an insight into ionic influence on dynamic water structures. The solutions studied are NaCl, NaI, KCl, CaCl₂ and MgCl₂. As cation concentration is increased, one notices an increase in the population of perturbed water for monovalent ions. However, this trend is reversed for divalent ions, especially for Mg²⁺. In this case, increasing concentration promotes order in the fluctuating H-bonded network.

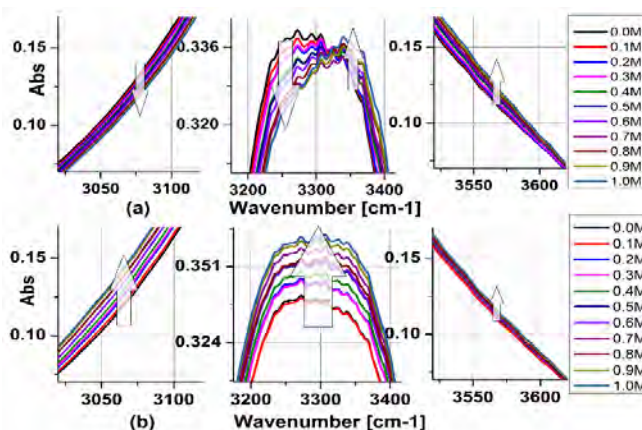


Figure 1. The experimental data for MgCl₂ and for NaI concentrations from 0-1 M. Panels (a)-(c) present the detailed behaviour of the peak and the wings of the OH-stretching mode for MgCl₂ and panels (d)-(f) present the same for NaI. The arrows indicate the change in behaviour as concentrations are increased. An immediate difference between the divalent and monovalent cation is the absence of an isobestic point in the data for the former. An isobestic point indicates a change in the balance between fully coordinated and partially coordinated populations.

Acknowledgments

The authors would like to thank Prof. Yuri Feldman and Dr. Cindy Galindo of the Applied Physics Institute of the Hebrew University of Jerusalem for their helpful comments and discussions

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Dynamics of Hydrated Soft Matters Studied by Broadband Dielectric Spectroscopy and Molecular Dynamics Simulations

Keisuke Tominaga^{1*}, Yuki Fuji², Ikuo Kurisaki³, Shigenori Tanaka⁴

¹ Molecular Photoscience Research Center, Kobe University, Japan

² Department of Chemistry, Graduate School of Science, Kobe University, Japan

³ Waseda Research Institute for Science and Engineering, Waseda University, Japan

⁴ Department of Computational Science, Graduate School of System Informatics, Kobe University, Japan

Email: *tominaga@kobe-u.ac.jp

We have been studying temperature dependence of dielectric response of aqueous solutions and hydrated soft matters such as proteins and lipid bilayers from the sub-GHz to THz frequency range. The broad frequency range is covered by several spectrometers. A vector network analyzer is used for the sub-GHz to 20 GHz region, and two time-domain spectrometers covers sub-THz region (30 GHz to 300 GHz) and THz region (0.2 THz to 2.0 THz). When it is necessary, we use a FTIR spectrometer for the far-IR region (50 cm⁻¹ to 700 cm⁻¹). Temperatures for the measurement can be controlled for all the spectrometers from -40°C to room temperature. This allows us to observe temperature dependence of the complex dielectric spectra for the almost entire spectral region. By using this system we measured temperature dependent dielectric response of the dehydrated and hydrated states of various soft matters such as globule protein [1], membrane protein [2], and lipid bilayer [3]. Generally, there is a low-frequency vibrational modes due to the global motions of the soft matters in the THz frequency region, which does not show large temperature dependence. In the GHz region a spectral component due to the relaxation dynamics of the hydration water molecules is observed, and this spectrum shifts to the higher frequency side when temperature increases. At around -40°C the low-frequency relaxation component and the high-frequency vibrational component overlaps, which causes sudden increase in the intensity of the absorption spectrum in the THz region.

Furthermore, we performed molecular dynamics simulations for hydrated globule proteins to interpret these experimental observations. The decomposed total dipole moments into protein, hydration water, and their cross correlation contributions enables us to describe the dielectric relaxation processes independently. Furthermore, these contributions are divided into the local contributions in terms of the residue and the backbone components in lysozymes. The whole line shapes of the spectra were well reproduced in the range from 0.1 GHz to 2.0 THz.

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Contribution of Dielectric Spectroscopy in Scrutinizing Protein Stabilization Mechanisms and the Role of Water

Tatiana Starciuc^{1*}, Natalia T Correia^{1*} and Alain Hedoux^{1*}

¹ University of Lille, Cité Scientifique, 59650 Villeneuve-d'Ascq, France

Email: * tatiana.starciuc@astrazeneca.com or natalia.correia@univ-lille.fr or alain.hedoux@univ-lille.fr

Broadband dielectric spectroscopy (BDS) is the technique of choice for characterizing molecular mobility in various materials, especially amorphous systems¹. This technique is well-established for the characterization of small molecules in simple systems but requires thorough method development to unlock its use for complex materials such as mixtures of small molecules or biomolecules. Over the past decades, the scientific community in the field contributed to the characterization of the molecular mobility of novel APIs^{2,3} and commonly used excipients^{4,5}, deciphering the full relaxation map of single component systems and tentatively extending their behavior to complex formulated mixtures. This approach is informative but remains incomplete due to its limited ability to account for molecular interactions typically occurring in complex mixtures of molecules.

This work aims to overcome this challenge and presents a new methodology developed to unlock BDS's potential to characterize the mobility of different components in a complex formulation of lysozyme and excipients. By combining BDS and Raman spectroscopy, coupled with in-situ monitoring of the freeze-drying process, it was shown that lysozyme is better protected during primary drying by sucrose, due to its lower affinity to water, inducing less pronounced microsegregation of pure component phases. By contrast, trehalose, assisted by water, was found to be more efficient than sucrose during storage, due to its ability to reduce the local molecular mobility of the complex system⁶. The results of a second part of this study (data not yet published), highlight that the bioprotective properties of trehalose can be further tuned by adding a specific amount of glycerol to the mixture, which slows down the local mobility of the matrix components. In addition, it was observed that the local mobility of the trehalose-water-lysozyme system is less affected by the water removal process in the presence of glycerol, which may lead to increased protein stabilization during processing and long-term storage.

To conclude, this work shows that the BDS methodology can be tuned to unlock a fundamental understanding of the physical mechanisms underlying API stability. Its use remains challenging when applied to complex formulations. However, this work shows one of the possible approaches to unlocking its potential by thoroughly characterizing the molecular mobility of single components, as a first step, followed by the application of appropriate methodology to describe complex systems.

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Disclosure

This work was funded and conducted at University of Lille, France, by Tatiana Starciuc (and co-workers), who is currently affiliated with AstraZeneca.

Water state in lipidic mesophase during phase transition

Yang Yao^{1*}, Sara Catalini², Bence Kutus³, Johannes Hunger³, Fanni Juranyi⁴, and Raffaele Mezzenga^{5,6*}

¹ Department of Chemistry, University of Basel, Switzerland

² European Laboratory for Non-Linear Spectroscopy, LENS, Italy

³ Max Planck Institute for Polymer Research, MPIP, Germany

⁴ Paul Scherrer Institut, Switzerland

⁵ Department of Health Sciences and Technology, ETH Zurich, Switzerland

⁶ Department of Materials, ETH Zurich, Switzerland

Email: * yang.yao@unibas.ch, raffaele.mezzenga@hest.ethz.ch

Water's role in biological systems, especially within confined environments, remains incompletely understood despite its fundamental importance. [1] The behavior of water at the nanoscale confines differs from its bulk properties regarding crystallization, nucleation, and molecular dynamics. [2,3] Herein, we present our research on the state of water within a biomimetic soft confinement provided by lipidic mesophases during phase transition induced by heating. Utilizing a combination of techniques, including Fourier transform infrared spectroscopy and broadband dielectric spectroscopy (BDS), we investigate the hydrogen bond network and molecular dynamics of confined water during the phase transition within dimodan-based lipidic mesophases. Our findings reveal the presence of two distinct fractions of water—bound and interstitial free water—with differing dynamics. [4] Furthermore, in lipidic mesophases with lower water content, such as those based on phytantriol, we combine BDS with pump-probe infrared and quasi-elastic neutron scattering to investigate this system. This enables a comprehensive understanding of the dynamics and the interaction between lipid and water molecules during the phase transition from lamellar phase to reverse micelle phase.

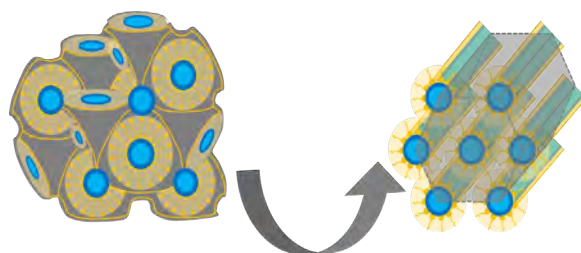


Figure 1. Phase transition from cubic to reverse hexagonal phase in lipidic mesophase.

Acknowledgments

We acknowledge support from SNSF Grant Nr. 200769. Y. Yao acknowledges SERI-funded ERC Starting Grant Nr. MB23.00006.

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S05

Charge Transport and Interfacial Effects

Elucidating the Transport of Electrons and Molecules in a Solid Electrolyte Interphase (SEI) close to Battery Operation Potentials using a Four-Electrode-Based Generator-Collector Setup

B. Roling^{1*}, F. T. Krauss¹, I. Pantenburg¹, V. Lehmann¹, J. O. Weiershäuser¹, M. Stich², A. Bund²

¹ Department of Chemistry, University of Marburg, Marburg, Germany

² Technische Universität Ilmenau, Ilmenau, Germany

Email: * roling@staff.uni-marburg.de

The solid electrolyte interphase (SEI) is a passivation layer in lithium-ion batteries, which has a strong impact on the battery lifetime. The SEI is formed by reductive decomposition of the electrolyte at the anode during the first charging of the battery and consists of inorganic as well as of organic decomposition products.^{1,2} In the ideal case, SEI growth is a self-terminating process, and the SEI passivates the electrode completely against further electrolyte decomposition. However, a slow yet significant long-term growth of real SEIs is observed, which contributes to battery aging.^{3,4}

Despite the passivation of the anode against electrolyte decomposition, the SEI allows for electron transfer reactions between anode and redox shuttle molecules, which are added to the electrolyte as an internal overcharge protection. In order to elucidate the origin of these poorly understood passivation properties of the SEI with regard to different molecules, we used a four-electrode-based generator-collector setup to distinguish between electrolyte reduction current and the redox molecule (ferrocenium Fc^+) reduction current at an SEI-covered glassy carbon electrode. The experiments were carried out in situ during potentiostatic SEI formation close to battery operation potentials. The measured generator and collector currents were used to calculate passivation factors of the SEI with regard to electrolyte reduction and with regard to Fc^+ reduction. These passivation factors show huge differences in their absolute values and in their temporal evolution. By making simple assumptions about molecule transport, electron transport, and charge transfer reaction rates in the SEI, distinct passivation mechanisms are identified, strong indication is found for a transition during SEI growth from redox molecule reduction at the electrode | SEI interface to reduction at the SEI | electrolyte interface, and good estimates for the transport coefficients of both electrons and redox molecules are derived.

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Achieving superionic conductivity in polymer electrolytes

Catalin Gainaru^{1,*}, Ain Uddin¹, Michelle Lehmann¹, Tomonori Saito¹, Alexei Sokolov¹

¹ Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Email: * gainarucp@ornl.gov

Developing polymer electrolytes with high ionic conductivity is critical for many energy storage and conversion technologies. This requires understanding of mechanisms controlling energy barrier for ion transport in polymers [1,2]. Our recent studies revealed that the energy barrier for charge transport in glassy polymer electrolytes is temperature dependent, a behavior which can be rationalized by the variations of dielectric permittivity and instantaneous shear modulus with temperature even in the glassy state of these materials [3]. These new findings additionally suggest that the energy barrier for hopping of small ions (Li, Na) can be strongly reduced by the addition of atomic groups which can increase the polarity of the polymer matrix. However, another consequence of strengthening the local interactions is the slowing down of segmental dynamics, which in turn is known to have a negative impact on the ionic conductivity. In the present contribution we demonstrate that this tradeoff can be mitigated by the addition of zwitterionic groups, which can lead to more than ten orders of magnitude decoupling between ion transport and segmental dynamics in the investigated polymer electrolytes. Consequently, the energy barrier and the conductivity of Li ions in glassy polymeric conductors can now reach levels comparable to those previously reported for superionic inorganic ceramics. These results provide new venues for a design of polymer-based solid-state electrolytes with enhanced conductivity for energy storage applications.

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Relaxation Dynamics and Ionic Conductivity in Structural Battery Electrolytes

Achilleas Pipertzis¹, Nicole Abdou², Johanna Xu³, Leif E. Asp³,
Anna Martinelli² and Jan Swenson^{1*}

¹ Department of Physics, Chalmers University of Technology, Gothenburg 41296, Sweden

² Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg 41296, Sweden.

³ Department of Industrial and Materials Science, Chalmers University of Technology, Gothenburg 41296, Sweden.

Email: * jan.swenson@chalmers.se

Structural batteries (SBs) represent a promising mass-less energy storage system” that can store electrical energy within load-bearing components.[1] Confining liquid electrolytes into cross-linked porous polymer matrices (i.e. ethoxylated bisphenol A dimethacrylate) synthesized by induced phase-separation can result in promising bi-continuous SBEs.[2,3] Herein, the liquid electrolyte is based on the ethyl-imidazolium cation [C₂HIm] and the bis(trifluoromethanesulfonyl)imide [TFSI] anion, doped with LiTFSI salt.[3] The effect of confinement was studied by means of differential scanning calorimetry (DSC), temperature-modulated DSC and dielectric spectroscopy. We report that the confined liquid phase exhibits the following characteristics: (i) a distinctly reduced degree of crystallinity; (ii) a broader distribution of relaxation times; (iii) reduced dielectric strength; (iv) a reduced cooperativity length scale at the liquid-to-glass transition temperature (T_g); and (v) a speeding-up of local T_g -related ion dynamics. The latter is indicative of weak interfacial interactions between the two nanophases and a strong geometrical confinement effect, which dictates both the ion dynamics and the coupled structural relaxation, hence lowering T_g . By decreasing the IL content, the pore size dedreases and the dynamics become faster. On the other hand, the dc-conductivity exhibits an opposite trend by changing composition, indicating the presence of non-percolating pathways that limit the long-range translational ion diffusion between the two electrodes. This work provides promising information about the confinement of liquid electrolytes into porous polymer matrices, but also shows the difficulty to synthesize an ideal polymer network with percolating pathways.

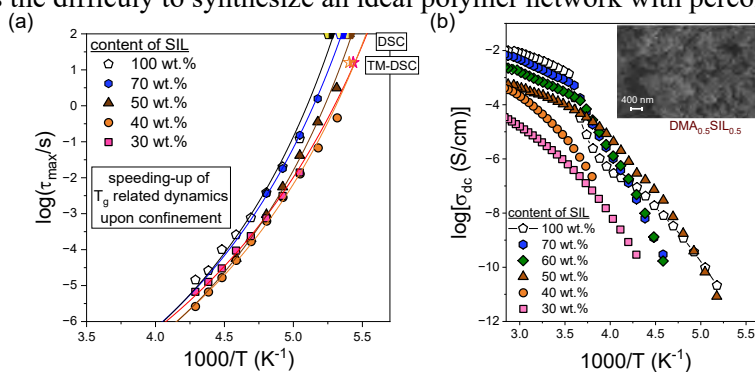


Figure 1. (a) Inverse temperature dependence of (a) relaxation times and (b) ionic conductivity values for the SBEs with different compositions, as indicated. The inset in (b) shows a SEM image.

Acknowledgments: This work was financially supported by a grant from the Area of Advance *Materials Science* at Chalmers University of Technology.

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Evidence of Liquid-Liquid Transitions in Ionic Liquids

Joshua Sangoro¹

¹ William G. Lowrie Department of Chemical & Biomolecular Engineering, The Ohio State University, Columbus, Ohio, USA

Email: * sangoro.1@osu.edu

A liquid-liquid transition (LLT) is a transformation from one liquid to another through a first-order transition. The LLT is fundamental to the understanding of the liquid state and has been reported in a few materials such as silicon, phosphorus, triphenyl phosphite, and water. Furthermore, it has been suggested that the unique properties of materials such as water, which is critical for life on the planet, are linked to the existence of the LLT. However, the experimental evidence for the existence of an LLT in many molecular liquids remains controversial, due to the prevalence and high propensity of the materials to crystallize. In this presentation, we will discuss recent experimental evidence of LLT in glass-forming ionic liquids that do not crystallize easily under normal laboratory conditions. We observe step-like increase in the static dielectric permittivity at the transition. Furthermore, the sizes of nonpolar local domains and ion-coordination numbers deduced from wide-angle X-ray scattering studies also change abruptly at the LLT [1], [2]. We independently corroborate these changes in local organization using Raman and Fourier-transform infrared spectroscopic techniques. The experimental access to the evolution of local order and structural dynamics across a liquid-liquid transition opens up unprecedented possibilities to advance the fundamental understanding of the nature of the liquid state.

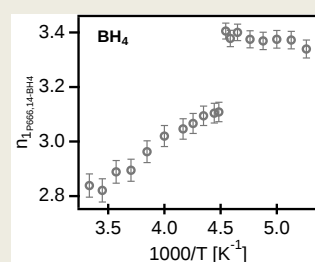


Figure 1: The ion coordination numbers obtained from the experimental radial distribution function showing a discontinuity at the LLT transition for P666,14-based ionic liquid (Harris et al. (2021) PNAS). Many other physical quantities including the static dielectric permittivity are discontinuous at the LLT.

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Insight into Electrical Conduction in Phosphate-Based Glasses: The Role of Transition Metal Oxides and the Mixed Glass Former Effect

L. Pavić*, and A. Šantić

Ruđer Bošković Institute, Bijenička cesta 54, Zagreb, Croatia

Email: * lpavic@irb.hr

In recent years, significant research efforts have been dedicated to exploring glasses as a more environmentally sustainable alternative for energy storage and conversion technologies. Phosphate glasses containing transition metal oxides (TMO) are well-known for their semiconducting nature with a polaronic conduction mechanism. Additionally, these glasses can accommodate a relatively high amount of alkali oxides, giving rise to ionic conductivity. Such extensive compositional and preparation variability enables tuning electrical conduction, making these materials attractive for application.

This contribution discusses the structure-property relationship in various glass systems, focusing on their glass-forming region and electrical properties. Depending on the composition, different types of conduction mechanisms can be present, ranging from purely electronic, and mixed electronic-ionic, to purely ionic. We utilize impedance spectroscopy (IS) for electrical characterization, correlating the structural features of a disordered glass network with long- and short-range charge carrier dynamics. The structural network composed of mixed glass-formers units facilitates ionic mobility, producing the well-known "mixed glass former effect" (MGFE). Replacing the conventional glass former (P_2O_5) with the conditional ones, such as TMOs, in alkali phosphate glasses, is highly promising due to the different roles TMOs can play. They can influence ionic conductivity similarly to classical MGFE and/or can actively contribute to conduction via polaronic transport. Moreover, it is shown that polaronic transport is strongly governed by the structural features of the glass network, such as the clustering of TM units, and cannot be directly related to the amount of TM oxide and the fraction of reduced TM ions. The ability to fine-tune the mechanism of electrical transport by simply controlling the oxide content and ratio in the glass composition is discussed based on the presented results. These findings are anticipated to drive future advancements in technology applications.

Acknowledgments

This work has been supported by the Croatian Science Foundation (CSF) under the projects IP-2018-01-5425 and DOK-2021-02-9665. Further, L. P. is pleased to acknowledge the support for this work from COST Action NETPORE (CA20126), supported by COST (European Cooperation in Science and Technology).

Decoding Ferroelectrics: Dielectric and Impedance Spectroscopy as Tools for Electrical Microstructure Assessment

Paula M. Vilarinho^{1,2}

¹ *Department of Materials and Ceramics Engineering, University of Aveiro, Portugal*

² *CICECO – Aveiro Institute of Materials, Portugal*

Email: paula.vilarinho@ua.pt

Why dielectric spectroscopy combined with impedance spectroscopy are relevant tools for the characterization of ferroelectric materials?

In this talk I will discuss the importance of using these two spectroscopies to fully characterise ferroelectrics.

Ferroelectrics are key materials with unique properties, like reversible spontaneous polarization, demonstrated in their P-E hysteresis loop. They lose ferroelectricity above the Curie temperature, becoming paraelectric. Their high dielectric constants, piezoelectricity, and reversible polarization are crucial for energy applications, including harvesting, storage, cooling, and photovoltaics. Ferroelectric ceramics, preferred for their cost-effectiveness and durability than single crystals. Ferroelectric single crystals have a highly ordered, continuous lattice with no grain boundaries, resulting in superior electrical properties and simpler domain structures, in contrast to ceramics that have randomly oriented grains and boundaries, adding microstructural complexity diminishing the electrical performance.

Characterizing the ferroelectric nature of a material involves several experimental techniques, being P-E hysteresis loop the most definitive test, while dielectric spectroscopy (DS), PFM, XRD, and thermal analysis provide complementary information about phase transitions, domain structures, and material stability. Impedance spectroscopy (IS) is not so commonly used. IS analyses resistive and capacitive behaviours across a system, crucial for electrochemical studies, while DS focuses on polarization and dielectric relaxation in insulating materials, both examining frequency-dependent electrical properties. However, when combined IS and DS one can get a more thorough and accurate analysis of material properties, what is particularly advantageous for materials with complex electrical behaviours.

In this talk I will present a detailed and comparative electrical investigation, using IS and DS, of high temperature self-flux grown $K1-x\text{Na}x\text{NbO}_3$ (KNN) single crystals and conventionally prepared KNN ceramics. The insights gained with the combination of IS with DS allow designing lead free KNN-based ferroelectrics with optimized performance for selective uses.

Ionic and Electronic Conductivity in Structural Negative Electrode Laminas

Achilleas Pipertzis^{1*}, Johanna Xu², Nicole Abdou³, Anna Martinelli³, Leif E. Asp², and Jan Swenson¹

¹ Department of Physics, Chalmers University of Technology, Gothenburg 41296, Sweden

² Department of Industrial and Materials Science, Chalmers University of Technology, Gothenburg 41296, Sweden

³ Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg 41296, Sweden

Email: * achilleas.pipertzis@chalmers.se

The concept of structural battery (SB) presents great potential for achieving substantial weight and volume savings. The SB design is based on multifunctional carbon fibre reinforced polymer composites, by combining the properties of traditional composite laminates and commercial Li-ion batteries [1]. A unidirectional electrode lamina consists of carbon fibres (CFs) embedded into structural battery electrolyte (SBE) and oriented in parallel along one direction yielding distinct anisotropy in electrical and mechanical properties. The heterogeneous SBE transfers mechanical loads to the CFs and provides high ionic conductivity [2]. Herein, the ion-conducting phase is based on a mixture of carbonate organic solvents doped with Li salt. Dielectric spectroscopy reveals a simultaneous combination of ionic and out-of-plane electronic conductivity in unidirectional electrode laminas, as depicted in Figure 1. The observed ionic conductivity closely mirrors that found in the free-standing SBEs. On the other hand, the through-thickness electronic conductivity is dictated by the inter-fiber contact points forming an interconnected network and the size of the electrically insulating SBE regions. For suppressing the out-of-plane electronic conductivity and potential short-circuits, either thick unidirectional electrode laminas (~700 μm) or thin electrode laminas (~100-200 μm) bearing a glass-fiber separator are required. Subsequently, the SBE+separator+CFs half-cell underwent ten galvanostatic charge/discharge cycles, followed by either potentiation static lithiation (discharge) or delithiation (charge). We report that the fully-delithiated sample exhibits slightly increased ionic conductivity, compared to pristine laminate. The latter reflects changes in the tortuosity of the SBE, caused by the presence of open microcracks, formed due to the expansion/contraction of CFs upon cycling [3]. To summarize, our experimental work verifies the multifunctionality governing SBs and provides promising routes for designing novel structural battery cells.

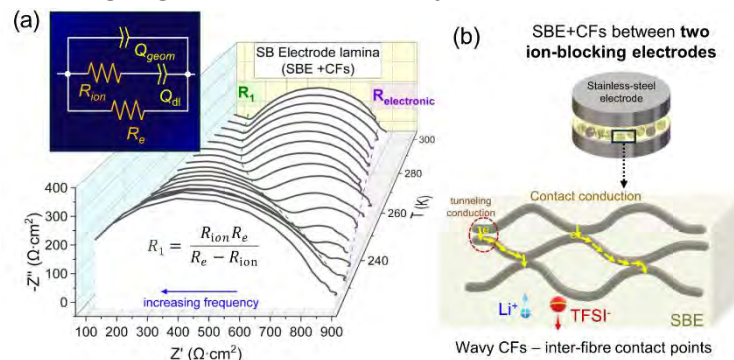


Figure 1. (a) Impedance data and (b) schematic representation of the two-electrode cell geometry and the undulation nature of CFs yielding inter-fibre contact points.

Acknowledgments: This work was financially supported by a grant from the Area of Advance Materials Science at Chalmers University of Technology.

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Molecular mobility and interfacial polarization study on model two-phase epoxy-amine networks

Carolina Franzon¹, Aurélien Roggero^{1,*}, Sébastien Pruvost¹, Jean-François Gérard¹

¹ Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, CNRS UMR 5223, Ingénierie des Matériaux Polymères F-69621 Villeurbanne, France

Email: * aurelien.roggero@insa-lyon.fr

Maxwell-Wagner-Sillars (MWS) polarization is observed when performing BDS measurements on polymer-based composite materials, or semicrystalline polymers. Although its origin is clearly ascribed to the interface between two phases with distinct dielectric properties [1], it is often difficult to extract valuable information about the studied material from the analysis of this dielectric phenomenon. To this end, model heterogeneous polymer networks have been developed which satisfy most of the assumptions of Wagner's model [2]: spherical inclusions constituting a minority phase in a continuous matrix, with perfect adhesion.

Cross-linked epoxy-amine microgels (CEMs) were synthesized by precipitation polymerization [3], in the form of spheres about 6 μm in diameter. The CEMs were then dispersed in an epoxy-amine matrix of similar chemical nature, resulting after curing in a network exhibiting topological cross-linking heterogeneity which can be fine tuned by adjusting the crosslinking degree of each of phase. This cross-linking heterogeneity induces a contrast in dielectric properties, giving rise to MWS polarization.

BDS was used to study molecular mobility of the two phases (matrix and inclusions) and MWS polarization in this model heterogeneous material (Figure 1). Wagner's model and two sets of data inputs (either mean ϵ' and σ' values or raw experimental spectra) were used to model the theoretical MWS polarization and compare it with the experimental one. The good agreement obtained between Wagner's historical model and experiment on a real heterogeneous system provides a better understanding of the parameters that govern MWS polarization and hints at links with the physico-chemical structure of the heterogeneous material.

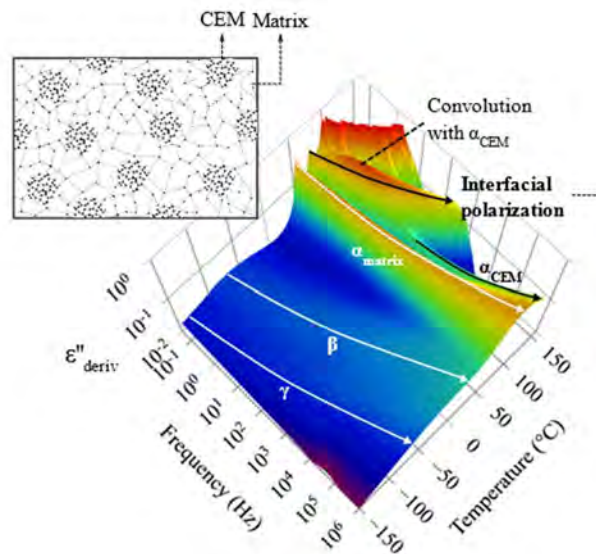


Figure 1. 3D relaxation map of the model heterogeneous epoxy network (inset: schematic representation of the network's topology)

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BDS on the nanoscale: restricted crystallization and conductivity of polymers in finite size

Martin Tress^{1*}, Alaa Y. A. Hassan¹ and Wing Kit Or¹

¹ Peter Debye Institute for Soft Matter Research, Leipzig University, 04103 Leipzig, Germany

* Martin.Tress@uni-leipzig.de

The impact of nanometric confinement on polymers has been studied extensively, especially in thin films and nanopores. Despite the strong interfacial and geometric constraints that can be achieved in these experiments, there is still a large number of polymer molecules interacting. Here we present an approach to study small aggregates of as few as ten chains and examine their crystallizability and conductivity using dielectric spectroscopy [1,2]. For that, a nano-structured electrode arrangement is combined with several physico-chemical surface modifications to deposit a regular pattern of gold nanoparticles onto which end-functionalized polymer chains are grafted to create ensembles of individualized chain aggregates.

For polycaprolactone, crystallization is completely suppressed in these aggregates although their volume is large enough to permit that according to classical nucleation theory. The latter is also demonstrated with spin-cast droplets of comparable volume (though a much broader distribution of sizes is obtained in these) [1]. A specific analysis suggests that the spatial constraints play only a minor role while the immobilization of the chains due to the grafting prevents proper crystalline arrangement.

In polyethylene oxide, pronounced changes in the ionconductivity are observed in the grafted aggregates compared to the bulk. Especially a pronounced reduction in slope of the spectral conductivity signature indicates a considerable alteration of the type of charge transport [2]. This can be understood as a switch from fast inter-chain ion hopping, which dominates in bulk, to slower intra-chain ion hopping in the aggregates. We attribute these changes to the specific chain configuration and orientation forced by the grafting to the surface. Despite the highly specialized and in some sense extreme arrangement, the impact of chain orientation on ionic charge transport may be a more general phenomenon. If that is the case, it may explain significantly increased electrode polarization and interfacial resistance in ion-conducting polymers in general, which often diminishes their performance. This suggests that bottle-brush architectures could improve polymeric electrolytes for various fields ranging from solid-state electrolyte batteries to ion-conducting fuel cell membranes which may help to face current ecological and economic challenges with the development of polymeric electrolytes for efficient, light-weight and low-cost energy storage devices.

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Dynamics of Ionic Liquid-Water Mixtures at Ambient and Elevated Pressure

Amith Kumar Murali¹, Marian Paluch¹, R. Casalini², Alynna Lange³, Andreas Taubert³,
Zaneta Wojnarowska^{1*}

¹ First Institute of Physics, the University of Silesia in Katowice, 75 Pulku Piechoty 1A, 41–500 Chorzow, Poland

² Chemistry Division, Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC 20375, USA

³ Institute of Chemistry, University of Potsdam, Karl-Liebknecht-Straße 24-25, 14469 Potsdam-Golm, Germany

Email: * zaneta.wojnarowska@us.edu.pl

The use of acidic ionic liquids and solids as electrolytes in fuel cells is an emerging field due to their efficient proton conductivity and good thermal stability. Despite multiple reports describing the conducting properties of acidic ILs, little is known about the charge transport mechanism near liquid-glass transition and the structural factors governing proton hopping. To address these issues, we studied two acidic imidazolium based ILs with the same cation, however, different anions - bulk tosylate vs. small methanesulfonate. Their water mixtures were also examined. Ambient-pressure dielectric studies of anhydrous and water-saturated materials (up to 50 wt % of H₂O) performed in close vicinity of T_g, have revealed significant differences in charge transport mechanism in these two types of protic systems. Thereby, we demonstrated the effect of molecular architecture on proton hopping, which is crucial in the potential electrochemical applications of acidic ILs. Furthermore, high-pressure dielectric measurements of pure ILs and their aqueous mixtures enable us to address the fundamental issue: the validity of the density scaling concept for IL and fast water dynamics. We found that all isothermal and isobaric relaxation data describing the time scale of charge transport (τ_σ) and fast dynamics within the water clusters (τ_v) reveal visual evidence of a liquid-glass transition. Furthermore, both relaxation processes satisfy the ρ^γ/T scaling concept with a single exponent $\gamma=0.58$. Thus, the scaling exponent is a state-point independent parameter for the dynamics of water clusters confined in ionic liquid investigated in the pressure range up to 300 MPa.

Acknowledgments

This research was funded in whole by National Science Centre, Poland [Opus 21, 2021/41/B/ST5/00840].

S06

**Monitoring of Chemical Reactions,
Crystallization process and Physical Ageing**

Density Scaling and Singel Parameter Aging

Tina Hecksher and Kristine Niss*

¹ Roskilde University, Denmark

Email: * kniss@ruc.dk

The aging rate of glasses has traditionally been modeled as a function of temperature, T , and fictive temperature, while density, ρ , is not explicitly included as a parameter. However, this description does not naturally connect to the modern understanding of what governs the relaxation rate in equilibrium. In equilibrium, it is well known that the relaxation rate, γ_{eq} , depends on temperature and density. In addition, a large class of systems obeys density scaling, which means the rate specifically depends on the scaling parameter, $\Gamma = e(\rho)/T$, where $e(\rho)$ is a system specific function.

Here we present a conjecture on how density scaling may be generalized to describe aging [1]. Moreover, we discuss how this connects to single parameter aging [2,3] and other recent related results in literature [4,5].

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Time and temperature dependence of nucleation and crystallization in amorphous pharmaceuticals

N. S. Krishna Kumar¹, Rahul Lalge¹, Raj Suryanarayanan¹

¹ Department of Pharmaceutics, School of Pharmacy, University of Minnesota, Minneapolis, Minnesota 55455, United States.

Email: * surya001@umn.edu

Amorphization of crystalline drugs is a promising approach to enhance oral bioavailability. However, the amorphous state can revert to a crystalline form, diminishing its solubility advantage. Therefore, comprehending the factors affecting the physical stability of amorphous pharmaceuticals is crucial. The amorphous-to-crystalline transformation typically occurs through two steps: nucleation and crystal growth. The time-temperature-transformation (TTT) diagram provides the time and temperature dependence of the first evidence of crystallization. The TTT curves are the boundary between the completely amorphous and crystal growth regions (amorphous + crystalline; Figure 1; red curve). However, nucleation propensity has a different time and temperature dependence (Figure 1, green curve). In amorphous solid dispersions (ASDs), which are drug-polymer molecular mixtures, the crystallization onset time increased significantly due to the strength of drug-polymer interaction and polymer concentration (Figure 2). The molecular mobility decreased as a function of the strength of drug-polymer interaction and polymer concentration, revealing the role of mobility in reducing the crystallization onset time. Further, we developed a method to obtain the nucleation TTT diagram based on the accelerated crystallization of the nucleated systems. With a decrease in temperature, nucleation was facilitated until the temperature was reached with the shortest nucleation time. Further decrease in temperature increased the nucleation time as mobility limitations inhibit the rate of nuclei formation. Nucleated ASDs are “ticking time-bombs”, with the potential for crystallization during product storage. The TTT diagram enables us to determine the contributions of kinetics and thermodynamics in nucleation and crystallization.

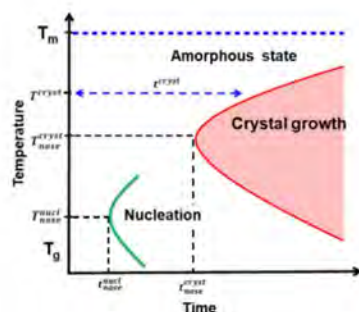


Figure 1. Schematic of TTT diagram for crystallization (green curve) and nucleation (red curve). T_m is the melting point, and T_g is the glass transition temperature.

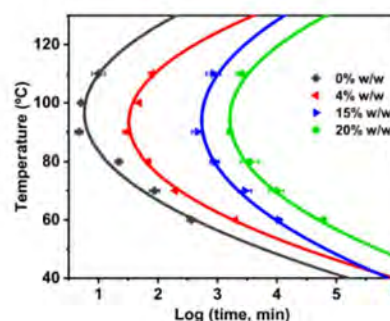


Figure 2. TTT diagram of nifedipine ASDs with PVP concentration ranging from 0 to 20% w/w.

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Hydrogen bonding during cold crystallization of Poly(alkylene 2,5-furanoate)s

Tiberio A. Ezquerra¹, Oscar Toledano^{1,2,+}, Oscar Gálvez^{2,+}, Mikel Sanz^{2,+}, Esther Rebollar³, Aurora Nogales¹, Gonzalo Santoro¹, Mari Cruz García-Gutiérrez¹

¹*Instituto de Estructura de la Materia, IEM-CSIC, Serrano 121, 28006 Madrid, Spain*

²*Universidad Nacional de Educación a Distancia (UNED), Depto. Física Interdisciplinar, Fac. Ciencias Av. de Esparta s/n, 28232, Las Rozas, Madrid, Spain.*

³*Instituto de Química Física Blas Cabrera, IQF-CSIC, Serrano 119, 28006 Madrid, Spain*

+NANOesMAT, UNED, Unidad Asociada al CSIC por el IEM y el IQF, Av. de Esparta s/n, 28232, Las Rozas, Madrid, Spain.

Email: * t.ezquerra@csic.es

The growing interest in lower carbon footprint polymers, as an alternative to petroleum based ones, originates from the increasing societal need for sustainable polymer materials derived from renewable sources potentially integrated in a circular economy concept. Recently, fully biobased polyesters derived from furandicarboxylic acid (FDCA) have received significant attention as potential substitutes for their petrochemical-based benzene aromatic counterparts. In particular, the role of intermolecular hydrogen bonds in the amorphous phase have been proposed to play an important role in the enhanced gas barrier properties of poly(alkylene 2,5-furanoate). Here we will present in-situ isothermal crystallization experiments of some relevant poly(alkylene 2,5-furandicarboxylate) as revealed by Broadband Dielectric Spectroscopy (BDS), time Fourier Transform Infrared Spectroscopy (FTIR) and grazing incidence wide angle X-ray scattering (GIWAXS). Special emphasis will be devoted to the potential of combining this battery of techniques to monitor in real-time the evolution of hydrogen bonding during crystallization. In addition, we will show how Density Functional Theory (DFT) ab initio calculations can be very useful in order to better understand the influence of hydrogen bonding on crystallization. Our results demonstrate that hydrogen bonding is present in both the crystalline and the amorphous phase and its rearrangement can be considered as a significant driving force for crystallization of poly(alkylene 2,5-furanoate)s.

Acknowledgments

Grants PID2022-138635NB-I00, PID2019-107514GB-I00 / AEI / 10.13039/501100011033, PID2019-106125GB-I00/ AEI / 10.13039/501100011033, TED2021-129845B-I00 and TED2021-131914B-I00 funded by MCIN/AEI/10.13039/, RYC2020-029810-I funded by MCIN/AEI/ 10.13039/501100011033 and by “ESF Investing in your future”.

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Modelling of the Evolving Glass Transition Temperature During Cure of Diels-Alder Thermo-reversible Networks

Jessica Mangialetto^{1*}, Niko Van den Brande¹ and Michael Wübbenhorst²

¹Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Pleinlaan 2, Brussels, Belgium

²Laboratory for Soft Matter and Biophysics, KU Leuven, Celestijnenlaan 200d, Leuven, Belgium

Email: * Jessica.Mangialetto@vub.be

Studies using Broadband Dielectric Spectroscopy (BDS) to explore reversible covalent network formation are notably limited, especially for systems based on Diels-Alder (DA) cycloadditions, despite the extensive use of this technique for irreversible network curing. Such dynamic networks based on thermo-reversible DA reactions hold promise as self-healing materials due to their ability to break and reform DA, leading to repeatable healing cycles and enhanced lifetime. In this context, this study [1] employs BDS to systematically investigate a dynamic network formed via the thermoreversible DA reaction between a 4-functional furan-functionalized Jeffamine and a 2-functional maleimide. The focus is put on the investigation of the evolution during the network cure of the cooperative segmental dynamics as sensed by the dielectric α -relaxation by measurement in (non-)isothermal conditions between 10^{-1} and 10^7 Hz.

In a first place, the relaxation times (τ_α) associated with the α -relaxation are determined by Havriliak-Negami fits [2] of dielectric spectra measured upon heating, immediately after partial isothermal network cure at 55 °C for different reaction times. The Vogel-Fulcher-Tammann (VFT) law is then fitted to τ_α data only including temperatures without noticeable kinetic changes. Subsequently, a more general approach is attempted by fitting a unique set of VFT parameters for all experiments with a Vogel temperature (T_V) for each experiment to take into consideration the degree of cure. Lastly, this approach was extended to describe all experimental relaxation traces, with and without including effects of the reaction by introducing a kinetic model to predict the cure conversion (Figure 1) [3].

Building upon this comprehensive characterization, a novel technique for continuous cure monitoring is proposed and validated via simulation of a system curing isothermally at 55°C. This technique enables real-time computation of the dynamic glass transition temperature (T_g) from the relaxation time (τ_α), utilizing only three VFT parameters obtained from the global fitting procedure. Such an approach might stimulate new applications of BDS-based cure monitoring.

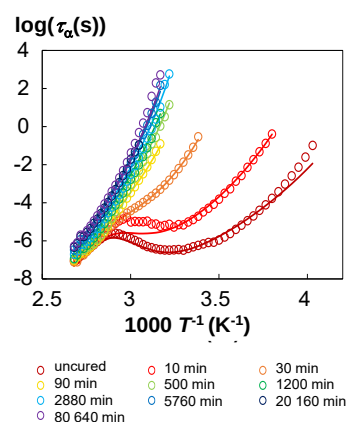


Figure 1. Relaxation time τ_α vs $1000 T^{-1}$. Symbols: experiment τ_α retrieved from heating segments following partial cure at 55 °C. Full lines: simulated τ_α based on the global VFT fit including the kinetic model.

Acknowledgments

The authors thank the Research Foundation - Flanders (FWO-Vlaanderen) for financial support under grants for the PhD fellowship (1128520N) and postdoctoral fellowship (1203524N) of Jessica Mangialetto.

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S07

Ferroelectrics and Ceramics

Structural (dis-)order, dielectric response and phase transition properties of electrocaloric ferroelectrics

Torsten Granzow^{1,*}, Junning Li¹, Youri Nouchokgwe¹, Veronika Kovacova¹, Ashwath Aravindhan^{1,2}, Uros Prah¹, Sakyo Hirose³, Pranab Biswas², Emmanuel Defay¹

¹ Luxembourg Institute of Science & Technology, 41 rue du Brill, 4422 Belvaux, Luxembourg

² University of Luxembourg, 4365 Esch Sur Alzette, Luxembourg

³ Murata Mfg Co, Nagaokakyo, Kyoto 6178555, Japan

Email: * torsten.granzow@list.lu

Temperature control, ranging from air conditioning or heating in buildings or cars over fridges and freezers to active coolers for microelectronics, constitutes an essential aspect of modern life and is responsible for a significant fraction of energy use and thereby also the carbon footprint of a society. Electrocaloric cooling, which relies on a variation of entropy and temperature in a material under the action of an electric field, promises to be an energy-efficient, well scalable, environmentally friendly, and noiseless alternative to conventional cooling devices based on vapor compression technology using hydrofluorocarbon refrigerants. To be effective, an electrocaloric material must switch reversibly between a disordered, high-entropy state and an ordered low-entropy state with an electric field. Materials with a ferroelectric instability are prime candidates; in this case, the high entropy state has low – ideally zero – electric polarization, and the low entropy state is characterized by a high polarization.

This presentation looks at the correlation between dielectric response, phase transitions and electrocaloric effect of perovskite-structured oxides representing three material classes: antiferroelectric lead zirconate (PbZrO_3 , PZO), ferroelectric relaxor lead scandium tantalate ($\text{Pb}[\text{Sc}_{1/2}\text{Ta}_{1/2}]\text{O}_3$, PST), and lead-free ferroelectric barium titanate (BaTiO_3 , BTO) in the vicinity of the Curie temperature. Solution-deposited thin films are used as ideal model systems; as practical applications require a large thermal mass, their properties will be compared to those of multilayer ceramic capacitors (MLCs).

The investigation of PZO reveals how a ferroelectric phase is stabilized against the original antiferroelectric phase by repeated high-field electric cycling. This is reflected both in the high-field response as well as the temperature-dependent dielectric permittivity in a broad frequency range and makes the material unsuitable for large-scale electrocaloric applications.

In contrast, PST with a high degree of B-site disorder displays a typical relaxor behavior, with low remanent polarization under high-field excitation, a very broad peak of the dielectric constant with temperature, and strong dielectric dispersion, while ordered samples tend towards a more ferroelectric character. Counter-intuitively, the dependence of the dielectric response on the amplitude of the driving field shows clear Rayleigh behavior for the relaxor system, but not the more ferroelectric materials. The influence of different dopants on the dielectric response is discussed, and the consequences for the suitability of PST for large-scale electrocaloric applications is demonstrated.

Last, but not least, dielectric spectroscopy on modified BTO reveals both the variation of the ferroelectric character with doping, but also high dielectric losses that seem to prohibit applications under high electric field. This allows an outlook on the future of ferroelectric electrocalorics for refrigeration applications.

Acknowledgments

Financial support by the Fonds National de la Recherche (FNR) of Luxembourg through BRIDGES2021/MS/CECOHA/Defay, THERMODIMATC20/MS/Defay, and BRIDGES2021/MS/ELINLOSS/Granzow is gratefully acknowledged.

Order – Disorder Phase Transitions in Hybrid Organic – Inorganic Perovskites – Insights from Broadband Dielectric Spectroscopy

Adam Sieradzki^{1*}, Andrzej Nowok¹, Katarzyna Fedoruk – Piskorska¹, Mirosław Mączka², Anna Gągor², Anna Szeremeta³, Sebastian Pawlus³

¹ Department of Experimental Physics, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland.

² Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Box 1410, 50-950 Wrocław, Poland.

³ August Chelkowski Institute of Physics, University of Silesia in Katowice, ul. 75 Pułku Piechoty 1, 41-500 Chorzów, Poland

Email: * adam.sieradzki@pwr.edu.pl

Hybrid organic-inorganic perovskites have emerged as a promising and rapidly evolving class of compounds, offering tunable optoelectronic properties and a plethora of potential applications.[1] This family of materials present a rich landscape of lattice dynamics and a complex dielectric response. The field-induced alignment of the polar molecular cations, defying their typical thermal fluctuations, gives rise to orientational polarization, the appearance of which underlies dielectrically-active relaxation phenomena.[2]

The dielectric relaxation processes are, however, predominantly characteristic of disordered high-temperature phases of hybrid organic-inorganic compounds and tend to disappear during the transformation to the structurally-ordered low-temperature (LT) structures. In fact, only a few examples of hybrid organic-inorganic compounds exhibit dielectrically-active residual relaxation dynamics of molecular cations in the LT phase, the origin of which has not been fully understood yet.

In this study, we aim to delve deeper into the nature of low-temperature disorder and dynamics in hybrid perovskite-like systems, analyzing various compound examples. Through the utilization of X-ray diffraction (XRD), Raman spectroscopy, and broadband dielectric spectroscopy (BDS), we demonstrate that the order-disorder first-order structural transformation in these compounds does not entirely suppress the molecular dynamics within the organic building blocks. We will discuss the mechanism of this motion and analyze its implications for the optoelectronic properties of these materials.

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A Feedback Model for Relaxor Ferroelectrics

Herbert Kliem and Andreas Leschhorn

Saarland University, 66123 Saarbruecken, Germany

Email: h.kliem@mx.uni-saarland.de

Relaxor ferroelectric ceramics and also relaxor organic materials exhibit unusually high dielectric permittivities in a broad temperature range. The relaxation times display in an Arrhenius plot a nonlinear curve, i.e. a Vogel-Fulcher-Tammann empirical law, instead of a straight line.

By cooling down from high temperatures, relaxors do not show a spontaneous polarization as expected for ferroelectrics, unless they are subjected to high electrical fields. The hysteresis loop of the polarization in electrical fields can turn into a double loop in restricted temperature ranges.

The physical model for an explanation of the relaxor behaviour developed by the authors [1] is based on interacting charges or interacting polar nanoregions fluctuating thermally activated in asymmetric double well potentials. The transition rates of the charges within the wells depend on the local fields. The intrinsic asymmetries are caused by disorder in the material and evoke the relaxor behaviour. For ordered systems with intrinsically symmetrical double well potentials a ferroelectric behaviour is calculated.

The double wells with their charges are equivalent to dipoles, which flip their direction, when the charge in a double well changes its position from one well to the other. These dipoles generate electrical fields, which act on the other double wells and increase or decrease their asymmetry. This electrostatic interaction is considered by a mean field approach according to Weiss [2]. In this Weiss approach the average fields at the dipoles are proportional to the polarization. The correctness of this approach is proved by a numerical calculation.

So the local fields at the double wells and therefore the charge's transition rates, are given by the applied field and the Weiss field, which is proportional to the polarization. This corresponds to a feedback loop, where the polarization can enhance itself. Besides the geometry of the system, the coupling strength in this loop depends on the temperature and on the intrinsic asymmetry of the double wells.

The following results are obtained for systems with an intrinsic asymmetry of the double wells:

We compute frequency dependent high permittivities in a broad temperature range and a Vogel-Fulcher-Tammann law for the relaxation times. At low temperatures a hysteresis of the polarization in electrical fields arises. This turns with increasing temperature into a double loop, which finally degrades in high temperatures to a single curve. For the chosen asymmetry, no spontaneous polarization, i.e. no polarization without electrical field, appears. It should be noted, that with a change of the system's parameters, e.g. coupling strength and intrinsic asymmetry, the system can be transformed from a dielectric to a ferroelectric or to a relaxor.

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Insights into the aging mechanism of ZnO ceramics from broadband dielectric spectroscopy

Men Guo¹, Gilad Orr², Pau Ben Ishai^{1*} and Shlomo Glasser²

¹ THz & Dielectric Science laboratory, Department of Physics, Ariel University, Ariel 4070000, Israel

² Crystal Science laboratory, Department of Physics, Ariel University, Ariel 4070000, Israel

Email: * paulbi@ariel.ac.il

ZnO ceramics, with excellent nonlinear I – V characteristics, are the core element in metal oxide arresters to protect electrical equipment from the harm of overvoltage. However, aging phenomenon appears when ZnO ceramics are subjected to the operation voltage for a long time. As a results, the leakage current and the residual voltage usually increase, but the nonlinear coefficient decreases [1]. Therefore, the long-term electrical stability of ZnO ceramics needs to be enhanced, which is based on clear understanding of the aging mechanism. Considering the difference between static and alternating electric field, there must be different dominant defect dynamics in ZnO ceramics under different waveforms, but they have not been distinguished in previously proposed aging mechanisms.

In this study, broadband dielectric spectroscopy (BDS), a non-destructive material characterization method [2], was adopted to induce the evolution of defects during aging. ZnO ceramics from a same batch were subjected to AC and DC voltage for aging tests. During aging, the ambient temperature was sustained at 408K. Maximal values of AC aging voltage and DC aging voltage were set to $0.9U_B$ and $0.8U_B$, respectively (U_B is the breakdown voltage obtained at $1 \text{ mA}\cdot\text{cm}^{-2}$). Aging tests lasted more than 1000 hours. J – E characteristics were measured using a multi-meter (Keithley DMM6500) and a high-voltage DC power (HVTOP, R2-P20W200) at room temperature. BDS was measured using an impedance analyzer (Novocontrol, Concept 80) in a frequency range of 10^{-1} – 10^6 Hz in a temperature range of 163–473K. J – E characteristics in the low-temperature region were also measured at 363–403K using the HVB 4000 test interface of Novocontrol. Cole–Cole model was employed to fit dielectric spectra [3].

Dielectric strengths of both zinc interstitials (Zn_i) and oxygen vacancies (V_O) decreased during aging. After AC aging, the double Schottky barrier height (Φ_B) remained around 0.59 eV. After DC aging, the forward-biased Φ_B decreased from 0.60 eV to 0.58 eV, but the reverse-biased Φ_B increased from 0.54 eV to 0.56 eV. Given electron-flipping nature of the relaxations, the same tendencies of relaxation strengths during aging, but quite different migration energy of Zn_i (0.57 eV) and V_O (2 eV), a dynamic of the occupation of the interface states by electrons in the early stage of aging was proposed. After the stage, the J – E curve (in the positive direction) uplifted to the low-current region because electrons trapped at the interfaces increased Φ_B and the depletion width. In the later stage of DC aging, Zn_i migrated to and accumulated at grain boundaries, increasing the donor density and thus decreasing the depletion width, resulting in deterioration in J – E characteristics. This study distinguished dominant processes in ZnO ceramics under different electrical stresses and the aging mechanism was further revealed by detailed analysis of the dielectric spectra.

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S08

**BDS in Relation to Other Spectroscopic or
Scattering Techniques**

Coupling of shear rheology with SAXS and BDS in rubber nanocomposites

Anne-Caroline Genix^{1*}, Numera Shafqat¹, Clément Robin², Anatoli Serghei³, René Fulchiron³ and Julian Oberdisse¹

¹ Laboratoire Charles Coulomb (L2C), Université de Montpellier, CNRS, Montpellier, France

² Hutchinson Research and Innovation Center, Châlette-sur-Loing, France

³ Ingénierie des Matériaux Polymères (IMP-UMR 5223), Univ Lyon, CNRS, Villeurbanne, France

Email: *anne-caroline.genix@umontpellier.fr

Rubber-based nanocomposites prepared by solid-phase mixing with precipitated silica or carbon black are typically strongly aggregated systems with different levels of spatial organization, as highlighted by our group in the past [1, 2]. Our strategy is to investigate such systems based on the study of simplified industrial samples with ingredients limited to a strict minimum. Small-angle X-ray scattering (SAXS) can then be used to study the filler microstructure in rubber nanocomposites with different filler loading. The size and mass of primary particles and small aggregates are determined using a model of inter-aggregate polydisperse hard sphere interactions based on a correlation hole analysis. Another key feature of rubber nanocomposites is the influence of filler surfaces on polymer dynamics, and an original application of dielectric spectroscopy to measure the adsorption isotherm of coating agents on silica embedded in the polymer matrix will be presented. [3]

A major advance was then to couple SAXS measurements on synchrotron beamlines with in-situ shear rheology to provide microstructural evidence for macroscopic rheological effects, which leads to disruption of the filler network and subsequent flocculation. The Payne effect has been characterized in rubber nanocomposites filled with carbon black, but with only small signatures in the scattering under oscillatory shear. In parallel, we have also coupled shear rheology with fast acquisition dielectric measurements to follow the change in electrical conductivity due to the destruction/formation of conductive pathways.

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Molecular mechanisms of glass aging

Daniele Cangialosi^{1,2}

¹ Centro de Física de Materiales CFM (CSIC-UPV/EHU) and Materials Physics Center MPC, Paseo Manuel de Lardizabal 5, 20018, San Sebastián, Spain

² Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain

Email: * daniele.cangialosi@ehu.eus

A supercooled liquid cooled at a given rate transforms into a glass at the so-called glass transition temperature, T_g ; and, once in the glassy state, slowly evolves with time, a phenomenon addressed as physical aging or structural relaxation. The conventional view exclusively addresses the main α relaxation as mediating both glass transition and physical aging. While this view generally holds in a relatively sharp cooling rate and temperature range in proximity of the laboratory T_g ; in this contribution, I will show that, extending the cooling rate and temperature range of physical aging, the description of the two kinetics phenomena requires introducing at least one additional molecular mechanism, beyond the exclusive role of the α relaxation [1-3]. The mild temperature dependence of these mechanisms allows explaining why at low cooling rates the T_g might be found to be lower than expected only accounting for the α relaxation [4]; and why aging persists at temperatures way below T_g , where the α relaxation is expected to reach experimentally inaccessible time scales.

Acknowledgments

I acknowledge the Grant No. PID2021-123438NB-I00 funded by MCIN/AEI/10.13039/5011000 11033 and by “ERDF A way of making Europe”; the financial support of Eusko Jaurlaritza, code: IT1566-22; the Grant No. PID2020-114506GB-I00 funded by the Spanish Minister of Science and Innovation; and TED2021-129457B-I00 funded by the Spanish Minister of Science and Innovation.

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Glass spectrum, excess wing phenomenon, and master curves in molecular glass formers

Ernst A. Rössler* and Manuel Becher

Nordbayerisches NMR Zentrum, Universität Bayreuth, 95440 Bayreuth, Germany

Email: * ernst.roessler@uni-bayreuth.de

The relaxation spectra of molecular glass formers solely displaying an α -peak and excess wing contribution collected by dielectric spectroscopy (DS), depolarized light scattering (DLS) and nuclear magnetic resonance (NMR) relaxometry [1] are reanalyzed to pin down their different spectral evolution [2]. Below T_g , a generic dielectric relaxation pattern is reinspected: A power-law spectrum with an exponential temperature dependence of its amplitude is observed and confirmed by NMR relaxation. Among many different glasses, its amplitude is found to be virtually the same at T_g . This is interpreted as a relaxation analog to the Lindemann criterion.

Above T_g , the power-law spectrum persists as an excess wing, yet, it is truncated at low frequencies by the emergence of the α -process. The question addressed is how does the original glass spectrum ranging from the sub-Hertz to the GHz range alter upon further heating. We show that master curve construction encompassing both α -peak *and* emerging excess wing works for DLS and NMR. It reveals the self-part of the slow dynamics' spectrum. Master curves are to be understood as a result of a more extensive scaling covering all temperatures instead of strict frequency-temperature superposition. Hence, deuteron NMR relaxation probed at a *single* frequency as well as proton field-cycling (FC) NMR provide the correct susceptibility when plotted as a function of $\omega\tau_{DLS}$ – see Fig. 1(a). DLS (photon correlation and tandem Fabry-Perot/double monochromator spectroscopy) and NMR display identical relaxation spectra. Comparing different systems, we do not find a generic structural relaxation at variance with recent claims [3] – Fig. 1(b). DS spectra show particularities, which render master curve construction obsolete. The DS peak is enhanced or suppressed with respect to that of DLS or NMR, yet, not correlated to the polarity of the liquid.

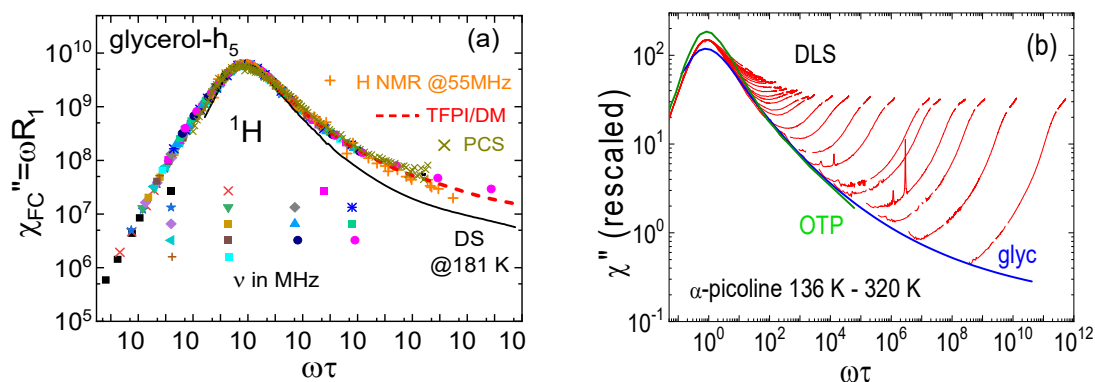


Figure 1. (a) FC ¹H NMR master curves of glycerol-h₅ (colored points); added: single-frequency ²H NMR (orange), photon correlation spectroscopy (PCS, dark yellow) [3], tandem Fabry-Perot/double monochromator (TFPI/DM, red dashed line) and dielectric spectra (DS, black line), all rescaled. (b) DLS spectra of picoline (red), glycerol (blue) and of o-terphenyl (green) showing different spectral widths.

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The spectral shape of structural relaxation in supercooled liquids: light scattering vs. dielectric spectroscopy

Thomas Blochowicz^{1*}, Till Böhmer¹, Rolf Zeißler¹, Florian Pabst² and Jan. P. Gabriel³

¹ Institute for Condensed Matter Physics, Technical University of Darmstadt, Germany

² SISSA – Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy

³ Institute of Material Physics in Space, German Aerospace Center, Germany

Email: * thomas.blochowicz@physik.tu-darmstadt.de

The non-exponential character of structural relaxation is one of the outstanding features in glassy systems, which despite decades of scientific efforts still remains to be fully understood. Dielectric loss spectra typically show a wide variety of α -peak shapes with power law exponents ranging from 0.35 to 1 on the high frequency side of the main relaxation peak. By contrast, recent studies have shown that corresponding spectra obtained by depolarized dynamic light scattering (DDLS) in a wide range of supercooled liquids, including simple van der Waals, hydrogen bonding and ionic liquids, follow, to good approximation, a generic line shape with a high-frequency power law $\omega^{-1/2}$. In order to reconcile both observations it is argued, that in the dielectric spectra pronounced dipolar cross-correlation contributions tend to mask the generic behavior while such cross-correlations are much less pronounced in DDLS [1].

In the talk first of all the reasoning is summarized that leads to the conclusion that there is a generic spectral shape of glassy dynamics and how a detailed comparison of dielectric and light scattering spectra in many cases allows to separate cross-correlation contributions [2, 3]. We also discuss, why certain substances deviate from simple generic behavior and under which conditions cross-correlations can be extracted by a straight forward comparison of experimental techniques. This is exemplified for the prominent case of water, where the addition of LiCl leads to suppression of cross-correlations in the dielectric response so that dielectric and DDLS results coincide at high salt concentrations.

Moreover, for a wide variety of supercooled liquids we establish a quantitative relation between the dielectric relaxation shape and the amount of static dipolar cross-correlations quantified by the Kirkwood-Fröhlich correlation factor g_k , thereby rationalizing earlier observed correlations between the relaxation shape and the dielectric strength [4]. Finally, we discuss how cross-correlations influence the recovery in aging experiments, in particular when recovery is monitored using time resolved multispeckle dynamic light scattering in an aging molecular liquid [5].

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Orientational dynamics in supercooled glycerol computed from MD simulations: self and cross contributions

Marceau Hénot^{1*}, Pierre-Michel Déjardin² and François Ladieu¹

¹ SPEC, CEA, CNRS, Université Paris-Saclay, 91191, Gif-sur-Yvette France

² Laboratoire de Modélisation Pluridisciplinaire et Simulations, Université de Perpignan, 66860 Perpignan, France.

Email: * marceau.henot@cea.fr

The relaxation processes of molecular liquids close to the glass transition are known to be non-exponential as a consequence of spatially heterogeneous dynamics. Dielectric spectroscopy (DS) is a powerful tool to characterize the structural relaxation of polar liquids. It has recently been shown that while it exists large differences in the shape of dielectric spectra corresponding to various molecular liquids, they all display the same $\omega^{-1/2}$ high-frequency slope when characterized through depolarized dynamic light scattering (DDLS) [1]. This is seen as a consequence to the different sensitivities of DS and DDLS to molecular cross-correlations [1], [2]. This approach could help better understand the generic features of the dynamic slowdown that accompanies the glass transition.

We present here an investigation of the orientational dynamics in supercooled glycerol using molecular dynamics (MD) simulations. We obtained precise equilibrium relaxation spectra between 323 and 253 K for the self part and total (self + cross) correlation for the first two ranks ℓ of the Legendre polynomial. In agreement with experimental work on glycerol [1], we show that the sensitivity to cross-correlation is much weaker for $\ell = 2$ (pertaining to DDLS) than for $\ell = 1$ (pertaining to DS). This supports the pertinence of directly comparing DS and DDLS spectra in order to separate self and cross contributions. Moreover, we show that, for glycerol, the net cross-correlation originates only from the first shell of neighboring molecules. Accessing the angular dependence of the static correlation allows us to get a microscopic understanding of why the rank-1 correlation function is more sensitive to cross-correlation than its rank-2 counterpart [3].

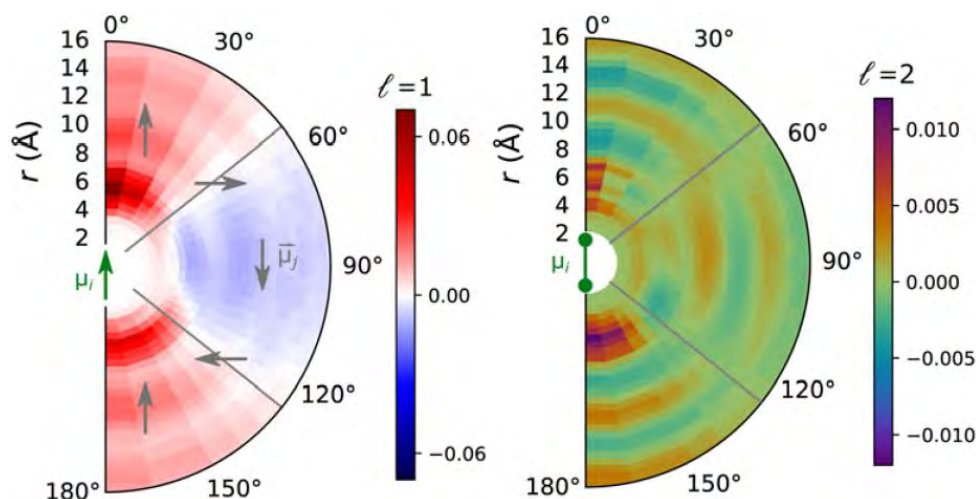


Figure 1. Angular and distance dependence of the static cross-correlation for $\ell = 1$ (left, pertaining to DS) and $\ell = 2$ (right, pertaining to DDLS), from ref. [3].

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Effect of hydrogen bonds on molecular mobility in P(MMA-co-MAA)/cellulose nanofibers composites

Valentina Cavallo^{1,2}, Aurélien Roggero¹, Alberto Fina², Jean-François Gerard¹ and Sébastien Pruvost^{1,*}

¹ Université de Lyon, CNRS, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, UMR 5223, Ingénierie des Matériaux Polymères, CEDEX, F-69621 Villeurbanne, France

² Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino, V.le Teresa Michel, 5, 15121, Alessandria, Italy

Email: * sebastien.pruvost@insa-lyon.fr

PMMA is a well-known amorphous polymer characterized by optical transparency and good processability. However, owing to its high brittleness, the modification of its chemical structure or its use in the design of composites and nanocomposites has been widely investigated to enhance its mechanical strength. The effect of the introduction of interchain H-bonds has been reported in different methacrylate-based copolymers. The main modification obtained following the introduction of H-bonds forming groups is the effect on the molecular mobility which causes an increase in T_g. In fact, when PMMA is copolymerized with different types of comonomers, *i.e.* methacrylic acid (MAA), methacrylamide (MAAM) and 2-ureido-4[1H]-pyrimidinone methyl methacrylate (UPyMA), a large positive deviation from the theoretical calculation of T_g was observed and correlated with the presence of intermolecular H-bonds.

In the present study, a P(MMA-co-MAA) copolymer was designed as a matrix to disperse cellulose nanofibers (CNF). In fact, thanks to the polar nature of MAA unit, the formation of H-bonds with the nanofibers can be established [1]. Here, we propose a multi-technique approach to investigate molecular mobility, starting from PMMA homopolymer used as a simple amorphous model and focusing on the influence of the introduction of a polar unit in the chain (MAA), able to bring H-bond forming moieties, and subsequently the addition in such systems of organic polar fillers (CNF) to study the combination of their effects. Two P(MMA-co-MAA) composites were processed containing 5 and 15%wt of CNFs. The introduction of cellulose nanofibers was found to have an effect on sub-glass relaxations (β and γ) and α relaxation and a β' relaxation appeared. A discussion will be focused on the relationships between molecular dynamics and the interfacial interactions between fillers and the polymer matrix.

Acknowledgments

The French Ministry of Education and Research is gratefully recognized for providing a grant for this project and the Ecole Doctorale Matériaux de Lyon ED034 for their financial support.

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Old news: dielectric spectroscopy is a good probe to study structural relaxation of glass forming systems

Silvia Arrese-Igor^{1*}, Arantxa Arbe¹, Lola Ruiz-Martín^{2,3}, Bela Farago³, Juan Colmenero⁴ and Angel Alegria⁴

¹ Centro de Física de Materiales CSIC-UPV/EHU, Paseo Manuel de Lardizabal 5, 20018, Spain

² Materials Physics Center MPC, Paseo Manuel de Lardizabal 5, 20018, Spain

³ Institute Laue Langevin, Av des Martyrs 71, 38000 France

⁴ Universidad del Pais Vasco UPV/EHU, Paseo Manuel de Lardizabal 5, 20018, Spain

Email: * silvia.arreseigor@ehu.eus

The transition from equilibrium to non-equilibrium state triggered by the arrest of molecular motions at the glass transition of glass forming systems still remains an intriguing phenomena. The study of the associated dynamics has been therefore approached applying many different techniques, where the use of dielectric spectroscopy has been particularly extensive. Although from a general point of view all the techniques lead to a common picture for the phenomenology and characteristics of the glass transition, the detailed comparison of the results obtained by different experimental techniques for particular systems and samples is not always trivial. Although the fact that dielectric spectroscopy is sensible to intermolecular dipolar interactions is at the basis of its formulation, recently, this old known characteristic has attracted quite an amount of attention. This was mainly thrived by the high correlation found between the dielectric strength and the width of the dielectric α -relaxation [1] in contrast to other techniques [2-5] and the postulation of slow Debye components in the dielectric response of several polar glass forming systems (even devoid of hydrogen bonds) [6-7]. Different results and views opened a debate on the way dipolar-dipolar interactions manifest when measuring dynamics by different techniques and the role of the mentioned cross correlations on the glass transition. Data will be presented for several systems and techniques –including also neutron scattering and calorimetry- that corroborate previous broadly accepted ‘dogma’, i.e. that dielectric spectroscopy is in general a good test of the structural relaxation, ALSO for polar systems. Comparing various systems grouped attending to different characteristics, the objective will be to generalize the observed phenomenology trying to point out specific aspects for particular cases.

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S09

Confinement Effects

Signature of the Adsorbed Layer on the Glass Transition of Thin Polymer Films: Broadband Dielectric Spectroscopy and Related Techniques

Andreas Schönhals^{1,2}, Hassan Omar¹, Andreas Hertwig¹ and Paulina Szymoniak¹

¹ Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

² Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

Email: * Andreas.Schoenhals@bam.de

In well annealed thin polymer films with non-repulsive polymer/substrate interaction with a substrate an irreversibly adsorbed layer is expected to form. These adsorbed layers have shown a great potential for technological applications [1]. However, the growth kinetics and the molecular mobility of the adsorbed layer is still not fully understood. This concerns also the influence of the adsorbed layer on the thickness dependence of the glass transition temperature of thin films. This is partly due to the difficult accessibility of these layers in thin films. Here, the irreversibly adsorbed layers of semi-rigid mail chain polymers like polycarbonate or polysulfone are revealed by solvent-leaching experiments. First, the growth kinetics of these layers is investigated as a function of annealing time. The film thickness, topography and the quality of the adsorbed layer is controlled by Atomic Force Microscopy (AFM). Secondly, the molecular mobility of the adsorbed layer is investigated by Broadband Dielectric Spectroscopy (BDS). A developed nanostructured capacitor arrangement is employed to measure the layer with a free surface. In addition to the dielectric experiments, spectroscopic Ellipsometry measurements are carried out to estimate the glass transition of the thin films. The thickness dependence of the glass transition of the thin films is correlated with the adsorbed layer [2,3].

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Nanopores as separation membranes for blends comprising polymers of different architecture and microstructure

George Floudas^{1,2*}, Panagiotis Kardasis,¹ Yun Dong²

¹ University of Ioannina, Dept. of Physics, Ioannina, Greece

² Max Planck Institute for Polymer Research, Mainz, Germany,
E-mail: gfloudas@uoi.gr

Capillary force can drag polymer chains into nanopores [1]. We discuss the effect of capillary action on the imbibition and subsequent adsorption of polymer blends comprising different chain architectures. This is made possible by following the evolution of the normal mode with *in situ* nanodielectric spectroscopy. The method provides *simultaneous* access to the kinetics of imbibition and to the molecular [2-5] dynamics *during* flow at the segmental and chain length scales. We have already discussed the case of blends comprising long/short *cis*-1,4-polyisoprenes (PI) [5]. By taking advantage of the disparity in the imbibition speeds, we have demonstrated that shorter chains penetrate first and, in addition, that they adsorb first on the AAO walls providing an example of fractionation in the absence of solvent. Here we discuss the effect of polymer architecture and polymer microstructure. For this purpose we employ blends of (a) linear/star *cis*-1,4-polyisoprenes, (b) linear/branched polydienes (*cis*-1,4-polyisoprene with *cis*-1,4-polyfarnesene), and (c) PIs with different microstructure (different 1,2 and 3,4 content). Because of differences in the imbibition speeds, nanoporous membranes facilitate the separation of the different topologies. Lastly, we investigate the way that ionic systems penetrate nanopores [6-8]. The aim here is to identify the principles underlying ion transport within nanochannels and to suggest new processes with efficient ion transport. Applications range from nanofluidic circuits, nanopore-based sensing devices, and bioinspired energy conversion systems. To this end, we employ the archetypal polymer electrolyte PEO/LiTFSI [6], and different ionic liquids [7] as well as mixtures of polymerized ionic liquids with ionic liquids [8].

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Molecular dynamics of ultrathin films of liquid crystal obtained via organic molecular beam deposition

Anna Drzewicz^{1*} and Michael Wübbenhorst²

¹ Institute of Nuclear Physics Polish Academy of Sciences, PL-31342 Krakow, Poland

² Laboratory for Soft Matter and Biophysics, Department of Physics and Astronomy, Catholic University of Leuven, Leuven, 3001, Belgium

Email: * anna.drzewicz@ifj.edu.pl

The miniaturization of devices causes an increase in scientists' interest in the possibility of creating thin layers of liquid crystals and their properties. The organic molecular beam deposition (OMBD) method can produce the organic thin layers in ultra-high vacuum by evaporating the material whose the molecules impinge on a cold substrate [1]. In this paper, we have verified the possibility to create thin films of liquid crystal [2,3] below the glass transition temperature by the OMBD method. We have also investigated the effect of OMBD measurement parameters on the layer thickness and the α -relaxation dynamics of compound under study. Some striking differences in relaxation dynamics related with glassy state of thin films compared to the sample in the bulk form have been observed.

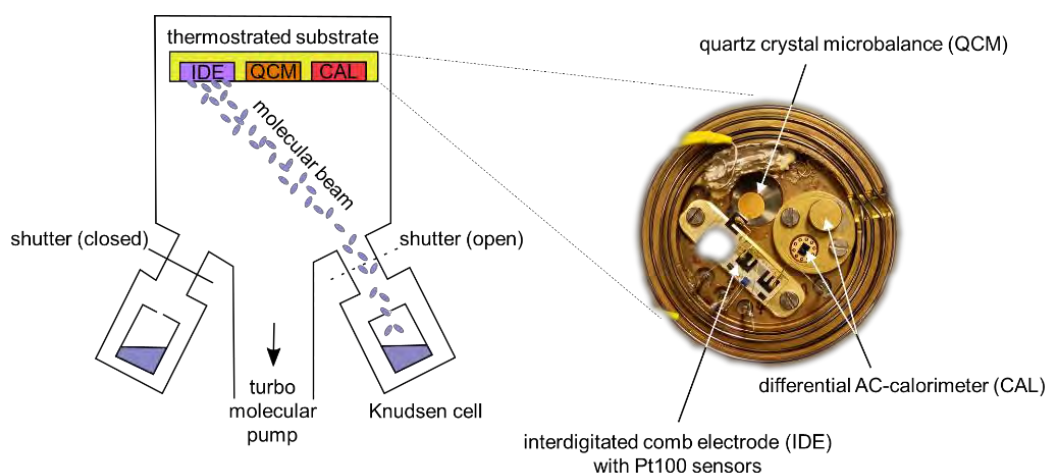


Figure 1. Scheme of the OMBD vacuum cell including two Knudsen cells and a temperature-controlled target containing the interdigitated comb electrodes, the quartz crystal microbalance and the differential AC-calorimeter.

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A.D. acknowledged the National Science Centre (Grant MINIATURA 5: UMO-2021-05/X/ST3/00888) for financial support.

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Dielectric evidence of high kinetic stability in vapour-deposited binary glasses with large T_g contrast

E. Thoms^{1,*}, M. E. Tracy², R. Richert¹, and M. D. Ediger²

¹ School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, USA

² Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

Email: *ethoms@asu.edu

Glasses formed by physical vapour deposition (PVD) can exhibit an increased kinetic stability compared to liquid cooled glasses, corresponding to the effects obtained by ageing for thousands or millions of years. *In-situ* dielectric measurements during deposition onto an interdigitated electrode can be employed to observe the growth and properties of the film [1]. For neat systems, we find proof of the formation of a constant thickness mobile layer on the film surface, which has been shown to be a prerequisite for ultrastability, allowing molecules to move to energetically favourable locations before being immobilised by subsequent deposition.

Ultrastability can be of interest for both basic research and technical application. Prominent examples for the later are vapour deposited organic light emitting diode (OLED) displays, where performance loss via ageing or crystallisation can be countered by the employment of ultrastable glasses. However, technical devices typically require multi-component glasses, and research on (ultra)stable glasses to date has been focussed on single-component systems [2].

To close this gap, we studied mixtures of molecular vitrifying materials, in particular methyl-*m*-toluate (MMT) and methyl-acetate (MA), as an example for a non-trivial mixture, with the glass temperature of MMT being nearly 50% higher than that of MA. As a point of reference, the bulk dielectric properties of these mixtures have been determined across the entire composition range. For the PVD samples, we show by *in-situ* measurements that the neat components form stable films. More interestingly, we have verified that all compositions form similarly stable films as the neat components. That is to say, the results show that the ability of the pure components to form stable glasses is preserved in mixtures, even for non-ideal mixing behaviour due to high T_g contrast. Moreover, as typical for neat systems, the highest kinetic stability for each composition is achieved for deposition near $0.85 \times T_g$ of the particular mixture.

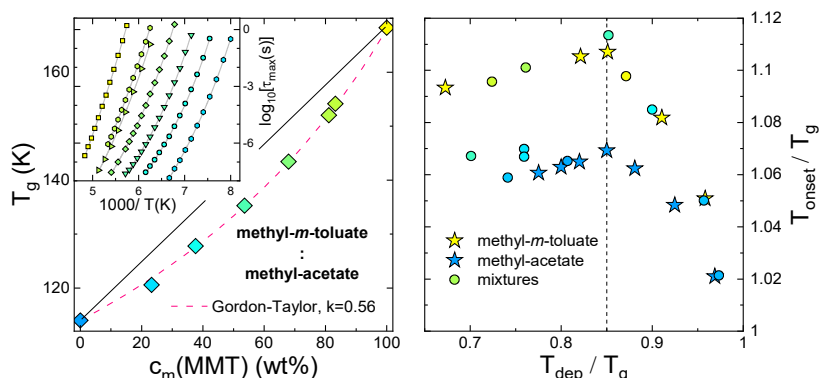


Figure: T_g for bulk systems, derived from VFT-fits (inset), is well described by a Gordon-Taylor equation, showing non-ideal mixing behaviour (left). Kinetic stability (right) of both neat and binary vapour deposited glasses is increased, with a maximum near $T_{\text{dep}} = 0.85 \times T_g$ (dashed line).

Acknowledgments

This work was supported by the National Science Foundation under Grant No. CHE-2153944.

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The influence of pore walls nanostructurization on the dynamics of low and high molecular weight systems

Kamil Kaminski^{1*}, Magdalena Tarnacka,¹ and Marian Paluch¹

¹ Institute of Physics, Faculty of Science and Technology, University of Silesia in Katowice, 75 Pulkę Piechoty 1A, 41-500 Chorzów, Poland

Email: *kamil.kaminski@us.edu.pl

Herein we show that the nanostructured interface obtained via modulation of the pore size has a strong impact on the segmental and chain dynamics of high (poly(propylene glycol) (PPG) derivatives with various molecular weights ($M_n = 4000$ g/mol and $M_n = 2000$ g/mol) as well as low molecular weight phenyl alcohols. In each case a significant acceleration of the dynamics was observed for samples infiltrated into ordinary alumina templates ($D_p = 36$ nm), while bulklike behavior was found for the materials incorporated into membranes of modulated diameter ($19 \text{ nm} < D_p < 28 \text{ nm}$) [1],[2]. We demonstrated that the modulation-induced roughness reduces surface interactions of polymer chains near the interface with respect to the ones adsorbed to the ordinary nanochannels. The confirmation of this supposition came from the calorimetric investigations where single glass transition was observed for the PPG and phenyl alcohols infiltrated into modulated AAO pores while for the other systems two T_g's were detected. That probably indicates the difference in tendency to form interfacial layer in both cases. Our results highlight the crucial role of the interface on the overall behavior of confined materials.

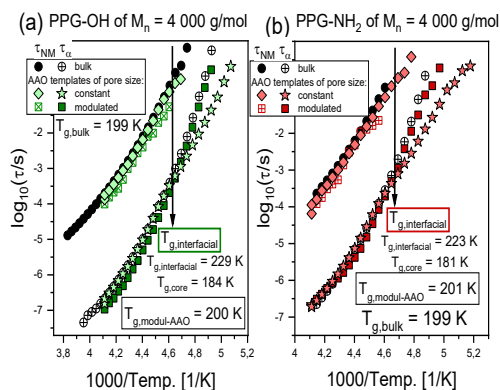


Figure 1. Segmental and normal mode relaxation times measured for PPG infiltrated into ordinary and modified AAO membranes

Acknowledgments

This work was supported from the Polish National Science Centre within the OPUS project (Dec. no 2022/47/B/ST4/00236)

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The influence of pressure and volume changes on the non-equilibrium segmental dynamics of polymers

Katarzyna Chat^{1,*} and Karolina Adrjanowicz^{2,3}

¹ Institute of Nuclear Physics Polish Academy of Sciences, Krakow, Poland

² Institute of Physics, University of Silesia, Chorzow, Poland

³ Center for Education and Interdisciplinary Research (SMCEBI), Chorzow, Poland

Email: * katarzyna.chat@ifj.edu.pl

Numerous studies show that the effects caused by nanoconfinement on the behavior of soft matter can be reduced or completely eliminated by prolonged annealing. The time required to equilibrate the nanopore-confined system depends primarily on the temperature, pore size and molecular weight of the polymer.^[1,2,3] In this talk, we would like to discuss the role of pressure and density changes in the context of the non-equilibrium segmental dynamics of low-molecular-weight poly(phenylmethyl siloxane) (PMPS 2.5k) confined in AAO nanopores. For this purpose, we have carried out time-dependent measurements at the annealing temperature preceded by the intermediate jumps from higher (“down jump”) or lower (“up jump”) temperatures. Figure 1 shows segmental relaxation times for PMPS 2.5k confined in 60 nm nanopores on the initial and final stage of annealing after the up and down jump. We have shown that pressure and volume changes are extremely important parameters in the context of equilibration of polymers in confined geometry. Under down jumps conditions, the polymer must eliminate excess free volume to recover bulk properties, whereas, in the case of up jumps, the system gains volume during the annealing processes, with corresponding pressure changes. This study reveals the interconnected relationship between thermal history and pressure/density changes in the equilibration process of polymers confined within nanopores.

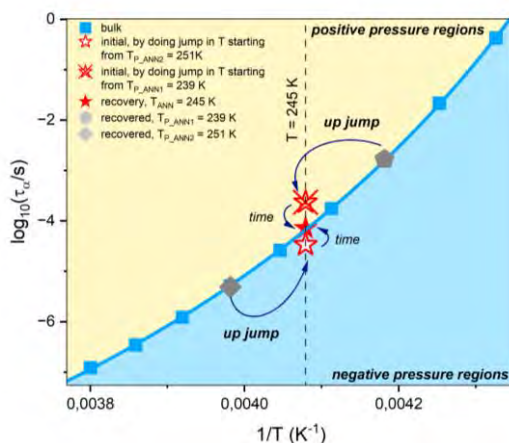


Figure 1. Temperature dependence of the segmental relaxation time for PMPS 2.5k in bulk and confined in 60 nm nanopores. The α -relaxation times for confined samples were recorded after jumps from lower and higher pre-annealing temperature to the annealing temperature $T_{ANN} = 245$ K at the initial and the final stages of the prolonged annealing.

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The impact of confinement on the behavior of associating materials. The case of phenyl alcohols

**M. Tarnacka^{1*}, N. Soszka², B. Hachula², M. Geppert Rybczyńska²,
K. Prusik³, A. Talik-Just¹, M. Paluch¹, K. Kamiński¹**

¹ August Chelkowski Institute of Physics, University of Silesia in Katowice, 75 Pułku Piechoty 1a, 41-500 Chorzów, Poland

² Institute of Chemistry, University of Silesia in Katowice, Szkolna 9, 40-006 Katowice, Poland

³ Institute of Materials Engineering, University of Silesia in Katowice, 75 Pułku Piechoty 1a, 41-500 Chorzów, Poland

Email: * magdalena.tarnacka@us.edu.pl

The effect of 2D confinement on the associating behavior of phenyl-substituted monohydroxyl alcohols (phenyl alcohols, PhAs) has been studied with the use of Infrared (FTIR) and Dielectric Spectroscopy (BDS) as well as Differential Scanning Calorimetry (DSC). Interestingly, the dielectric response of PhAs infiltrated within native silica mesopores revealed the presence of an additional relaxation process, particularly pronounced for longer aliphatic chains. It was observed that this additional mobility is most likely not related to the vitrification of the interfacial layer, $T_{g,interfacial}$. Its molecular origin is yet to be clarified. However, FTIR measurements showed that the incorporation of PhAs into silica membranes inhibits a complete association over the entire temperature range. Moreover, nanogeometrical restriction has a relatively small impact on the H-bonds strength of infiltrated PhAs, as seen in the ν_{OH} peak position. However, it alters the ν_{OH} bandwidths, i.e., the confined samples are characterized by broader OH bands than those in bulk, indicating greater heterogeneity in the distribution of H-bonded systems in nanoconfinement. Interestingly, the activation energy values of the dissociation process, E_a , for confined PhAs were lower than those determined for the bulk samples. This result correlates well with the lower association degree of infiltrated PhAs compared to their bulk counterparts, resulting from the spatial restriction. Thus, all experimental methods used consistently confirmed the formation of an additional interfacial layer in infiltrated PhAs in which the alcohol molecules strongly interact with the pore walls. We believe that the presented results offer a better understanding of the processes occurring for associating liquids in nanoconfinement [1].

Acknowledgments. This work was financial supported the National Science Centre, Poland [Dec. no 2022/47/B/ST4/00236].

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S10

Modeling, Theory and Simulation

Kramers-Kronig relations expressed as a convolution pair and its uses in Broadband Dielectric Spectroscopy

Carlos J. Dias

i3N/CENIMAT, Department of Materials Science, NOVA School of Science and Technology, NOVA University of Lisbon, Caparica, Portugal

Kramers-Kronig relations are used extensively in electrical, mechanical/rheological, thermal and acoustic measurements because they link the real-part to the imaginary-part of the complex ratio of oscillating quantities. These relations are independent of any model and assess whether the real and imaginary parts of data is associated with a system having time-invariant properties and minimum-phase, passive response.

Here we propose to obtain both the real and the imaginary parts of the dielectric constant using a **convolution pair** which relates the complex counterparts when these quantities are expressed in the logarithmic scale of frequency.

It was reported [1], that the imaginary part of the dielectric constant can be obtained by a convolution operation of its real part with the hyperbolic secant function. This convolution function performs an operation on the real part, similar but not exactly, known as the Hamon approximation.

Here we will show that the real-part is obtained from the imaginary-part with another function which performs a kind of integration of the imaginary part in the log-scale of frequency.

It should be noted that these convolution functions give exact and precise values of their complex counterparts as can be seen in the figure below, if no experimental errors are involved and if the data can be appropriately extended two decades to either side frequency axis.

In this work the application of these relations will be used to gain insight into the relaxation of various polymers and materials especially in view of determining and distinguishing its bulk relaxation from what should be identified as electrode polarization. Other uses of these relations can be envisaged which will be addressed in this communication.

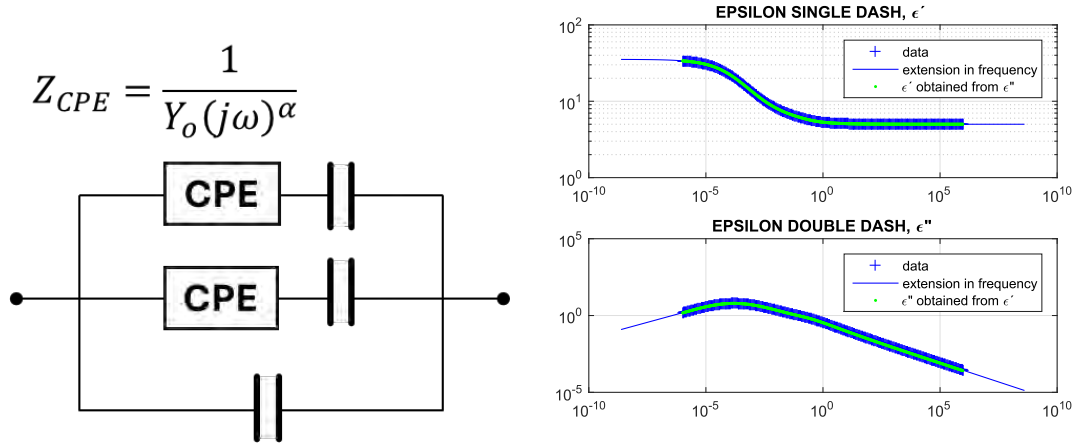


Figure 1. A simple example of the application of Kramers-Kronig relations using the proposed convolution transformation pair.

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Investigation of the nature of the translational and orientational disorder in pharmaceutical cocrystals from molecular dynamics simulations and dielectric relaxation spectroscopy experiments

L. Roca-Paixão¹, N. T. Correia¹, H. Zhao¹, F. Danède¹,
M. T. Viciosa² and F. Affouard^{1*}

¹ University of Lille, CNRS, INRA, ENSCL,

UMR 8207-UMET-Unité Matériaux et Transformations, F-59650 Villeneuve d'Ascq, France.

² Centro de Química Estrutural, Institute of Molecular Sciences, Department of Chemical Engineering,
Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal.

Email: * frederic.affouard@univ-lille.fr

The nature of the disorder in nanoporous organic Carbamazepine/Tartaric Acid cocrystal is investigated through complementary molecular dynamics simulations and broadband dielectric spectroscopy experiments [1,2]. We especially highlight that the Tartaric Acid molecules present in the channel-like cocrystalline architecture show both translational and rotational dynamical disorder. Such understanding presents a fundamental significance, but also a possible interest for the control of particle transport in pharmaceutical processes. Translational dynamics can be described as an unusual single-file diffusion process at short times while at longer times the classical diffusion (Fickian) is recovered. Rotational dynamics is interpreted as rotational jumps between preferred orientations. Freezing out of the rotational molecular mobility is detected in concomitantly with the presence of a kink in the temperature evolution of the crystalline cell volume usually associated with the glass transition phenomenon. It reveals a remarkable link between the molecular mobility of the molecules in the channels and the overall crystal anharmonicity.

Acknowledgments

This project has received funding from the Interreg 2 Seas program 2014-2020 co-funded by the European Regional Development Fund under subsidy contracts 2S01-059_IMODE and 2S07-033_Site Drug.

The project ARCHI-CM, Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche, Région Hauts-de-France and European Regional Development Fund (FEDER) are also acknowledged for supporting and funding this work.

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Solved and unsolved problems relating to the Random Barrier Model

Jeppe C. Dyre¹

¹“Glass and Time”, IMFUFA, Department of Science and Environment, Roskilde University,
P. O. Box 260, DK-4000 Roskilde, Denmark

Email: dyre@ruc.dk

The random barrier model (RBM) was constructed to provide a minimal model for explaining the strongly frequency-dependent ac conductivity of various disordered solids, ranging from doped semiconductors at low temperatures, over electronically and ionically conducting polymers, to the modelling of ion conduction and neutral-atom diffusion in glass-forming liquids and glasses. The model considers the motion of non-interacting particles hopping stochastically on a cubic lattice with nearest-neighbor jumps and randomly varying energy barriers, assuming identical lattice energies. Despite these gross simplifications, the model provides a good description of the generally observed transition from a frequency-independent conductivity at low frequencies to an ac conductivity that varies as frequency to an exponent close to, but below unity.

The RBM becomes particularly simple in the limit of extreme disorder defined as whenever the energy-barrier distribution is much broader than $k_B T$. In this limit the model's particle dynamics is controlled by percolation and, as a consequence, in properly scaled units the dynamics becomes independent of the energy-barrier distribution, i.e., universal.

The talk briefly reviews the history of the RBM followed by an account of how the model is solved analytically by reference to percolation arguments [1]. The paper goes on to discuss outstanding challenges, including how to justify that all particle sites have the same energy and how to justify ignoring Coulomb interactions between charge carriers as well as self-exclusion. While the RBM becomes a zero-parameter model in the extreme disorder limit that is mainly of interest, the talk can hopefully inspire to future works aiming at a generalized one-parameter RBM based on sound physical assumptions. In this way one may hopefully arrive at a model that can fit data better than the current RBM, thereby making it possible to reveal sample-specific details of the transport physics.

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EIS smart tool: An application software for the analysis and modeling of impedance spectroscopy data with multi-curve fitting

**B.M.G. Melo^{1*}, Francisco J. A. Loureiro^{2,3}, Duncan P. Fagg^{2,3}, Luiz Pereira¹,
L.C. Costa¹ and M.P.F. Graça¹**

¹ i3N, Department of Physics, University of Aveiro, Aveiro 3810-193, Portugal

² TEMA, Department of Mechanical Engineering, University of Aveiro, 3810-193 Aveiro, Portugal

³ LASI - Intelligent Systems Associate Laboratory, 4800-058 Guimarães, Portugal

Email: * bmelo@ua.pt

Impedance spectroscopy is a crucial technique to describe ionic transport properties, allowing to separate electrochemical cell components or processes based on direct electrical elements (resistor, capacitor, inductor) using Equivalent Circuit Models (ECMs). The analysis using ECMs has also been extended to more complex transfer functions, including the constant phase element or even chemical elements such as the Warburg or Gerischer, to represent the diffusion processes.

With respect to dielectric materials, their dielectric relaxations are often studied with empirical models such as the Cole-Cole (CC), the Cole-Davidson (CD), and the Havriliak-Negami (HN). According to these models, the dielectric relaxation is characterized by a distribution of relaxation times instead of a single relaxation time. By choosing the appropriate distribution function, it should be possible to fit the experimental dielectric response of many different materials.

In this work, we present a MATLAB application software for the visualization, analysis, and modeling of impedance spectroscopy data.

This free software, available from <https://github.com/bmgmelo>, provides an intuitive and time-saving tool for analyzing impedance spectroscopy data in multiple immittance functions (Z^* , ϵ^* , M^* , Y^* , $\tan(\delta)$, σ^*) as a function of temperature and frequency. Some of the relevant features provided are: fitting impedance data to a user-defined equivalent circuit model; fitting complex data (ϵ^* and M^*) according to the Havriliak-Negami function; analysis tools for distinguishing between the long-range conductivity peak and the localized relaxation processes; and studying the impedance data with the distribution function of relaxation times formalism (impedance data is directly imported to the DRTtools [1]).

Most impedance spectroscopy commercial software solutions use the Levenberg-Marquardt or Nelder-Mead algorithms for complex nonlinear least-square problems. We provide alternative algorithms with boundary conditions since we believe they could offer some advantages such as restraining numerical solutions where one of the fitting parameters has no physical meaning.

Special interest was given to developing a software tool able to fit complex dielectric modulus data (M^*) according to the Havriliak-Negami model. In this, we developed a new multi-variable numerical algorithm, that fits simultaneously the complex M^* and ϵ^* values using the Havriliak-Negami function. This new algorithm provides the general solution to both immittance functions. Moreover, it allows fitting complex dielectric modulus data (M^*) while minimizing the overlapped effect of the dc-conductivity peak and highlighting the ϵ' contribution which is independent of the conductivity contribution.

Several study cases will be discussed (proton conductors, lithium-ion batteries, polymers), showing the application of this software and how it could be a useful tool for the dielectric community.

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Nonlinear dielectric spectroscopy of liquids and protein solutions

Dmitry Matyushov*¹

¹*School of Molecular Sciences, Arizona State University, Tempe, USA*

Email: *dmitrym@asu.edu

This talk will discuss theories of nonlinear dielectric response from simple liquids to dilute protein solutions to intrinsically disordered proteins (IDPs) [1,2]. The nonlinear dielectric effect (NDE) is traditionally connected to saturation of individual dipoles in strong electric fields. Recent experiments have shown that the temperature effect on the NDE is inconsistent with this view and it should be alternatively related to binary and multipolar dipolar correlations [3]. The theory predicts a positive NDE in dilute solutions of polar molecules in less polar solvents. This prediction is applied to protein solution showing a sharp contrast between the nonlinear response of proteins relative to the water solvent. Nonlinear dielectric response can serve as a sensitive tool for monitoring protein conformations and physiological activity. Computer simulations are used to understand the origin of field-induced alteration of dielectric relaxation. The main field effect comes from slowing down of single-particle rotational dynamics [4]. Theories of nonlinear dielectric relaxation need to mostly account for the field effect on single-dipole rotations. The theoretical formalism was applied to analyze long, 1.5 μ s, MD simulations of IDPs. Solutions of IDPs produce a large increment of the linear dielectric constant due to their strongly fluctuating dipole moments. Statistics of the dipole moment are non-Gaussian, contributing a component to the NDE response. Electrolyte screening and reduction of density fluctuations of proteins in solution are required to observe the intrinsic non-Gaussian fluctuations of the dipole moment connected to conformational flexibility of IDPs.

Acknowledgments

This research was supported by the National Science Foundation (CHE-2154465).

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Dielectric Spectra from First-Principles Simulations : Water, Salty Water and Others

Florian Pabst^{1,*}, Stefano Baroni¹

¹ *Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy*

Email: * fpabst@sissa.it

When mixed with certain kinds of salts, the dielectric spectrum of water shows a peculiarity: The main dielectric peak, often associated with the structural α -relaxation, shifts to higher frequencies upon adding salt, although the viscosity increases [1]. Since viscosity and the α -relaxation timescale are proportional, this questions the assignment of the main dielectric peak. Indeed, over the past few years, it has been established that the dielectric spectrum of all kinds of liquids may contain a strong contribution from the cross-part of the dipole correlation function, superimposed on the self-part [2], the latter commonly regarded as the α -relaxation. It has been shown by extensive first-principles simulations that this is also true for neat water [3]. Here, we use machine learning methods to train a neural network potential on density functional theory (DFT) data in order to combine the accuracy of first-principles simulations with the computational speed of classical force fields. A second neural network is trained on maximally localized Wannier functions to get state-of-the-art molecular dipole moments from the electronic structure. With that, it is possible to efficiently calculate dielectric spectra over a broad concentration and temperature range with first-principles accuracy. We use calcium perchlorate, a salt hypothesized to depress the freezing point so that liquid salty water might exist on Mars, to show that the cross-part of the dipole correlation function is suppressed upon addition of salt. This leads to the shift of the main peak to higher frequencies, while the self-part follows the viscosity. Implications of these findings for the dielectric spectra of other types of liquids are discussed.

Acknowledgments

Financial support by the Italian Ministerial grant PRIN 2022 "ARES - Assessing the origin and stability of Martian subglacial waters" is gratefully acknowledged.

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Inversion of Coaxial Transmission Line Data Using Numerical Simulation

Kazunori Takahashi^{1,2*}

¹ OYO Corporation, 1-66-2 Miyahara, Kita-ku, Saitama, Japan

² Geophysical Survey Systems Inc., 40 Simon St., NH, USA

Email: * takahashi-kazu@oyonet.oyo.co.jp

The coaxial transmission line measurement has been employed to measure complex permittivity at microwave frequencies. The Nicolson-Ross-Wier (NRW) method is one of the common methods to invert the data. Another method for the same purpose but using a numerical simulation [1], instead of a theoretically derived formulation, is proposed in this presentation.

The proposed method employs the finite-difference time-domain (FDTD) method, which is a transient electromagnetic simulation based on Maxwell's equations. The wideband frequency response from a sample is modelled, compared to the measurement, and the modelled complex permittivity that simulates the measurement the best is determined as the solution. In order to verify the idea, air, ethanol, and water were measured in a frequency range of 1 MHz – 10 GHz.

As the propagation in a coaxial transmission line is in the TEM mode, the forward modelling was performed using a 1D model. The simulation was run for each frequency. The downhill simplex method was used to minimise the cost function, which was the normalised error between measured and modelled S-parameters. The NRW method was used to set the initial guess at the lowest frequency, and the solution of the previous frequency was used for other frequencies onwards which implicitly assumes the continuity of the dielectric spectrum over frequency. Figure 1 shows the obtained complex permittivities of air, ethanol, and water, compared to those obtained by the NRW method and those found in the literature. The permittivities obtained by the method agree well with the literature values and did not show divergences at the frequencies where wavelength matches integer multiples of the sample length. The permittivity of water deviated from the literature value in higher frequencies, which may have been caused by higher-order propagation modes and the frequency limit of the calibration standards used for the measurement. The former is expected to be overcome by employing a 2D or 3D FDTD model in the forward modelling at the expense of the computation time.

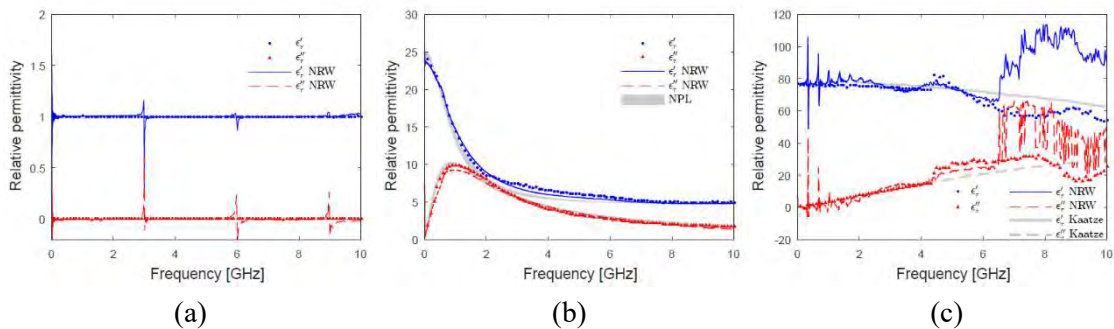


Figure 1. Complex permittivity of (a) air, (b) ethanol, and (c) water obtained using the proposed method, NRW method, and found in the literature[2][3].

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On the Kirkwood correlation factor of dense isotropic polar fluids

Pierre-Michel Déjardin¹

¹ *Laboratoire de Modélisations Pluridisciplinaires et Simulations, Université de Perpignan Via Domitia,
52 avenue Paul Alduy, F-66860 Perpignan, France*
Email: * dejardip@univ-perp.fr

A new formula for the Kirkwood correlation factor g_K occurring in the Kirkwood-Fröhlich theory of the dielectric constant of polar fluids is obtained from Dynamic Density Functional Theory [1,2]. After an approximation on the rotational part of the triplet rotational partial density is made, this formula can be evaluated, analytically in the simplest situations, and numerically in more complex ones. It is then argued that, since molecules are also polarizable, comparing g_K with 1 to deduce pair orientational ordering is meaningless in general, making only sense when the polarizability of the molecules is zero. The correlation factor is then computed for a model potential involving, in particular (but not only) permanent dipole-dipole, induction, and dispersion interaction energies [3]. The theory is shown to successfully agree with the experimental temperature dependence of the dielectric constant of around 10 simple polar fluids of different nature.

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Introducing a Mechanistic Perspective on the Slow Arrhenius Process (SAP) in Glass Forming Systems

Ronald P. White^{1*}, Simone Napolitano² and Jane E.G. Lipson¹

¹ Department of Chemistry, Dartmouth College, Hanover, NH 03755, USA

² Polymer and Soft Matter Dynamics, Experimental Soft Matter and Thermal Physics (EST), Université libre de Bruxelles (ULB), 1050 Brussels, Belgium

Email: * ronald.p.white@dartmouth.edu

Recent experimental work is revealing an important route to molecular relaxation in glass forming systems, the slow Arrhenius process (SAP). The SAP has been shown [1] to be a driving factor in a number of routes to material equilibration. It operates over a temperature range that spans melt and glassy states, coexisting in dielectric spectra together with the well-known α -process. Here we will provide new mechanistic insight into the SAP [2] and connect its activation energy to both dynamic and thermodynamic system properties. The former include the glass transition temperature (T_g) and viscosity (activation energy for flow). By applying thermodynamic model analysis [3] to pressure-volume-temperature data we also demonstrate links to thermodynamic properties such as coefficient of thermal expansion, segmental entropy, cohesive energy, and heat capacity. These insights allow us to introduce a molecular level mechanism for the SAP that is consistent with experimental observations and markedly distinct from the α -process. (See Figure 1.) It is initiated by thermal fluctuations that lead to deformation of the amorphous packing in localized regions, creating points of flexibility for a material's overall stress relaxation (rheology), and consolidating free space for volume relaxation (physical aging). As characterized in Figure 1, it is qualitatively different from the α -process in several key ways: it requires only minimal translation by individual segments, and there is neither cage breaking nor segmental diffusion.

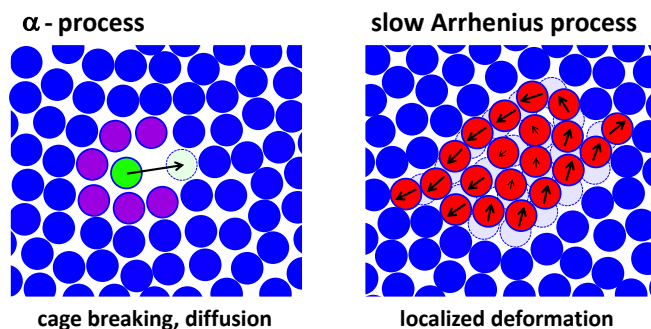


Figure 1. Contrast of molecular level mechanisms. Motions in the α -process (left) involve large segmental translations, equal to or greater than a near neighbor distance. The slow Arrhenius process (right) reshapes amorphous packing based on smaller translations, all well less than a near neighbor distance.

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S11

Industrial and Technological Applications

Improving electrical insulating properties by using conductive materials: the interplay between permittivity and conductivity

Anatoli Serghei

University Claude Bernard Lyon 1, Ingénierie des Matériaux Polymères,
CNRS, Villeurbanne, France
Email: * anatoli.serghei@univ-lyon1.fr

The partial discharge is a harmful phenomenon that progressively deteriorates the insulating performance of insulating materials, ultimately leading to a dielectric breakdown that gives rise to a total, irreversible and permanent loss of electrical insulation. This phenomenon sets off above a certain voltage threshold called the partial discharge inception voltage (PDIV). Insulating materials operating above this voltage threshold are continuously exposed to this phenomenon, being thereby subjected to damages that significantly reduce their life time. Increasing the PDIV of insulating materials represents thus an important challenge to avoid the negative impact of the partial discharge and the consequent deterioration of the insulating properties. Here we show that the integration of conductive materials into insulators surprisingly leads to a substantial increase of the partial discharge inception voltage (Fig. 1). This effect, originating from an interplay between the contribution of permittivity and conductivity, is systematically investigated in our study, both theoretically and experimentally, and its scaling laws in respect to the permittivity and conductivity are analyzed in detail. This new finding could have a huge impact on eliminating the impact of partial discharge on the electrical performance of insulating materials.

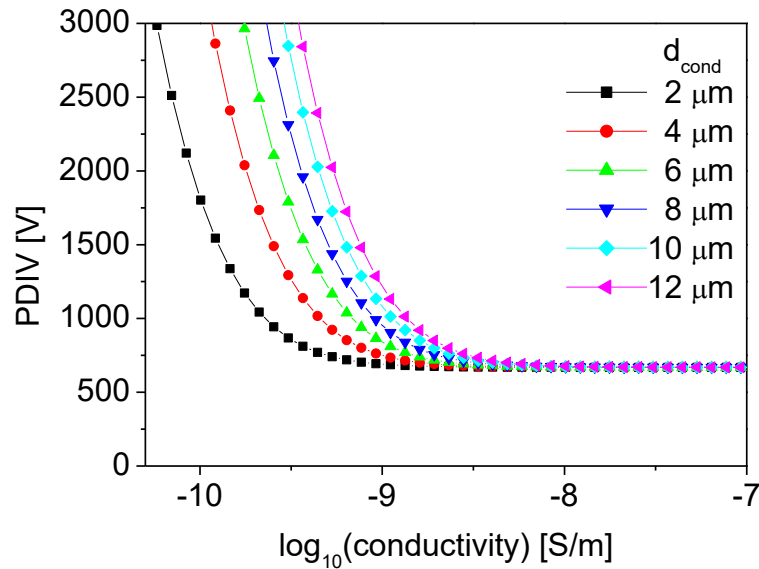


Figure 1. Partial discharge inception voltage as a function of conductivity, for conductive layers of different thicknesses, as indicated, integrated into insulating materials.

Broaden the use of dielectric spectroscopy to non-polar polymers: implementation of dipolar probes by gamma irradiation

Nathan Dintilhac¹, Simon Lewandowski², Laure Gevaux³ and Eric Dantras^{1*}

¹ CIRIMAT – Université Toulouse III Paul Sabatier, Physique des Polymères, 118 route de Narbonne, 31062, France

² ONERA/DPHY, Université de Toulouse, F-31055, Toulouse, France

³ CNES – French Space Agency, 18 avenue Edouard Belin Cedex 9, F-31401, Toulouse, France
Email: * eric.dantras@univ-tlse3.fr

Zero Pressure Balloons (ZPBs) enable the transport of scientific equipment up to a stratospheric altitude, in order to carry out experiments such as atmospheric composition studies, instruments validation for future satellites, or astrophysics study. Linear Low Density Polyethylene (LLDPE) thin films are the polymer used for ZPB envelope. Analyses as mechanical spectroscopy or Fourier Transform Infrared, have been already carried out to explore its microstructure evolution as a function of environmental stress (UV, ozone, temperature cycle, mechanical load, etc...). Dielectric techniques have been rarely used because of their intrinsic principle based on the dipolar nature of the macromolecule [1]. A non-polar polymer will have a very poor signal-to-noise ratio [2]. This work presents a protocol for implementing dipoles on an apolar LLDPE, by gamma irradiation.

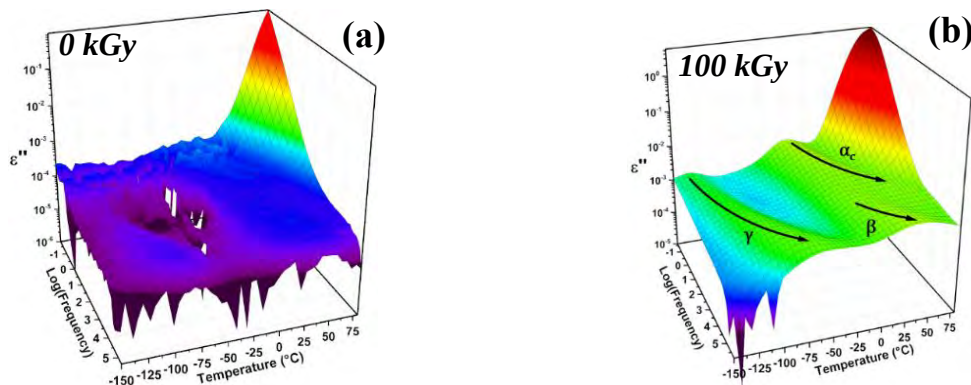


Figure 1. 3D relaxation map of virgin (a) and irradiated (b) LLDPE at 100 kGy measured by Broadband Dielectric Spectroscopy.

Infrared analyses showed that carbonyl bonds were implemented on the LLDPE macromolecule after irradiation. The addition of polar sites was followed by the evolution of $\epsilon''(\omega, T)$ dielectric loss values. A significant improvement in the signal-to-noise ratio was observed (Figure 1), enabling the molecular mobility study [3]. For example, establishing behavior laws as well as associated activation energies of β and α_c relaxation modes, are now possible.

Acknowledgments

The authors would like to thanks ONERA for their MEGA facility and CNES for their financial support in this project.

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Through-vial impedance spectroscopy as a process analytical technology for developing pharmaceutical freeze-drying cycles

Geoff Smith¹, * Pathum Wijesekara¹ and Paul Matejtschuk²

¹ School of Pharmacy, De Montfort University, Leicester, LE1 9BH, UK

² Medicines and Healthcare Regulatory Agency (MHRA), South Mimms, Potters Bar, UK
Email: * gsmith02@dmu.ac.uk

In the majority of freeze-drying processes, the drug product solution is contained within small glass bottles (vials) and taken through a series of stages; from an initial freezing stage (with optional annealing stage) to a primary drying stage (in which the ice fraction is removed by sublimation), to a secondary drying stage (in which adsorbed water is removed by evaporation). The format of a glass vial container is ideally suited to an application for impedance/dielectric spectroscopy in characterising the freeze-drying cycle, because the vertical glass wall container provides a suitable structure to support an electrode system and maintain its geometry, and hence cell constant.

With the electrodes on the outside of the vial, the measurement of impedance is therefore taken through the wall of the container; hence the expression through-vial impedance spectroscopy (TVIS) was coined as the name for this method [1]. The electrical connections to these test vials are formed using a pair of coaxial cables which, if sufficiently small in diameter, can be flexible enough to not cause the vial to tip on flexing any one cable. This also means that it is easily possible to place the TVIS vials within a standard array of vials without disturbing the packing density and hence heat transfer processes.

This presentation will profile the unique capability of TVIS for the non-invasive characterisation of the ice fraction and the solids fraction, with case studies that demonstrate the accurate determination of

- (i) the solids fraction's stability (i.e., critical temperatures above which products collapse and the propensity to crystallise during drying).
- (ii) individual vial ice interface temperatures and sublimation rates, which then improve the robustness of the drying models that facilitate the safe-design of higher-temperatures processes, with potential reductions in processing time of up to 50% (without risking quality because of forced instabilities in the solids fraction).
- (iii) endpoints of each process stage (namely, the freezing stage, the sublimation of ice (primary drying) and the desorption of moisture (secondary drying) with potential reductions in process time of 10-15%.

Acknowledgments

This research is supported by the Digital_Lyo grant awarded by Innovate UK to the following organizations: De Montfort University, MHRA, Qrometric Ltd, IS Instruments Ltd, AstraZeneca plc, and Siemens.

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Microwave Dielectric Response of Cytoplasmic Water in Red Blood Cells Upon Glucose Uptake

Cindy Galindo¹, Leonid Livshits², Gregory Barshtein³, and Yuri Feldman¹

¹ Institute of Applied Physics, Hebrew University of Jerusalem, Israel

² Institute of Veterinary Physiology, University of Zurich, Switzerland

³ Biochemistry Department, The Faculty of Medicine, Hebrew University of Jerusalem, Israel

Email: * yurif@mail.huji.ac.il

Diabetes is one of the most prevalent diseases worldwide and its incidence continues to rise due to dietary changes and sedentary lifestyles. Current approaches for blood glucose level monitoring in diabetic patients are highly invasive. Consequently, considerable attention has been directed toward the advancement of non-invasive technologies. Previous studies have demonstrated the sensitivity of Microwave Dielectric Spectroscopy (MDS) to glucose changes in the blood. Nevertheless, a deeper understanding of the underlying mechanism driving this sensitivity is essential for the development of an optimal non-invasive device

This investigation primarily addresses this fundamental question: "**Why microwave dielectric spectroscopy (MDS) is sensitive to changes in blood glucose concentration?**". Here, we focus on specific aspects of the hypothesis that the alteration of water dynamics (monitored by MDS) due to glucose uptake by red blood cells (RBC) is related to intracellular sugar metabolism and associated homeostasis. The intricate cascade of reactions occurring within the intracellular compartment caused due to glucose is referred to as glycolysis. Glycolysis involves the production of adenosine triphosphate (ATP) molecules and the rearrangement of ions and water within the cytoplasm, both of which contribute to alterations in the dielectric properties of cytosol water. Several years ago, our research group initiated the use of MDS to characterize the state of water within the cytoplasm of RBCs (erythrocytes) and revealed a strong dependence of the dielectric response of water on changes in extracellular glucose concentration. Notably, a sensitivity threshold to glucose uptake was identified at a concentration of 10–12 mM. It was hypothesized that this threshold is influenced by *dipole-matrix* interactions between water dipoles and moieties, like adenosine triphosphate (ATP), generated during glycolysis. However, the issue of the specificity of this response remains unsolved, as alterations in ATP concentration also lead to variations in the cytosol environment overall, particularly in terms of electrolyte composition. Such a complex environment is expected to significantly impact the interaction between water and ATP.

In this research, our objective is to discern the primary factors influencing the properties of cytoplasmic water during glucose uptake. To achieve this goal, we conducted experiments employing MDS, in the frequency range of 0.5-40 GHz. We aimed to explore potential scenarios arising from glucose uptake within the red blood cells (RBCs) and their impact on the dielectric signature of intracellular water. To understand the microscopic details/heterogeneity of cytosol water upon glucose uptake by RBC, we examined the dependence of MDS water response on two key factors: 1) the transport of glucose facilitated by GLUT1 cell membrane protein, in both the presence and absence of GLUT1 inhibitors and 2) induced changes in the composition of cations (Na^+ , K^+ , Ca^{2+} , and Mg^{2+}).

The results of this research will support the further development and implementation of applied noninvasive glucose monitoring solutions.

Using artificial neural networks to predict the dynamics of molecular glass formers

Claudia Borredon¹, Luis A. Miccio^{2,3}, Silvina Cervený¹ and Gustavo A. Schwartz^{1*}

¹Centro de Física de Materiales (CSIC-UPV/EHU) 20018 San Sebastián, Spain

²Donostia International Physics Center, P. M. de Lardizábal 4, 20018 San Sebastián, Spain

³Institute of Materials Science and Technology Colón 10850, 7600 Mar del Plata, Argentina.

Email: * gustavo.schwartz@csic.es

The glass transition temperature and related dynamics are crucial for the development of industrial materials, strongly affected by these properties during production processes and in service-life. However, the temperature dependence of the structural relaxation time for a given glass former is only experimentally accessible after synthesizing it, implying a time-consuming and costly process. In this work, we combine artificial neural networks and disordered systems theory to predict the glass transition temperature and the temperature dependence of the main relaxation time based only on the knowledge of the molecule's chemical structure [1]. This approach provides a way to estimate the dynamics of molecular glass formers, with reasonable accuracy, even before synthesizing them. We tested the model to predict the glass transition temperature of organic molecular glass formers, pharmaceutical drugs, and essential amino acids and peptides [2]. In addition, we performed a chemical embedding from the last hidden layer of the artificial neural network architecture into an m -dimensional T_g -oriented space [3]. This embedding allows us to deal with chemical structures as if they were mathematical entities, therefore performing quantitative operations, so far hardly imaginable, being essential for both the design of new materials and the understanding of the structure-property relationships. We expect this methodology to boost industrial development, save time and resources, and accelerate the scientific understanding of structural relaxation dynamics.

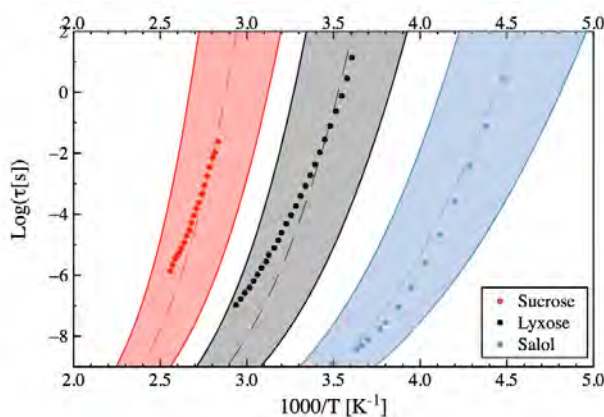


Figure 1. Relaxation map for sucrose, lyxose and salol. Dots represent experimental values measured by broadband dielectric spectroscopy, whereas shaded bands indicate the range of the relaxation times predicted by the joint numerical/theoretical approach proposed here.

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Broadband mechanical spectroscopy made available for dielectric setups

K. Eliassen¹, M. Mikkelsen¹, B. Jakobsen¹, N. B. Olsen¹, T. Christensen¹ and T. Hecksher^{1*}

¹ Dept. of Science and Environment, Roskilde University, Denmark

Email: * tihe@ruc.dk

Broadband shear mechanical spectroscopy (BMS) is a complimentary technique to broadband dielectric spectroscopy (BDS). Together, BDS and BMS is a powerful combination that can provide valuable insights that either one alone could not bring, e.g. in disentangling and interpreting different dynamical modes of e.g. alcohols [1,2] or polymers [3]. However, BMS usually is limited to fairly low frequencies and requires separate instrument.

We have developed a BMS technique, the so-called Piezo-electric Shear Gauge (PSG) [4], which has a wide frequency span reaching up to 70 kHz [5]. The working principle is a piezo electric (PZ) transducer that converts an imposed electrical field to a mechanical displacement thus shearing a sample in contact with the PZ transducer disc. The sample partially clamps the motion of the PZ disc, which can be measured as a lower electrical capacitance of the disc. Through modeling, this measured partially clamped capacitance can be translated into a shear modulus of the sample.

In collaboration with industrial partners, a simpler and more versatile version of the sample cell design has been devised [5], consisting of only one central PZ disc and two outer rigid supports. The new design allows for measurements of solid samples, such as polymers [6], and eases the implementation to a given experimental setup. Furthermore, the software for the data treatment was streamlined and published as open source software [7]. This makes the PSG technique available to anyone with a dielectric setup.

Here we describe the PSG technique and demonstrate that it produces measurements on polymer adhesives that are consistent with rheometer data, but covers a much larger range of frequencies.

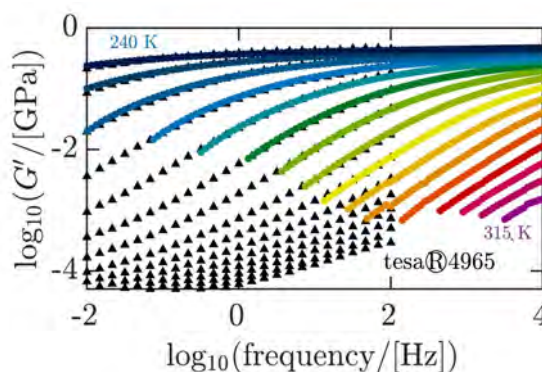


Figure 1. PSG data (colors) and rheology data (black triangles) of a commercial tape.

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**YOUNG
RESEARCHER
SESSION**

Phase Diagram, Glassy Dynamics, & Crystallization Kinetics of the Bio-based Polyester Poly(ethylene-2,5-furanoate)

Ioannis Tzourtzouklis^{1*}, D. N. Bikiaris², G. Z. Papageorgiou³ and G. Floudas^{1,4}

¹ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

² Laboratory of Polymer Chemistry and Technology Department of Chemistry Aristotle University of Thessaloniki, 541 24 Thessaloniki, Macedonia, Greece

³ Department of Chemistry, University of Ioannina, 45110 Ioannina, Greece

⁴ University Research Center of Ioannina (URCI)-Institute of Materials Science and Computing, 45110 Ioannina, Greece

Email: * ioannis.tzour@gmail.com

Global energy crisis along with the increased production of synthetic polymeric materials has led to the need for new green substitutes in order to reduce the environmental carbon footprint. To this end, recent studies have shown that poly(ethylene-2,5-furanoate) (PEF) is the most promising sustainable alternative of PET in packaging. As it derives from renewable sources (FDCA), is completely biobased and biodegradable [1]. In the present study, we report the P - T phase diagram and the origin of the sub-glass dynamics of PEF, through dielectric spectroscopy measurements performed as a function of temperature and pressure. Additionally, we report the effect of the crystallization kinetics in different dynamic parameters, using X-Ray Scattering (simultaneous SAXS and WAXS), DSC and Dielectric Spectroscopy. Regarding the P - T phase diagram, four different "phases" were detected; glass, quenched melt, crystalline, and "normal" melt [4]. We show that the cold crystallization temperature, T_{cc} , increases linearly (Clausius-Clapeyron) with pressure and is accompanied by a small volume change ($\Delta V = 0.021 \text{ cm}^3 \cdot \text{g}^{-1}$) [4]. Subsequently we address the molecular origin of the superior gas-blocking properties of PEF, by following the sub-glass β -process through the apparent activation volume (a quantity accessible via P -dependent DS measurements). Lastly, the isothermal crystallization kinetics of PEF were studied, using different probes: SAXS/WAXS for the domain spacing and degree of crystallization, DSC, for the degree of crystallinity and DS, for the evolution of the restricted amorphous fraction (RAF) and the totally amorphous fraction. The latter was used to identify dynamic changes of the amorphous and restricted amorphous fractions during crystallization [2],[3]. All probes (structural and dynamical) follow the same Avrami process with only slightly different exponent. In particular we discuss the evolution of the RAF.

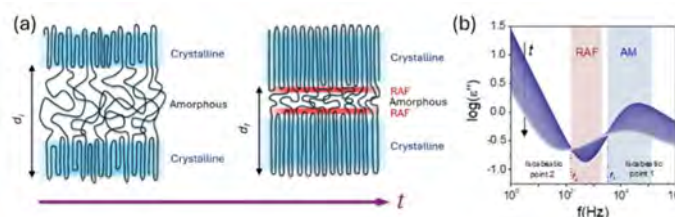


Figure 1. (a) Graphical representation of changes in the domain spacing during crystallization. (b) Dielectric loss curves during isothermal measurements at $T_c = 402 \text{ K}$. The Restricted amorphous fraction (RAF) emerges following long equilibration times [4].

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786.

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Decoupling viscosity and conductivity by leveraging Grotthuss diffusion in imidazole systems

Kaylie C. Glynn¹, Benworth B. Hansen¹, Enoch S. Mensah¹, Aikaterini Sanida¹ and Joshua R. Sangoro^{1*}

¹ The Ohio State University, 1960 Kenny Road, Columbus, OH 43210-1016, United States of America
Email: * sangoro.1@osu.edu

Next generation redox flow batteries (RFBs) will utilize complementary mechanisms of proton transport beyond simple vehicular diffusion, including mechanisms such as Grotthuss transport. Concentrated hydrogen-bonded electrolytes (CoHBEs), including ionic liquids and systems commonly referred to as deep eutectic solvents, offer a broad design space for proton-coupled electron transfer (PCET) by forming hydrogen bonded networks (HBN) in non-aqueous systems. Imidazole is a desirable system for studying Grotthuss PCET due to its ability to form chains, and in this work is paired with a proton donating species to create a model CoHBE to assess the dynamics and mechanisms of transport in the HBN. Broadband dielectric spectroscopy, dynamic mechanical spectroscopy, vibrational spectroscopy, and thermodynamic studies have been employed to analyze imidazole and levulinic acid mixtures across a broad range of compositions. The mixture shows a decoupling of the trends between viscosity and conductivity as a function of composition, suggesting transport mechanisms beyond simple vehicular diffusion. There are two compositions with regions of strongly glassy behaviors, one around a local eutectic minimum around 15 mol% imidazole and another much stronger glassy region from about 40 mol% imidazole to 70 mol% imidazole. Around 40 mol% imidazole, there is a local maximum in viscosity and minimum in diffusion, suggesting that in the imidazole rich regions above 40 mol% imidazole there is a frustration in the HBN, leading to glassy behavior, and an increase in the speed of the dynamics. Case studies of 60 mol% imidazole in this strongly glassy region have suggested evidence of multiple mechanisms, with a crossover temperature around 260K. Elucidating the proton transport mechanisms in this model CoHBE system enables strategic design of electrolyte systems for RFBs which utilize transport mechanisms beyond vehicular transport, improving transport independent of viscosity by leveraging Grotthuss diffusion.

Acknowledgments

This work was supported as part of the Breakthrough Electrolytes for Energy Storage and Systems (BEES2), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0019409.

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Investigation of the Effects of Cerium Oxide Addition on Bioglass 45S5

S.R. Gavinho^{1,*}, J.S. Regadas¹, B.M.G. Melo¹, A.C. Gonçalves¹, M.A. Valente¹, M.P.F. Graça¹

¹ *i3N and Physics Department, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

Email: * silviagavinho@ua.pt

Biomaterial coatings on dental implants are increasingly being used to address issues of rejection and implant loss. Bioglass® has emerged as a promising material for coating metal implants, enhancing the integration rate and strengthening the bond between bone and implant [1-3]. Multifunctional bioactive glasses can exhibit antibacterial, antitumor, and antioxidant effects through the addition of therapeutic ions. For instance, cerium ions have demonstrated antioxidant properties by mimicking enzymatic mechanisms and acting as scavengers of reactive oxygen species (ROS), which is crucial for reducing oxidative stress post-surgery [4,5]. Furthermore, bioglass surfaces can store electrical charge, which further promotes osseointegration [6]. This combination of properties makes bioglass an excellent candidate for advanced biomedical applications, such as dental and orthopedic implants, where enhanced biological performance and integration are critical.

In this study, glasses with various concentrations of cerium oxide (0.25, 0.5, 1, and 2 mol%) were developed and subjected to structural and electrical analysis. It was observed that the introduction of cerium did not alter the amorphous phase characteristic of the glass but led to an increase in the number of non-bridging oxygens (NBOs). This rise in NBOs had no effect on the electrical conductivity in either the AC or DC regime. Similarly, the consistent permittivity values of the glasses suggest that their storage capacity remains unaffected by the addition of CeO₂. In terms of impedance spectroscopy (IS) data, a decrease in resistance was noted with the inclusion of cerium oxide, indicating a favourable potential for applications as an antioxidant through the electro-Fenton reaction.

Acknowledgments

Acknowledgements: Work carried out with the support of the i3N, UIDB/50025/2020, UIDP/50025/2020 and LA/P/0037/2020 projects, as well as the following projects LISBOA-01-0247-FEDER-039985/POCI-01-0247-FEDER-039985.

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Water dynamics on calcium pectin-based hydrogels for application in water remediation

Francesco Coin^{1,2}, Alejandro Miccio^{1,2}, Aitor Larrañaga³ and Silvina Cervený^{1,4*}

¹ Centro de Física de Materiales (CSIC, UPV/EHU)-Materials Physics Center (MPC), Paseo Manuel de Lardizabal 5, San Sebastián 20018, Spain.

² Departamento Polímeros y Materiales Avanzados: Física, Química y Tecnología, University of the Basque Country (UPV/EHU), P. Manuel Lardizábal 3, 20018 San Sebastián, Spain.

³ SGIker, General Research Services, University of the Basque Country (UPV/EHU) (48080), Spain.

⁴ Donostia International Physics Center (DIPC), San Sebastián 20018, Spain.

Email: * silvina.cervený@ehu.es

Water is fundamental for social and economic progress, livelihoods, agriculture, health, and safety. Its scarcity and contamination, driven by population growth, industrial overuse, and climate change, pose significant challenges. Emerging contaminants, including pharmaceuticals, personal care products, and heavy metals, severely compromise water quality. Although there are solutions for this problem, such as coagulation, photocatalytic ozonation, or ion exchange, adsorption emerges as a cost-effective and scalable solution [1]. Recently, we have developed an eco-friendly pectin-based hydrogel crosslinked with selected agents (which act as adsorption sites) for adsorbing heavy metals and pharmaceuticals from contaminated water [2]. Since water mediates adsorption, it is useful to understand how water interacts with the hydrogel to elucidate the adsorption mechanism of the adsorbent.

In this work, we have studied the pectin-based hydrogel crosslinked with calcium by applying broadband dielectric spectroscopy (BDS) combined with X-ray diffraction (XRD), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to characterize its structure at different humidity levels (0 - 40 wt%) and analyze how water molecules are distributed inside the hydrogel. DSC and TGA results show a complex distribution of water molecules in both amorphous and semicrystalline regions. Moreover, water induces plastification in the amorphous region. XRD shows how water enters the semicrystalline areas, increasing the interlayer distance between chains by increasing the water content. Finally, by BDS, it is possible to detect the dynamics of water molecules in the semicrystalline areas, indicating that water is confined in regions of ~ approximately 1 nm [3].

Acknowledgments

This work was supported by CSIC (BILAT23076), and Basque Government (IT1566-22).

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Measurement of rotational relaxation time of water in biosystem by shortwave infrared micro spectroscopy

Kosei Kawai^{1*}, Junkai Zhang¹, Hiroaki Matsuura², Ryo Shirakashi²

¹ Department of mechanical engineering, The University of Tokyo, hongo7-3-1, bunkyo-ku, Tokyo, Japan

²Institute of industrial science, The University of Tokyo, komaba4-6-1, meguro-ku, Tokyo, Japan

Email: * kkawai@iis.u-tokyo.ac.jp

Dielectric spectroscopy is a simple but effective method for measuring the rotational relaxation time of water in a biosystem. However, dielectric spectroscopy using a physical probe has insufficient spatial resolution and is invasive for measuring water in a single cell *in vivo*, because the probe needs to contact the sample and the measurement range is limited by the size of the probe. We introduce a new method to measure the rotational relaxation times of water molecules in solution or biological samples with infrared micro spectroscopy, which is non-invasive and has a high spatial resolution, theoretically limited by diffraction limit [2], [3]. In this method, the water absorbance spectrum at 4500–5500 cm⁻¹ in the shortwave IR region (Fig.1), which is an exclusive combination band of stretching and bending vibrations of water molecules [1], is measured. The rotational relaxation time of water in the sample is calculated using the decomposed peaks of this spectrum and the extended Langevin equation. By measuring several solutions, the obtained relaxation time of water up to 80 psec had a 20% error ratio of the relaxation time measured by dielectric spectroscopy at a maximum (Fig.2) [2], [4]. The scanning IR micro spectroscopy in an area of 1.6 mm square with a spatial resolution of 200 μm square revealed the relative standard deviation of the relaxation time among the measured points is about 1.5% (Fig.3) [4].

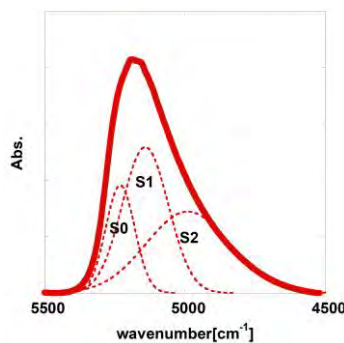


Figure 1. IR spectrum of 4500–5500 cm⁻¹

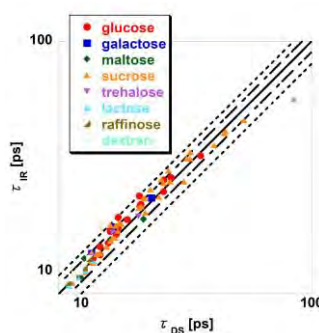


Figure 2. Relaxation time by dielectric spectroscopy, τ_{DS} , and by SWIR, τ_{IR} . ($\tau_{IR} = \tau_{DS}$ (black line), $\tau_{DS} \pm 10\%$ (black chained line), $\tau_{DS} \pm 20\%$ (black dotted line))

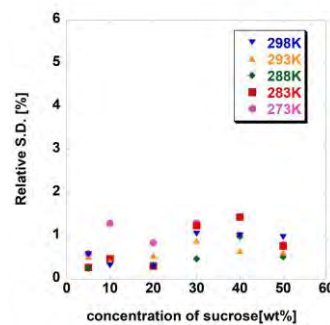


Figure 3. Relative standard deviation to concentration in two-dimensional distribution measurements of sucrose [4]

Acknowledgments

This work was supported by JST SPRING, Grant Number JPMJSP2108, and KAKENHI Grant Number 22H01409.

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Identifying dipolar cross correlation contributions to the dielectric response of water

Rolf Zeißler^{1*}, Florian Pabst² and Thomas Blochowicz¹

¹ *Institute for Condensed Matter Physics, Technical University Darmstadt, Darmstadt, Germany*

² *Scuola Internazionale Superiore di Studi Avanzati di Trieste, Trieste, Italy*

Email: * rolf.zeissler@pkm.tu-darmstadt.de

Differences in relaxation spectra of liquid water as measured by dielectric spectroscopy and other techniques have been intensively discussed over the past decades [1], [2]. Recent computational work suggests that the dielectric response of water is dominated by dipolar cross correlations introduced by the hydrogen bond network [3]. For other hydrogen bonding liquids, e.g. monoalcohols, it has been shown that dipolar cross correlations appear as a slow Debye-like contribution to the dielectric response and are absent or contribute only weakly to, e.g., depolarized dynamic light scattering (DDLS) spectra [4]. Here, we present the results of a combined BDS and DDLS study on water and aqueous lithium chloride solutions. We show that the discrepancy between dielectric loss and DDLS spectra diminishes with increasing mole fraction of lithium chloride. In agreement with recent ab initio molecular dynamics simulations [5] we conclude that disruption of the hydrogen bond network decreases the contribution of dipolar cross correlations to the dielectric loss. For a mole fraction of lithium chloride where dipolar cross correlations are sufficiently suppressed, we perform broadband DDLS measurements, accessing the dynamics from the liquid regime to the deeply supercooled regime covering more than 15 orders of magnitude in frequency. Comparison with BDS spectra shows the similarity over the full dynamic range.

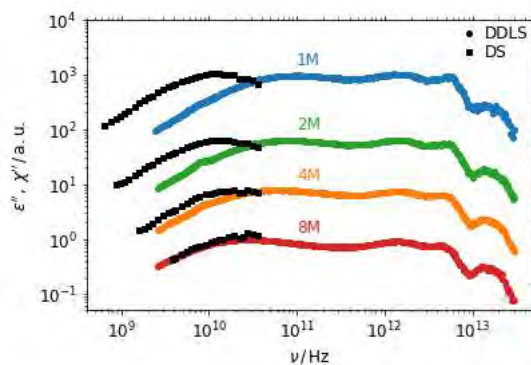


Figure 1. Comparison of dielectric loss (black squares) and DDLS susceptibility (colored circles) of aqueous lithium chloride solutions (from top to bottom: 1 molar to 8 molar) at 263 K.

Acknowledgments

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Water Dynamics in Aqueous Dipeptide Solutions Studied by BDS and ²H NMR

Sandra Krüger^{1*}, Elisa Steinrücken¹ and Michael Vogel¹

¹ Institute for Condensed Matter Physics, TU Darmstadt, Germany

Email: * sandra.krueger@pkm.tu-darmstadt.de

The interactions between water and biomolecules, in particular, the dynamics of water near biological surfaces are fundamental for understanding chemical processes related to biological functionality. To reduce the complexity of hydrated protein systems, we investigate aqueous dipeptide solutions as much simpler model systems. Explicitly, we study water dynamics in mixtures with N-acetyl-glycine-methylamide (NAGMA), N-acetyl-leucine-methylamide (NALMA) and N-acetyl-lysine-methylamide (NAKMA) serving as model protein backbones with different hydrophobicity. In addition to the amino acid composition of the dipeptides, the water concentration is varied, resulting in complete vitrification or partial freezing of water. In the latter case, the hydration layer near the dipeptide surface remains liquid.

We use broadband dielectric spectroscopy (BDS), differential scanning calorimetry (DSC) and various ²H nuclear magnetic resonance (NMR) methods to investigate the rotational dynamics in large time and temperature windows. In addition, we employ static field gradient (SFG) NMR to determine the self-diffusion coefficients of both water and dipeptide. At temperatures above a possible freezing point, we find that the water dynamics slows down with increasing dipeptide concentration, as expected. For a given concentration, water dynamics, however, slows down with increasing size of the dipeptide. Comparing rotational and diffusive motions, we find that the Stokes-Einstein-Debye relation is obeyed, see Fig. 1.

Below the freezing point, we disentangle the signal contributions of the liquid and frozen water fractions and the dipeptide. We observe that the rotational motion of the remaining liquid water fraction is independent of the nominal concentration of the solution and has an Arrhenius temperature dependence with an activation energy of 0.9 eV, for $T_m > T > 200$ K. In contrast to the high-temperature dynamics, water dynamics slows down with increasing hydrophobicity of the dipeptide, implying a significant influence of the amino acid type on hydration shell dynamics. For a completely supercoolable NAGMA solution, we observe that the α -relaxation has Vogel-Fulcher-Tammann temperature dependence, while a water relaxation separates in the highly viscous regime and follows an Arrhenius law with an activation energy of 0.5 eV below the glass transition temperature T_g , see Fig. 1. Nonetheless, ²H NMR reveals a quasi-isotropic rotational mechanism for water in this temperature range.

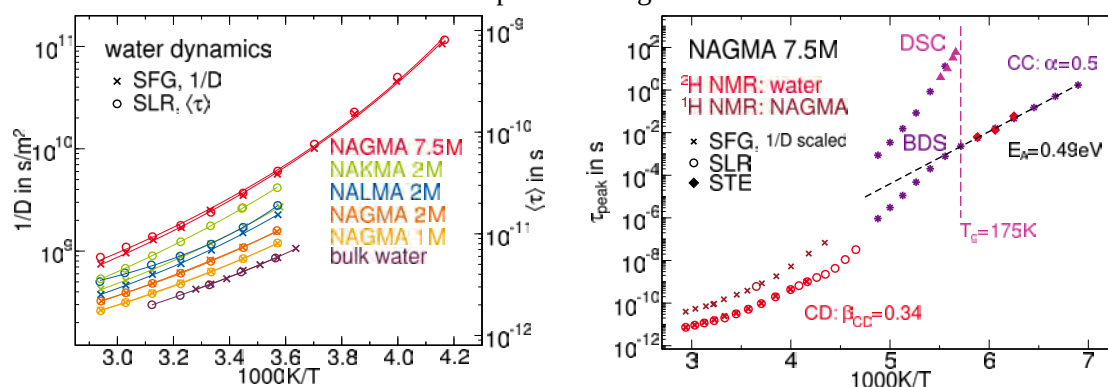


Figure 1: Results for mixtures of water with different dipeptides: (left) Correlation times and diffusion coefficients of water in the indicated dipeptide mixtures in the high temperature region. (right) Correlation times of water and NAGMA in supercoolable 7.5M NAGMA solution from BDS, NMR and DSC measurements.

Dynamically and Structurally Heterogeneous Ethanol/Water Mixtures

Vasileios Moschos^{1*}, and George Floudas^{1,2,3}

¹ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

² Max Planck Institute for Polymer Research, 55128 Mainz, Germany

³ University Research Centre of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina, Greece

Email: * v.moschos@uoi.gr

Aqueous monohydroxy alcohol solutions, such-as the 1-propanol/water mixture, display several peculiar features originating from hydrogen bonding, and in particular, antagonistic hydrophilic/hydrophobic interactions of the head/tail that give rise to local nano-heterogeneity [1], [2], [3]. Ethanol/water mixtures are of particular interest due to the polymorphism ethanol exhibits; pure ethanol can be prepared as an amorphous solid, a *bcc* plastic crystal or in fully ordered crystalline state (monoclinic) [4]. By combining structural (XRD) thermodynamic (Differential Scanning Calorimetry, DSC) and dynamical probes (Dielectric Spectroscopy, DS), the pertinent phase diagram of the binary mixture is established [5]. It comprises of different states of ethanol depending on temperature and composition, liquid water, hexagonal and amorphous ice and different hydrates. The phase diagram is discussed in terms of four regimes; three having in common a droplet arrangement of the minority component and one (ethanol-rich) where ethanol and water are molecularly mixed. Within regime II ($0.90 \leq X_V \leq 0.475$, X_V corresponds to the volume fraction of ethanol in the mixture) water droplets are moderately confined and water crystallizes via homogeneous nucleation well within *No Man's Land*. By probing the dynamics of the mixture with DS over a broad frequency and temperature range, different relaxation processes are identified, that comprise the α -process and the Debye (-like) process of ethanol and three additional processes associated with the dynamics of ethanol/water mixtures. Both equilibrium and non-equilibrium effects are studied by different thermal protocols (slow/fast cooling rates respectively). Differences and similarities of the ethanol/water phase diagram are discussed with respect to the 1-propanol/water binary system, where hydrophobic interactions dominate.

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786.

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Enhanced Ionic Conductivity in Single-Ion-Conducting Block Copolymer Electrolytes of PS-*b*-P(EO-*co*-GME)

Marianna Spyridakou^{1*}, Ioannis Tzourtzouklis¹, Tobias Gäb², Holger Frey², George Floudas^{1,2,3}

¹ Department of Physics, University of Ioannina, P.O. Box 1186, 45110 Ioannina, Greece

² Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

³ University Research Center of Ioannina (URCI)-Institute of Materials Science and Computing, 45110 Ioannina, Greece

Email: * spiridakoum@gmail.com

Single ion-conducting polymer electrolytes (SICPE) based polystyrene and poly(ethylene oxide) block copolymers (PS-*b*-PEO) hold great potential, as they combine superior durability and the ability to exclusive charge transport via lithium cations [1]. However, the incorporation of covalently attached anions into the flexible polyether block to yield SICPE is a synthetic challenge [1]. For this purpose, a new diblock copolymer electrolyte, polystyrene-*b*-poly(ethylene oxide-*co*-glycidyl methyl ether) (PS-*b*-P(EO-*co*-GME)), was synthesized bearing different [O]:[Li⁺] ratios and different compositions [2]. The P(EO-*co*-GME) block can be engineered to simultaneously suppress the PEO crystallization and significantly enhance ion conduction. This reflects the lower glass temperature of PGME as compared to PEO, its inability to crystallize due to branching and the presence of two oxygens that can better solubilize lithium salts. In all investigated samples, X-rays scattering (SAXS) revealed strong nanophase segregation between the PS and P(EO-*co*-GME) blocks, while the ordered morphology is maintained, even at higher temperatures. The thermodynamic properties (DSC) verified the vitrification of the two blocks, identifying two glass temperatures and further confirming the absence of PEO crystallization. Ionic conductivity measurements performed as a function of temperature revealed enhanced conductivity values, in comparison to previous studies in the related PS-*b*-P(EO-*co*-LiTfSAEGE) [3], due to the considerably high conduction of the PGME. At the same time, the mechanical stability of the system is maintained by the glass PS block. This provides a promising alternative for designing SPEs, which combine high ion conductivity with mechanical stability, both of which are important for future battery technologies.

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786.

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Evaluating polyantimonic acid membranes as solid-state fuel cell electrolytes

Sofia R. Mendes^{1,*} and Pedro M. Faia¹

¹ University of Coimbra, CEMMPRE – Electrical and Computer Engineering Department, FCTUC, Polo 2, Pinhal de Marrocos, Coimbra 3030-290, Portugal.
Email: * uc2002123458@student.uc.pt

In recent years, there has been a growing interest in discovering new ways to generate renewable electrical energy for fuel cell applications that are as low-polluting, efficient, and stable as possible[1]. The study of promising protonic materials as fuel cell membranes led to the study of polyantimonic acid (PAA) as a promising candidate. PAA does not agglomerate easily to produce bulk membranes, which is why it is necessary to add a binder[2]. Some studies already approach some binders, such as polysulfone and polytetrafluoroethylene, among others[2]. Polyvinyl alcohol (PVA) was the chosen binder for the present research.

Electrical evaluation by Electrical Impedance Spectroscopy (EIS) of the prepared membranes (membranes with 10:90, 15:85, 20:80 and 25:75 wt/wt % proportion of PVA:PAA, named PP10, PP15, PP20 and PP25, respectively) was carried at 0% of relative humidity (dry air) and different temperatures (25, 50, 75, 100, 150 and 200°C). In the figure are depicted some results of the evaluation of sample PP20. There was a change in the colour of the sample above 150°C, attributed to the chemical alteration of the binder, also reflected in the Nyquist diagrams (**Figure 1 (a)**). The repeatability tests provided acceptable ageing information (the Nyquist plots obtained one week after, **Figure 1 (b)**, show a slight increase of the overall observed impedance). Time stability evaluation is still ongoing. An equivalent circuit is being developed based on EIS results to better interpret the contributing phenomena to the overall electrical response found.

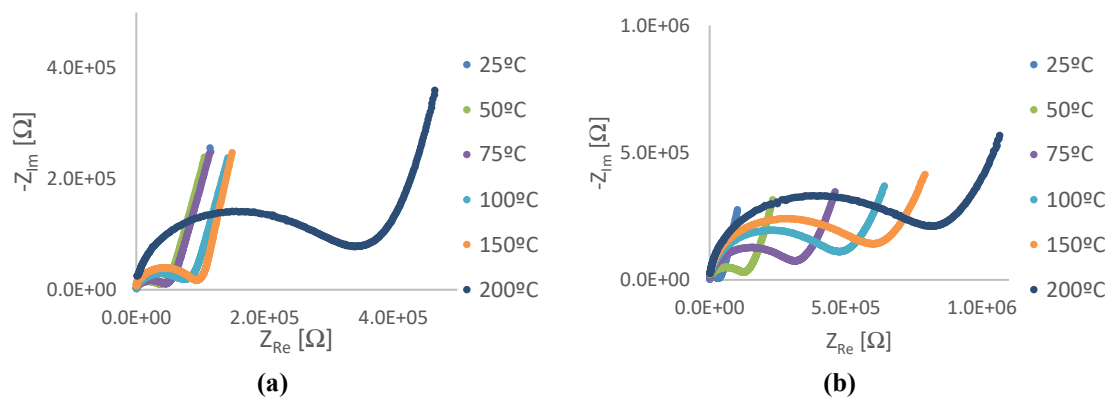


Figure 1. Nyquist diagram for PP20 (a) initial and (b) after a week.

Acknowledgments

This research was sponsored by FCT - Fundação para a Ciência e a Tecnologia, Portugal, and by scholarship UI/BD/152285/2021 (<https://doi.org/10.54499/UI/BD/152285/2021>).

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Phyto- and Phyto-Second Harmonic Generation- Photodynamic Therapy of Prostate Cancer Cells

Efrat Hochma¹, Paul Ben Ishai¹, Michael A. Firer^{2,3,4} and Refael Minnes¹

¹ *Department of Physics, Ariel University, Ariel, Israel*

² *Department of Chemical Engineering, Ariel University, Ariel, Israel*

³ *Adelson School of Medicine, Ariel University, Ariel, Israel*

⁴ *Ariel Center for Applied Cancer Research, Ariel University, Ariel, Israel*

Email: *firer@ariel.ac.il

Cancer therapy, from malignant tumor inhibition to cellular eradication treatment, remains a challenge. Especially regarding higher tissue penetration, reduced side effects and low energy consumption during treatment. Hence, phytochemicals and non-linear upconverting phyto-SHG-nanocomposites as cytotoxic sensitizers or photosensitizers deserve special attention. The dark and photo-response of Yemenite 'Etrog' leaf extracts applied to prostate PC3 cancer cells was investigated. An XTT cell viability assay along with light microscope observations revealed pronounced cytotoxic activity of the extract for long exposure times of 72 h upon concentrations of 175 mg/ml and 87.5 mg/ml, while phototoxic effect was obtained even at low concentration of 10.93 mg/ml and short introduction period of 1.5 h. For the longest time incubation of 72 h and for the highest extract concentration of 175 mg/ml, relative cell survival decreased by up to 60% (below the IC₅₀). In combined phyto-photodynamic therapy a reduction of 63% compared to unirradiated controls was obtained. The concentration of extract in cells versus the accumulation time was inversely related to fluorescence emission intensity readings. Based on ATR-FTIR analysis of the powdered leaves and their liquid crude ethanolic extract, biochemical fingerprints of both polar and non-polar phyto-constituents were identified. Next, perovskite Barium titanate (BT) nanoparticles were studied for optional conjugation to visible light-absorbing natural plant-derived photosensitizers, including Yemenite Citron ('Etrog') leaf extracts (EXT), rhein molecules (RH), and their BT/RH/EXT superpositions. The synthesis and conjugation formation of phyto-SHG-nano-systems was evaluated through STEM imaging and UV-VIS absorbance and emission spectra analysis. Optional operating mechanism pathways were suggested. Phyto- and phyto-nanoconjugates exhibiting dark and photodynamic activity can be applied as therapeutic and mediation-therapeutic agents in the medical field.

Shear Force Microwave Microscopy: Complex impedance imaging, and Single Entity Electrochemistry.

Maxwell Sparey,^a Gianluca Fabi,^a Georg Gramse,^a

^a Institute of Biophysics, Johannes Kepler Universität Linz, Gruberstraße 40, Linz, 4020

Maxwell.Sparey@jku.at Gianluca.Fabi@jku.at Georg.Gramse@jku.at

We are introducing Electrochemical Shear Force Microwave Microscopy (EC-SFMM), an innovative technique positioned at the convergence of Scanning Electrochemical Microscopy (SECM) [1] and Scanning Microwave Microscopy [2]. It enables high-sensitivity microwave spectrometry analysis in the frequency range of 1 GHz to 18 GHz with nm resolution, utilising a Vector Network Analyzer (VNA) and a Bipotentiostat operating in the mHz - KHz range. This approach harnesses the synergies of both methods to deliver high-resolution local cyclic voltammetry (LCV), local electrochemical impedance spectroscopy (LEIS) [1, 3, 4], topographic imaging [2, 4, 5] and capacitance mapping [3, 4].

Distinguished from the recently introduced EC-STM [3,4] technique, ec-SFMM locks onto the mechanical resonance] of a coaxial nano electrode probe [5] and uses the damping effect of the shear force for precise distance control. This marks a significant stride by extending the applicability to non-conductive samples. This marked advantage opens new avenues for understanding complex material properties in molecular electronics [6], materials science, and single-entity electrochemistry [7]. This presentation seeks to provide a clear exploration of SECM-SMM, delving into its fundamental principles, accompanied by experimental validation results, and showcasing its potential applications in nanoscale characterization. We will discuss this hybrid technique's technical intricacies, benefits, and practical considerations, offering insights into its role in advancing our comprehension of nanoscale phenomena. Join us for a straightforward examination of ec-SFMM and its promising contributions to the ever-evolving landscape of scanning probe microscopy.

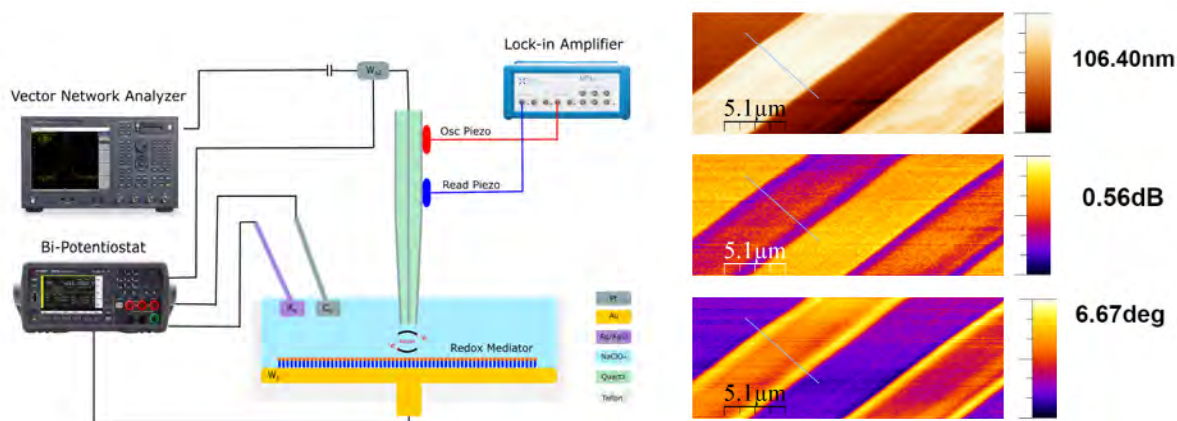


Fig 1. Overview Diagram of ec-SFMM showing electrochemical cell set-up, coaxial nanoelectrode probe, and benchtop electronics (Left). Topographic (Top) s11 Amplitude (Middle), s11 Phase (Bottom) Maps of an immersed Si/SiO₂ wafer (Left).

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Water Dynamics in Silica Confinements with Various Surface Chemistries Studied by BDS and NMR

Elisa Steinrücken^{1*} and Michael Vogel¹

¹ TU Darmstadt, Institute for Condensed Matter Physics, Hochschulstr. 6, 64289 Darmstadt, Germany

Email: * elisa.steinruecken@pkm.tu-darmstadt.de

In order to determine possible influences of different confinements, reorientational dynamics of water are studied in silica confinements with various pore diameters and surface chemistries combining broadband dielectric spectroscopy (BDS) and nuclear magnetic resonance (NMR). The crystallization of water is completely suppressed in pristine silica pores with a diameter of 2.1 nm. This allows the determination of the liquid's dynamics from room temperature to the glassy state. A wide transition range separates the Vogel-Fulcher-Tammann temperature dependence of the correlation times at $T > 215$ K from an Arrhenius behavior with an activation energie of $E_a = 0.5$ eV at $T < 160$ K, see Fig. 1. We show that the continuous transition in the temperature dependence is accompanied by a gradual change from asymmetrical dynamic BDS and NMR susceptibilities at high temperatures to symmetric ones at low temperatures. In the low temperature range, we observe that water reorientation comprises quasi-isotropic large-angle jumps. These results can be explained by a transition from bulk-like α relaxation to an interface-influenced, non-cooperative relaxation [1].

In larger silica pores with diameters of 2.8 nm or 5.4 nm partial crystallization leads to another crossover in the temperature-dependent dynamics of an unfreezable water fraction. Moreover, a static energy landscape, imposed by the interactions with the adjoining silica and ice interfaces leads to a pronounced heterogeneity of water dynamics.

For silica pores functionalized with basic lysine, neutral alanine, or acidic glutamic acid, we investigate the dependence of water dynamics on properties of the inner surfaces of silica confinements. While the temperature dependence of the correlation times is qualitatively similar to that in native silica confinement, the absolute values of the correlation times depend substantially on the type of the amino acid modifications, yielding a variation by up to two orders of magnitude. The reorientational dynamics of the water surface layer are slowed down the most for lysine functionalization, followed by alanine and glutamic acid [2]. This observation implies for biological and biomimetic systems that the mobility of water along protein surfaces varies greatly.

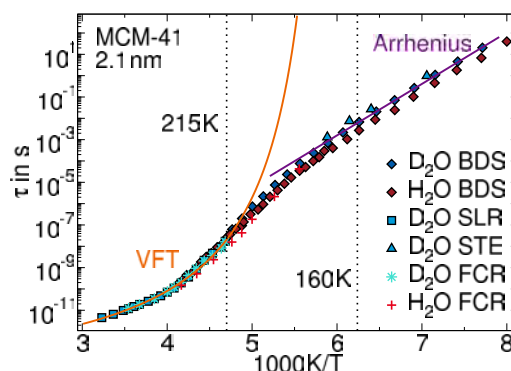


Figure 1: Correlation times of water in silica pores with diameter of 2.1 nm from BDS and various NMR methods [1], where BDS data for H₂O is taken from [3].

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Conductive P3HT nanotubes: structure/properties relationship and applications

Lucas Leveque*, Eric Drockenmuller, Laurent David, Guillaume Sudre,
and Anatoli Serghei

IMP Laboratoty – Université Lyon 1

*lucas.leveque@etu.univ-lyon1.fr

Organic semiconducting polymers have generated significant interest due to their potential applications in various fields such as flexible electronics, sensors, transistors[1], solar cells[2], particle detectors etc. Poly(3-hexylthiophene) (P3HT) has been extensively studied due to its excellent charge transport properties and ease of processing. In the recent years, the fabrication of P3HT nanostructures has received special attention in the field of nanotechnology, due to the unique properties that emerge at the nanoscale. Among various fabrication methods, the "template-assisted" method has proven its effectiveness in the preparation of different P3HT nanostructures, such as nanowires, nanotubes or nanopillars.

Here we report a systematic study of the conductive properties of P3HT nanotubes prepared using highly-ordered nanoporous AAO membranes (Anodized Aluminum Oxide) as templates and measurements cells. The electrical conductivity and the phase transitions of P3HT nanotubes were measured using Broadband Dielectric Spectroscopy (BDS), while their crystalline properties were investigated by Wide-Angle X-ray Scattering (WAXS) analysis conducted at the European Synchrotron Radiation Facility (ESRF).

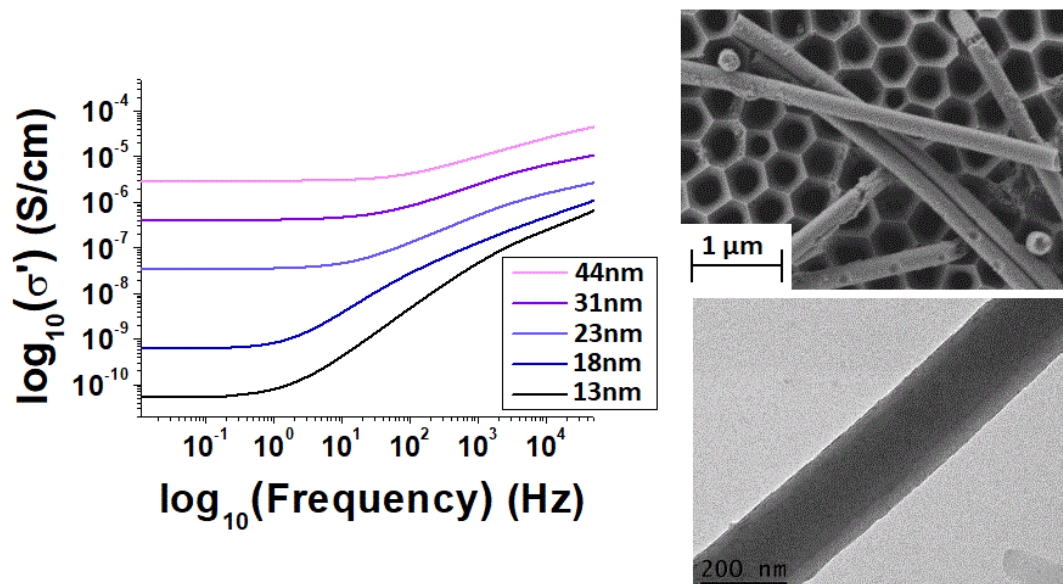


Figure 1 : (left) conductivity σ' vs. frequency for P3HT nanotubes of different thicknesses, as indicated. (right) SEM and TEM images of P3HT nanotubes.

We demonstrate that the interplay between interfacial and orientation effects at the nanoscale lead to an increase of conductivity by increasing the nanotube thickness. A conductivity value higher for the nanotubes than for the bulk is reported for thick nanotubes.

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How Do Polymers and Mixtures of Different Architecture Penetrate Nano Channels?

Panagiotis Kardasis,¹ * Georgios Sakellariou,² George Floudas^{1,3,4}

¹Department of Physics, University of Ioannina, 45110 Ioannina, Greece

²Department of Chemistry, National and Kapodistrian University of Athens, 15771 Athens, Greece

³University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina, Greece

⁴Max Planck Institute for Polymer Research, 55128 Mainz, Germany

Email: * p.kardasis@uoi.gr

The way that polymers penetrate narrow pores is of both academic and technological importance. It provides possibilities in several areas including sensors, biotechnology, drug delivery, and optoelectronics.[1] Using *in situ* nanodielectric spectroscopy (*nDS*), we report the imbibition kinetics of star *cis*-1,4-polyisoprenes in alumina nanopores (AAO) as a function of chain architecture (linear vs multiarm stars), pore size, molar mass, and temperature.[2] We demonstrate that the imbibition kinetics of star *cis*-1,4-polyisoprenes proceeds via a slow adsorption mechanism, about 2 orders of magnitude slower than in linear polyisoprenes.[3], [4] Such ultraslow timescales ($\sim 10^6$ s) have not been reported for any polymer at temperatures well above T_g . We have explored the different imbibition kinetics of linear and star topologies in separating the components of a homogeneous blend composed of linear/star chains. [5] Moreover, a simple relation ($\tau_{\text{ads}} \sim 10 \times t_{\text{peak}}$; τ_{ads} is the adsorption time and t_{peak} is the time needed for the complete filling of pores) was found for linear polymers and stars. This suggested that the characteristic timescale of imbibition (t_{peak}) governs the adsorption process of polymers.

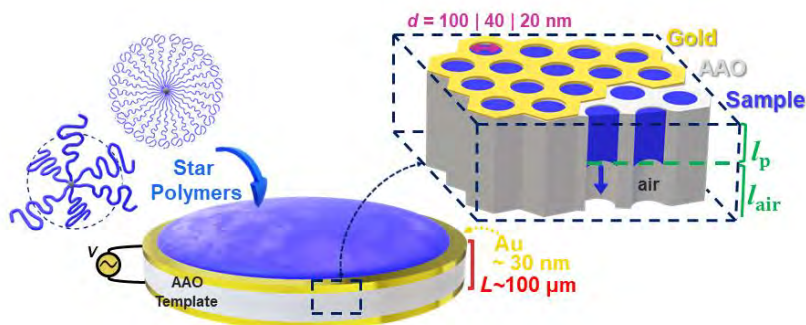


Figure 1. Schematic of the *nDS* geometry employed for the *in situ* imbibition of *cis*-1,4-polyisoprenes with different architectures (linear vs star PIs).

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786. P.K. was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the 4th Call for HFRI Ph.D. Fellowships (Fellowship Number: 9360).

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POSTERS

Molecular Dynamics and Self-assembly in Double Hydrophilic Copolymers with Densely Grafted Macromolecular Architecture

Achilleas Pipertzis^{1*}, Angeliki Chroni², Stergios Pispas², Jan Swenson¹

¹Department of Physics, Chalmers University of Technology, 41296, Gothenburg, Sweden

²Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Constantinou Ave., 11635 Athens.

Email: *achilleas.pipertzis@chalmers.se

Double hydrophilic copolymers with densely grafted architecture are promising for drug delivery applications [1], [2]. We investigate the self-assembly and dynamics of double hydrophilic block copolymers (DHBCs) composed of densely grafted poly(oligo ethylene glycol methacrylate) (POEGMA) and poly[(vinyl benzyl trimethylammonium chloride) (PVBTMAC) parent blocks by means of calorimetry, small and wide-angle X-ray scattering (SAXS/WAXS), and dielectric spectroscopy, as depicted in Figure 1 [3]. A weak segregation strength is evident from X-ray measurements, implying a disordered state and reflecting the inherent miscibility of the host homopolymers. The presence of intermixed POEGMA/PVBTMAC nanodomains results in homogeneous molecular dynamics, as evident by isothermal dielectric and temperature-modulated DSC measurements. The interfacial segmental relaxation freezes at approximately 40 K higher compared to the vitrification of bulk POEGMA segments. The interfacial process slows down by increasing the content of the hard PVBTMAC block. At temperatures below the interfacial glass transition temperature, the confined POEGMA segments in between the glassy intermixed regions contribute to a segmental process featuring: (i) reduced T_g , (ii) reduced dielectric strength, (iii) broader distribution of relaxation times and (iv) reduced fragility compared to the POEGMA homopolymer. Overall, this work provides insights about the self-assembly and molecular dynamics of bottle-brush hydrophilic copolymers.

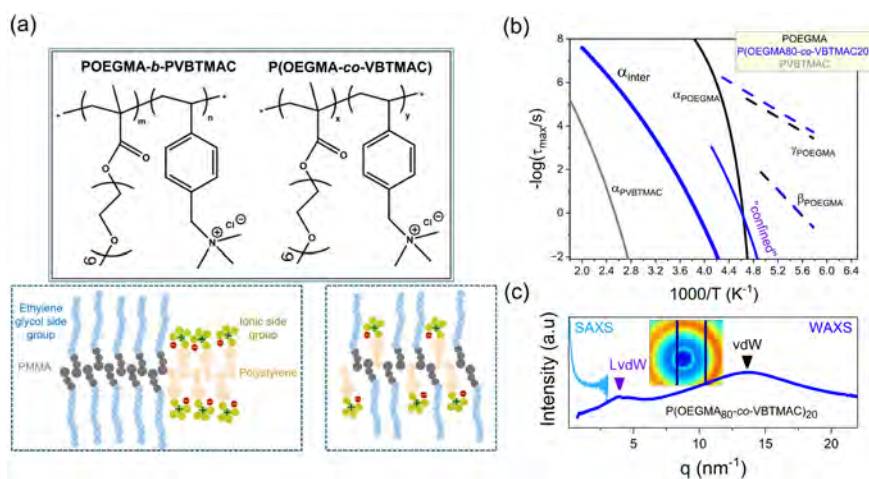


Figure 1. (a) Chemical structure and schematic representations of double hydrophilic copolymers. (b) Relaxation map and (c) SAXS/WAXS patterns of the unspecified copolymer with 80 wt.% of POEGMA.

Acknowledgments: This work was financially supported by a grant from the Area of Advance Materials Science at Chalmers University of Technology.

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Microplastics Evaluation by Electrical Spectroscopy

Diogo Gomes^{1,*}, Maria Rasteiro², Solange Magalhães² and Pedro Faia¹

¹ CEMMPRE - Electrical and Computer Engineering Department, FCTUC, University of Coimbra, Polo 2, Pinhal de Marrocos, 3030-290, Coimbra, Portugal

² CERES - Chemical Engineering Department, University of Coimbra, Polo 2, Pinhal de Marrocos, 3030-290, Coimbra, Portugal

Email: * diogomes2009@hotmail.com

Plastics are vital for society, but its usage has grown exponentially [1] and contributes to the growth of pollution worldwide. The World Health Organisation, WHO, already reported that microplastics, MPs, are found everywhere, in waste and fresh water, and in the air and soil [2]. Regarding water effluents, waste-water treatment plants, WWTP, only minimize the problem, trapping only larger size particles, while smaller ones remain in oxidation ponds or sewage sludges. Classic procedures for MPs detection are still quite laborious, and usually involve several steps and expensive equipment. However, to overcome these limitations, efforts have started using Electrical Impedance Spectroscopy, EIS. In EIS, impedance between a pair of electrodes is measured at diverse frequencies. When particles are present between the electrodes, they change the measured impedance according to their relative permittivity [3]. Consequently, impedance changes reflect both the material properties and the size of the particles. The present work aims on providing a method to detect/estimate MPs in water based on EIS. A measuring probe was developed allowing to evaluate the suspensions containing the MPs: Polyethylene, PE, and Polyethylene Terephthalate, PET, were used for preparing suspensions with two pH levels (one acid, one basic), with different concentrations. An experimental methodology was also defined to perform the tests (measures were done near the suspensions surface after heavy agitation). In Figure 1 are shown results of the obtained Nyquist plots, for the acid suspensions. As can be seen, we can differentiate solutions containing identical concentrations of PE and PET, Figure 1a), as well as solutions containing different concentrations of the same MP, Figure 1b).

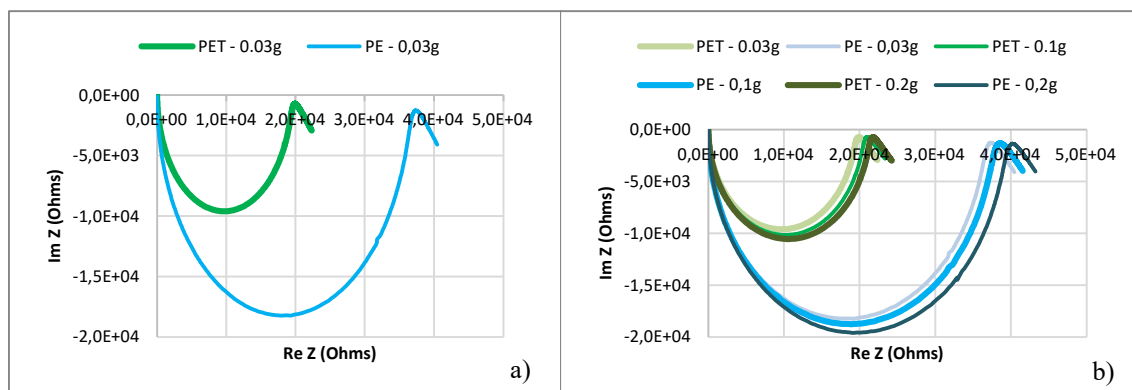


Figure 1. Nyquist plots for diverse PE and PET concentrations

Acknowledgments

Authors thank FCT—Fundação para a Ciência e a Tecnologia, Portugal, UIDB/00285/2020 and LA/P/0112/2020 projects, for the support.

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Molecular Dynamics and Viscoelastic Properties of the Biobased 1,4-Polymyrcene

Ioannis Tzourtzouklis,^{1*} Christoph Hahn,² Holger Frey,² and George Floudas^{1,3}

¹ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

² Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

³ University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina, Greece

Email: * ioannis.tzour@gmail.com

Terpenes is an important class of biomass compounds. They are naturally abundant, originating from plants that are used, e.g. in pharmaceutical products [1,2]. The most well-known example of polyterpene is natural rubber, i.e., *cis*-1,4-Polyisoprene (PI) comprising about half of the total rubber consumption worldwide. Among the variety of bio-based monomers, myrcene (Myr) has garnered considerable attention due to its convenient availability and structural similarity to isoprene and butadiene. Myrcene belongs to the class of monoterpenes that can be found in plants like conifers, wild thyme, hop, and bay leaves [3]. Here, we report the synthesis and dynamics of a series of polymyrcene homopolymers, all with identical microstructure (95% 1,4-units and 5% of 3,4-units), the latter by dielectric spectroscopy and rheology. The results show a decreasing glass temperature as compared to *cis*-1,4-Polyisoprene. Dielectric spectroscopy measurements as a function of pressure also were employed, suggesting that the measured apparent activation volume is lower than the molecular volume of the PMyr repeat unit, being closer to the corresponding PI value. This suggests that responsible for the segmental relaxation process is a part of the repeat unit [4]. Furthermore, we report the effect of chain thickening on the viscoelastic properties. The plateau modulus, G_N^0 , decreased, the entanglement molar mass increased (from 5 kg/mol in *cis*-1,4-Polyisoprene to 22 kg/mol in *cis*-1,4-Polymyrcene) and the packing length, p , increased (from 3.1 Å in PI to 4.7 Å in PMyr) as anticipated by chain thickening [4]. The plateau modulus, G_N^0 , followed the proposed empirical relation: $G_N^0 = 0.00226 k_B T / p^3$ further reflecting the proportionality between the tube diameter and the packing length [5].

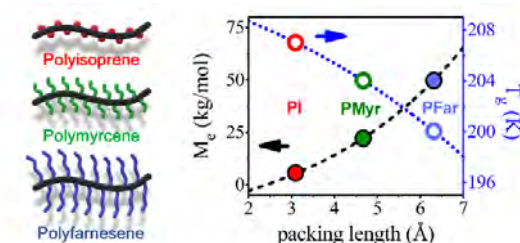


Figure 1. (a) Entanglement molar mass and glass transition temperature over packing length for the three different polymers, PI, PMyr and PFarn, with increasing side group length [6].

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786.

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Heterogeneous Local Environments in Mussel-Inspired Elastomers

Marianna Spyridakou^{1*}, Elpida Iliopoulou¹, Katerina Peponaki^{2,3}, Stelios Alexandris^{3,§}, Emmanouela Filippidi^{2,3}, George Floudas^{1,4,5}

¹ *Department of Physics, University of Ioannina, P.O. Box 1186, 451 10 Ioannina, Greece*

² *Department of Materials Science and Technology, University of Crete, Heraklion 71003, Greece*

³ *FORTH, Institute of Electronic Structure and Laser, Heraklion, Crete 71110, Greece*

⁴ *Max Planck Institute for Polymer Research, 55128 Mainz, Germany*

⁵ *University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina, Greece*

[§] *Current address: Chemical Engineering Department, Soft Matter, Rheology and Technology, KU Leuven, Leuven, Belgium*

Email: * spiridakoum@gmail.com

Creating homogeneous materials that combine high stiffness, ultimate strength and toughness is desirable for any structural material [1]. Strategies towards damage-tolerant polymeric networks with increased mechanical strength and toughness are based on interpenetrating double and triple network architectures¹ mechanically interlocked polymers or one single-network architectures e.g. with metal coordination bonds [3], Coulombic interactions or hydrogen bonding. In particular, mussels have provided various inspiration for engineered tough elastomers and hydrogels [2]. Materials with increased mechanical strength and toughness bearing mussel-inspired iron-catechol complexes and network architectures exhibit a number of dynamic features, e.g. high and broad glass “transition” temperature, not explored so far. By combining differential scanning calorimetry and dielectric spectroscopy, the latter as a function of temperature and pressure, we have explored the increase in the glass temperature, T_g , and the concomitant increase in the breadth of T_g , in bio-inspired networks bearing one (covalent) or two types (covalent and coordination) types of cross-links [3]. Cross-linked networks experience heterogeneous segmental dynamics that are responsible for the broad T_g range observed in the thermal measurements. The two distinct dynamics reflect the relaxation of segments in the vicinity versus more distant cross-linked units. The various topologies are shown to have different fragilities and tend to form stronger glasses with increasing network topology. In addition, the ionic conductivity is influenced by the segmental dynamics and the increased T_g in the networks. These features (reduced specific heat step, Δc_p , at T_g and “strong” dynamic behavior) are also found in permanently crosslinked polymers with dynamic network topology known as vitrimers [4]. The similarities in the two network systems are discussed.

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786.

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Dissecting the Role of Reduced Graphene Oxide on the Dielectric Properties of PEDOT:PSS-PVA Blends

Mydhili Varma^{1,2}, T. Kavin Kumar², S. Manivannan² and Paul Ben Ishai^{1*}

¹ The Dielectric & THz Science Laboratory, Department of Physics, Ariel University of Samaria, Ariel, 40700, Israel.

² Carbon Nanomaterials Laboratory, Department of Physics, National Institute of Technology, Tiruchirappalli 620015, India.

Email: * paulbi@ariel.ac.il

The superior traits of flexibility, high breakdown strength combined with high dielectric permittivity have paved the way for growing demand of polymer dielectrics in the flexible electronics industry, with the most used polymer being biaxially oriented polypropylene (BOPP). However, BOPP has low energy density ($1\text{--}2\text{ Jcm}^{-3}$), low dielectric permittivity of 2.2 at 100 kHz and low operating temperature, limiting its application in the electronic industry [1]. This has led to the development of many other polymer dielectrics with multiple strategies to satisfy market demand. One such strategy is interface design by introducing a range of interfaces and structures, such as addition of organic and inorganic fillers and formation of multilayer dielectric [2].

Herein, we present the fabrication of freestanding films of reduced graphene oxide-poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)-poly(vinyl alcohol) (RGO-PEDOT:PSS-PVA) composite through solution blending method at optimal synthesis conditions and optimal RGO concentration of 1mg/mL. The frequency and temperature dependent dielectric measurements were accomplished by using Hioki 3532-50 LCR Hi-Tester within temperature range 303-523 K for frequency range $10^2\text{--}10^6$ Hz. The Havriliak-Negami model was used to fit the dielectric spectra and the dc conductivity characteristics from fitting results suggests percolation of charge carriers at the optimal concentration of RGO. The temperature dependent dielectric spectra suggests that in the low temperature regime ($<358\text{ K}$), the polarization occurs due to the free water molecules present in the composite and this is supported by the thermogravimetric analysis of the sample. Above 358K, the steep rise in the dielectric constant (ϵ') and dielectric loss (ϵ'') to the order of 10^5 and 10^6 respectively at 100 Hz and 468 K suggests an increase in dc conductivity due to percolation of charge carriers. The RGO act as a channel for charge percolation and transport and form a barrier between the PVA and PEDOT:PSS through intermolecular hydrogen bonding and $\pi\text{--}\pi$ interaction between the thiophene ring in PEDOT:PSS and sp^2 carbon of RGO. The shift in FTIR and Raman spectra corresponding to the inter-ring stretching vibrations of PEDOT and vibrational modes of PSS with addition of RGO supports the claim [3]. Beyond 468 K, the values of ϵ' and ϵ'' , suggests the start of decomposition of the PVA and PSS components in the PEDOT:PSS-PVA matrix. The temperature dependent dielectric studies suggests the role of RGO in the polarization and relaxation mechanism of the composite and also, point towards the range of temperature at which the sample can be effectively used as dielectric for practical use.

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Relaxation Dynamics of Hydroxypropylmethylcellulose Acetate Succinate: via Dielectric and Mechanical Methods

S.X. Drakopoulos^{*1}, Y. Sao², R.D. Priestley^{1,2}

¹Princeton Materials Institute, Princeton University, Princeton, New Jersey, 08544, United States (USA)

²Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, 08540, United States (USA)

Email: * sd5541@princeton.edu

Hydroxypropylmethylcellulose Acetate Succinate (HPMCAS) is a highly functionalized natural cellulose derivative that is often used to promote drug–polymer interactions in the pharmaceutical industry [1]. Here, HPMCAS was compression molded by heating the powder sample at 130 °C (higher than the T_g) and applying 40 MPa of pressure. Specimens for both Broadband Dielectric Spectroscopy (BDS) and Dynamic Mechanical Analysis (DMA) were produced following the same manufacturing protocol. The BDS measurements were conducted by employing a Phecos temperature system with an integrated dielectric cell, and an Alpha-A frequency analyzer, all provided by Novocontrol Technologies, Germany. The dielectric experiment was done in the temperature and frequency ranges of -50 – 160 °C and 10^{-1} – 10^6 Hz, respectively. The DMA experiments were performed via a DMA8000 apparatus provided by PerkinElmer, USA. The sample was tested in the temperature and frequency ranges of -100 – 160 °C and 10^{-1} – 10^1 Hz, respectively.

For the dielectric analysis, the derivative permittivity function (ϵ''_{der}) was employed, which is approximately equal to the dipolar losses, and follows Eq. (1) as seen below:

$$\epsilon''_{der} = -\frac{\pi}{2} \frac{\partial \epsilon'}{\partial \ln \omega} \quad (1)$$

where ϵ' is the real part of dielectric permittivity and ω is the angular frequency equal to $2\pi f$ where f is the frequency of the externally applied electric field.

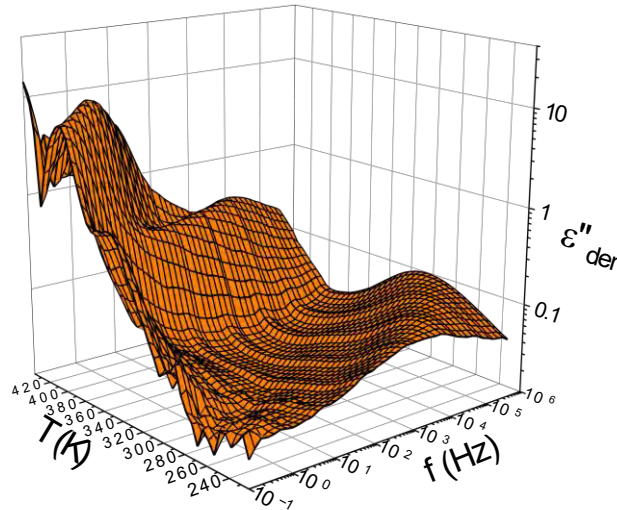


Figure 1. The derivative permittivity as a function of both temperature and frequency for HPMCAS.

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Unusual secondary relaxation in the glass-forming molecular rotors

Alfred Błażytko*, Marzena Rams-Baron and Marian Paluch

August Chelkowski Institute of Physics, University of Silesia in Katowice, 75 Pulku Piechoty 1, 41- 500 Chorzow, Poland

Email: * alfred.blazytko@us.edu.pl

Although the occurrence of secondary relaxations is an inherent feature of the glassy state, their origin and characteristics are still debated. The commonly used classification is based on their molecular origin and whether the whole (Johari-Goldstein (JG) relaxation) or part of the molecule (non-JG relaxation) is involved. The classification is often based on compliance with the coupling model or the sensitivity of the dynamics to density changes caused by compression.

Molecular rotors are gaining significant attention due to their application in artificial molecular machines and optoelectronic nanodevices. From the point of view of molecular dynamics, in rotor molecules with glass-forming ability, rotor mobility is the source of a secondary process with a well-defined molecular origin. We reported recently interesting dynamic behavior of fluorophenyl rotors in sizable molecules, showing that internal rotation behaves like a probe examining the environment around the rotating unit by specific C $\cdots$ H-F $\cdots$ C contacts. [1] Thus, in molecular rotors, we are dealing with relaxation which is unusual from the point of view of the current division, i.e. has an intramolecular origin (results from the rotation of a small fragment of the molecule) but is sensitive to molecular surroundings. One can expect, that such environment-sensitive internal relaxation should also detect changes in the environment underlying the glass transition phenomenon. In this context, a question arises about the relationship between secondary relaxation resulting from internal rotation and structural relaxation. It is not clear how it is coupled with structural relaxation and hence if it meets the criteria assigned to JG relaxation.

To investigate this problem, we performed dielectric molecular dynamics studies on a series of custom-designed structurally related rotor molecules belonging to the sizable glass formers.[2] Structurally, these materials comprise a bulky sizable core, acting in a solid state as the stator, and a rapidly rotating component, referred to as the rotor. In their chemical structure, we can distinguish (1) the rotating polar unit, (2) the non-polar core formed by diphenylamine and fluorene, and (3) alkyl chains that prevent crystallization and facilitate the formation of a stable glassy phase. We used a phenylene ring as a rotor and as the source of the secondary relaxation discussed in our study. To ensure that the internal rotation of the phenylene ring contributes to the dielectric response, we decorated the ring with a polar group that introduced a dipole moment to the molecule. By systematically altering several structural features of sizable molecules, i.e. linker length between the rotor and stator, as well as the size and position of the polar group (e.g., an F atom versus a -CF₃ group) attached to the phenylene ring, we modified the rotational freedom, steric hindrance and the degree of coupling with the rest of the sizable molecule. We observed that by modifying these parameters, the dynamic behavior attributable to JG or non-JG relaxation can be seen. The presented results deepen our understanding of the unusual behavior of secondary relaxation associated with internal rotation in molecular rotors - a phenomenon that has recently attracted a lot of interest from the scientific community.

Acknowledgments

This research was funded by the National Science Centre, Poland (Grant No. 2021/41/B/ST5/00992).

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Physical characterisation of a carbamazepine/oxalic acid cocrystal designed by liquid-assisted grinding

Fabian Puga¹, Hengli Zhao¹, Luisa Roca-Paixão¹, Florence Danède¹, Natália T. Correia^{*1} and Frédéric Affouard¹

¹Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207, UMET, Unité Matériaux et Transformations, F-59650 Villeneuve d'Ascq, France
Email : *natalia.correia@univ-lille.fr

In this work we present the first results of the physical characterisation of a cocrystal based on the active pharmaceutical ingredient carbamazepine and its coformer oxalic acid, using complementary experimental techniques: powder x-ray diffraction (PXRD), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Broadband Dielectric Spectroscopy (BDS).

A stoichiometry screening utilising liquid-assisted grinding (LAG), as previously described by some of the authors [1], has demonstrated that a pure carbamazepine (CBZ)/oxalic acid (OA) crystalline multicomponent system can be obtained at a stoichiometric ratio of CBZ:OA (3:1). The DSC curve corroborates the purity of the sample, exhibiting a single endothermic event associated with its melting, despite the potential impact of sublimation and/or degradation, as indicated by the TGA curve.

The PXRD pattern of the CBZ:OA (3:1) LAG product, which differs from the pure parent compounds, is reproduced with reasonable accuracy by the structure (refcode MOXWUS) proposed by Child *et al.* [2]. The latter was previously obtained using a solution-based cocrystallisation method that did not allow the OA content to be determined [3]. This multicomponent system exhibits a channel-like structure, comprising channels of nanometric dimensions that are filled with disordered oxalic acid molecules [2].

This study presents the initial insights obtained through BDS, which demonstrate a rotational dynamical disorder of the oxalic acid molecules present within the cocrystal channels.

Acknowledgments

This project has received funding from the Interreg 2 Seas program 2014-2020 co-funded by the European Regional Development Fund under subsidy contracts 2S01-059_IMODE and 2S07-033_Site Drug.

The project ARCHI-CM, Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur et de la Recherche, Région Hauts-de-France and European Regional Development Fund (FEDER) are also acknowledged for supporting and funding this work.

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The slow Arrhenius process beyond thin-film geometry

Federico Caporaletti¹, Simone Napolitano¹

¹ *Laboratory of Polymer and Soft Matter Dynamics, Université libre de Bruxelles (ULB), Brussels, Belgium*

Email: * federico.caporaletti@ulb.be

The slow Arrhenius process (SAP) [1] is a molecular relaxation mechanism observed both in polymers and small molecules [2]. The SAP, which has been detected in more than 30 systems, is active both in the liquid and glassy states, and its molecular time is characterized by a simple Arrhenius behavior, with 100 kJ/mol. The SAP shares the same activation barrier as the high-temperature flow. It obeys an enthalpy-entropy compensation law, meaning that its enthalpic (thermal barrier) and entropic (attempt frequency, $f_0 = 1/2\pi\tau_0$) components strongly correlate [3]. The SAP is also sensitive to the residual stresses present in a sample [4].

While the SAP is thought to provide an alternative equilibration pathway in glasses, its observation is limited to dielectric spectroscopy measurements performed in thin-film geometry obtained via a bottom-up approach [1].

This limitation has cast doubts on the universal character of the SAP, which has indeed been suggested to be connected to dielectrically specific phenomena such as Maxwell-Wagner and electrode polarization. Here, we show that the SAP can also be observed in different sample geometries, including bulk samples, and by employing other experimental techniques that are not sensitive to dipole re-orientational dynamics, such as rheology.

These results reinforce the idea that the SAP is a genuine feature of liquid dynamics and show that multiple experimental techniques are required to fully characterize its properties.

Acknowledgments

F.C. is a Chargé de Recherche of the Fonds de la recherche scientifique-FNRS. We acknowledge financial support from Action de Recherche Concertée ULB under grant ARC 20061 “SADI”.

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Comparative Analysis of the Structure, Thermodynamics, and Dynamics of Amorphous Forms of Trehalose

Kenneth Rojo¹, Florence Danède¹, Mounira Hamoudi², Frédéric Affouard¹ and Natália T. Correia^{*1}

¹Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207, UMET, Unité Matériaux et Transformations, F-59650 Villeneuve d'Ascq, France

²Univ. Lille, College of Pharmacy, INSERM U1008, 3 rue du Professeur Laguesse, 59006 Lille, France
Email : *natalia.correia@univ-lille.fr

This study examines the impact of different amorphization routes on amorphous trehalose, highlighting how water influences its structural, thermodynamic, and dynamic properties. Amorphous trehalose samples prepared by quench-melting, milling, freeze-drying, and spray-drying of β -trehalose crystal, plus the dehydration of trehalose crystal dihydrate. They were characterized using Powder X-ray Diffraction (PXRD), Temperature-Modulated Differential Scanning Calorimetry (TM-DSC), and Broadband Dielectric Spectroscopy (BDS).

The PXRD patterns demonstrate the influence of water on the shape of the diffusion halo. The intensity and 2θ position of an extended wing of the main diffusion halo are demonstrated to be correlated with the water content of amorphous trehalose. An increase in water content results in a shift of the peak towards higher 2θ values, accompanied by an enhancement in the intensity of the extended wing, which was hypothesized to be related and the precursor to Bragg peaks characteristic of the crystalline trehalose dihydrate.

The results of pinholed-pan TM-DSC measurements indicate that the glass transition temperature of dried amorphous trehalose forms remains approximately constant, irrespective of the amorphisation route employed. In contrast, closed-pan TM-DSC measurements indicate an inverse proportional relationship between the glass transition temperature (T_g), indicating that the water content of the as-prepared amorphous trehalose forms has a plasticizing effect on the glass transition.

BDS analyses of the two secondary relaxations observed in the glassy state of amorphous trehalose forms demonstrated that the intramolecular γ -relaxation, which is attributed to movements of the exocyclic $-\text{CH}_2\text{OH}$ side group of the glucose rings [1], is either minimally or not affected by changes in water content. In contrast, an inverse relationship is observed between the activation energy of the β -relaxation and the water content of amorphous trehalose. This demonstrates that the β -relaxation, which is attributed to a twisting mode of the glucose rings around the α,α -1,1 glycosidic linkage and involving the whole trehalose molecule [1], is influenced by water-induced plasticisation. The hypothesis proposed by Kudlik *et al.* [2] regarding a Johari-Goldstein (JG) β -relaxation is validated for all amorphous trehalose forms. The activation energy ($E_{a,JG}$) has been determined to have a value of approximately $24 RT_g$, while the T_g values have been observed to demonstrate a correlation with water content in accordance with the Gordon-Taylor equation.

Acknowledgments

K. Rojo acknowledges his master's degree scholarship from the BIOPHAM Erasmus Mundus program and his Master Thesis grant from MMT-UMET-Univ Lille.

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Local and global dynamics of *cis*-1,4-Polyfarnesene in PS-*b*-Polyfarnesene diblock copolymer as a function of phase state

Nikolaos Fotaras^{1,*}, Moritz Maximilian Simon², Holger Frey² and George Floudas^{1,3,4}

¹ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

² Department of Chemistry, Johannes Gutenberg University, 55128 Mainz, Germany

³ Max Planck Institute for Polymer Research, 55129 Mainz, Germany

⁴ University Research Center of Ioannina (URCI), Institute of Materials Science and Computing, 45110 Ioannina, Greece

Email: * nikolasfotaras@gmail.com

There is an increasing interest in sustainable bio-based polymer materials, like the 1,3-diene monomers isoprene and butadiene. Polyterpenes, based on *cis*-1,4-Polyfarnesene (PFarn), are a promising alternative combining the bio-based background with the abundance of their natural resources. In contrast to polyisoprene (PI), which is a linear polymer, polyfarnesene (PFarn) consists of three isoprene units forming a branch structure similar to this of a bottlebrush-like polymer. This architectural difference leads to a “chain thickening”, which affects both the local and the global (chain) dynamics. As a result, there is an increase in entanglement molar mass, from 5 kg·mol⁻¹ for PI to 50 kg·mol⁻¹ for PFarn, and the packing length from 3.1 Å to 6.3 Å, respectively [1]. Herein, we report the study of dynamics (Broadband Dielectric Spectroscopy), viscoelastic properties (Rheology) and self-assembly (SAXS), of the PS-*b*-PFarn diblock copolymer over the entire composition range from 0.1 to 0.9 polyfarnesene volume fraction (ϕ_{PFarn}). The phase diagram of the diblock system is established comprising of classical (spheres, cylinders, lamellae) and non-classical (double gyroid) microphases, without any conformational asymmetry ($\alpha_{\text{PS}} \approx \alpha_{\text{PFarn}}$), resulting in an almost symmetric phase diagram. The diblock structure of PS-*b*-PFarn influences the dynamics, with the dielectric loss curves revealing two segmental processes one for each component respectively. Another segmental processes, is also present, related to the side group of PFarn accompanied by a very weak broad process associated with the PFarn normal mode. The effect of curvature of the PS-PFarn interface for symmetric and asymmetric systems (lamellae and hexagonal packed cylinders microphases) has also been studied [2], [3].

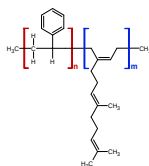


Figure 1. Chemical structure of the diblock copolymer PS-*b*-PFarn.

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786.

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Variation of Activation Volume as an Indicator of the Change in Clusterization Phenomenon in Flurbiprofen Enantiomers and the Racemate

Paulina Jesionek^{1,2*}, Barbara Hachula¹, Karolina Jurkiewicz³, Patryk Włodarczyk⁴, Marek Hreczka^{4,5}, Kamil Kamiński³ and Ewa Kamińska²

¹ *Institute of Chemistry, Faculty of Science and Technology, University of Silesia in Katowice, Szkolna 9, 40-007 Katowice, Poland*

² *Department of Pharmacognosy and Phytochemistry, Faculty of Pharmaceutical Sciences in Sosnowiec, Medical University of Silesia in Katowice, Jagiellonska 4, 41-200 Sosnowiec, Poland*

³ *Institute of Physics, Faculty of Science and Technology, University of Silesia in Katowice, 75 Pulku Piechoty 1, 41-500 Chorzow, Poland*

⁴ *Łukasiewicz Research Network - Institute of Non-Ferrous Metals, Sowinskiego 5 St., 44-100, Gliwice, Poland*

⁵ *Department of Mechatronics, Silesian University of Technology, Akademicka 10A St., 44-100, Gliwice, Poland*

Email: *paulina.jesionek@us.edu.pl

In recent years, chiral compounds, i.e., enantiomers (*R*- and *S*- isomers), as well as the racemate (a mixture of equal amounts of these compounds), have been the subject of intense research in many scientific fields, including chemistry, physics, and pharmacy. This is because, despite the substantial similarity in the physicochemical properties of enantiomers, they can differ significantly in their biological, toxicological, and pharmacokinetic properties.

Particular attention is paid to 2-arylpropionic acids, the so-called profens (e.g., ibuprofen (IBP), ketoprofen (KTP), or flurbiprofen (FLP))- one of the most popular active pharmaceutical ingredients (APIs) with anti-inflammatory, analgesic, and antipyretic properties. Due to the presence of carboxylic moiety capable of forming hydrogen (H)-bonds in the close vicinity of the chiral carbon atom, which can influence the spatial molecular organization, self-assembly phenomenon, etc., this group of compounds is thoroughly studied from physical, chemical, and pharmaceutical perspectives.

In this work, we present the results of structural, spectroscopic, thermal, and dielectric studies performed for *R*-, *S*-, and *RS*- FLP. They were additionally supported by the outcomes of Molecular Dynamics (MD) simulations and DFT calculations. According to the collected diffractograms, thermograms, infrared, and dielectric spectra, it was concluded that enantiomers have properties very similar to those of the racemate. However, deeper data analysis revealed unexpected variations in the activation volume between *R*-, *S*-, and *RS*- FLP. Further MD simulations enabled us to assign this peculiarity to a higher population of the small clusters (di, tri-, and tetramers) in pure enantiomers. Finally, DFT computations revealed very specific and enormously strong F – Π interactions that may control local molecular arrangement in the supercooled liquid phase and the crystals of the studied compounds.

Acknowledgments

This research was funded by the National Science Centre (Poland), grant number: Opus 21 No. 2021/41/B/NZ7/01654.

Is There a Relationship Between Wettability and the Rates of Equilibration of Hydrogen-Bonded Oligomer PMMS under Confinement?

Sara Zimny^{1,2*}, Magdalena Tarnacka², Monika Geppert-Rybczyńska¹ and Kamil Kamiński²

¹ *Institute of Chemistry, University of Silesia in Katowice, Szkolna 9, 40-006 Katowice, Poland*

² *Institute of Physics, University of Silesia in Katowice, 75 Pułku Piechoty 1, 41-500 Chorzów, Poland*

Email: * sara.zimny@us.edu.pl

Soft materials subjected to nanospatial restriction have already been investigated for decades. So far, these studies have shown that their basic physical parameters, i.e. viscosity, diffusion, relaxation times, as well as phase transition temperatures, can be modified by changing the type of confinement (soft vs. hard), degree of confinement, finite size, as well as interfacial interactions. The latter is possible by appropriate physical or chemical modification of the substrate, making it more attractive, repulsive, rough, hydrophilic, etc. Extensive studies of polymers supported as layers of different thicknesses have shown that all the above-mentioned parameters, resulting from the applied spatial constraint, can be completely or partially removed in the process of annealing, which restores the characteristics of the system at the macroscale. It is worth mentioning experiments on polystyrene, polyvinyl acetate or poly(methyl methacrylate), where prolonged annealing was applied, after which rheological properties similar to the solid substance were recovered. Further studies indicated that the recovery of solid-substance dynamics of polymers in spatial confinement may be related to the free volume equilibration process, as well as the formation of an irreversibly adsorbed layer. Despite so many experimental and simulation studies focusing on the behaviour of polymers deposited as thin films during annealing, there is so much less research in the case of materials infiltrated into mesoporous matrices.

The purpose of our research was to carry out annealing experiments of poly(mercaptopropyl)-methylsiloxane (PMMS) incorporated into two types of mesoporous matrices (made of anodic alumina (AAO) and silica oxide (SiO₂)) with different pore diameters ($d=8-120$ nm), using different thermal protocols. We conducted the study using broadband dielectric spectroscopy (BDS) with complementary differential scanning calorimetry (DSC), as well as temperature-dependent measurements of wettability angles (θ). Through temperature-dependent dielectric studies, PMMS relaxation times deviated from the macroscale behaviour when approaching the glass transition temperature (T_g). Further dielectric analysis of isothermal experiments for samples incorporated into porous matrices cooled at different rates showed that the equilibrium rate constants increase as the temperature decreases and depends weakly on the cooling rate or thermal history of the sample. In contrast, the activation energy of the equilibration process, E_a , varies with the pore diameter and the material of the mesoporous matrix. The change in E_a can be explained by considering the temperature dependence of θ of PMMS, which indicates a noticeable change in wettability between PMMS and substrate when the temperature is lowered. Consequently, it can be expected that adsorption-desorption processes occurring at the polymer-pore wall interface at lower temperatures must be perturbed. Our data provide a better understanding of the equilibrium processes occurring in liquids infiltrated into mesopores, which will significantly affect the better use of this type of material in the future.

Acknowledgements

The research was fully funded by the National Science Center (Poland), grant number: the OPUS project (Dec. no 2022/47/B/ST4/00236).

Improving the stability of amorphous drugs by deposition on the surface of silica nanoparticles

M. Teresa Viciosa,^{1*} Hermínio P. Diogo,¹ Joaquim Moura Ramos,¹ Madalena Dionísio,² Tiago D. Martins,¹ José Paulo Farinha¹

¹ Centro de Química Estrutural, Instituto Superior Técnico, University of Lisbon, Lisbon, Portugal.

² LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, NOVA University of Lisbon, Caparica, Portugal.

Email: * teresaviciosa@tecnico.ulisboa.pt

Aceclofenac (ACF) (2-[(2, 6-dichlorophenyl) amine] phenylacetoxycetic acid) is a non-steroidal anti-inflammatory drug commonly used in the treatment of rheumatoid arthritis, osteoarthritis and inflammatory diseases including the area of odontology. Recent formulations have been developed with the aim of overcoming its low solubility in water (around 0.0035 mg.mL⁻¹ [1]), which is a limiting factor in its bioavailability.

Some of these formulations exploit the advantages of the amorphous form, as is the case, for example, of drug release composites based on silica nanoparticles [2]. However, there is still a lack of in-depth understanding of the physico-chemical aspects that determine the promising results obtained.

In the present work, the main goal is to demonstrate the complex behaviour of the amorphous form of ACF, evaluating its molecular mobility in the bulk state, and its modifications when ACF is deposited on the surface of silica nanoparticles (SiNPs). For this aim, spherical SiNPs were prepared in the laboratory with precise size control (diameter ~50 nm). [3]

Differential scanning calorimetry (DSC) and dielectric relaxation spectroscopy (DRS) have been the main techniques used to evaluate the mobility of amorphous ACF obtained after cooling from the liquid state either in bulk or in a physical mixture of SiNPs and 30%wt of ACF. The shift detected in the glass transition temperature when compared to pure amorphous ACF suggests that molecular interactions with the silica surface promote stabilisation in this physical state, reducing or even eliminating the tendency to recrystallize.

Based on this promising result, the next step will be to expand the surface area available to increase the payload capacity.

Acknowledgments

This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, Projects UIDB/00100/2020 (<https://doi.org/10.54499/UIDB/00100/2020>), UIDP/00100/2020 (<https://doi.org/10.54499/UIDP/00100/2020>), and IMS-LA/P/0056/2020UIDB/00100/2020 (<https://doi.org/10.54499/LA/P/0056/2020>).

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Rheo-dielectric study of transformer oil-based magnetic nanofluid

Michal Rajnak^{1,2*}, Katarina Paulovicova¹, Jana Tothova² and Bystrík Dolník²

¹ Institute of Experimental Physics SAS, Watsonova 47, 04001 Kosice, Slovakia

² Faculty of Electrical Engineering and Informatics, Technical University of Kosice, Letna 9, 04200 Kosiice, Slovakia

Email: * rajnak@saske.sk

Nano-functionalization of transformer oils is an attractive approach to enhancing their thermal and dielectric performance [1]. Among various nanoparticle materials, magnetic nanoparticles are of special interest as their suspensions are magnetically controllable. This controllability has been found for a low-frequency dielectric response of such nanofluids (ferrofluids) when exposed to a magnetic field [2,3]. The nanoparticle interfacial polarization and charge migration dominate the low-frequency dielectric spectrum. The knowledge on dielectric behavior of nano-functionalized transformer oils under magnetic field is important especially in the view of applications in electrical equipment generating magnetic field, e.g. power transformers [4]. One must also realize that in such equipment the liquid flows by means of natural or forced convection or even due to the thermo-osmosis. Such a flow can be characterized by a gradient in velocity. However, there is a lack of dielectric studies of magnetic nanofluids under the shear flow conditions. In this paper we study the low-frequency dielectric response of naphthenic transformer oil and nanofluids containing iron oxide nanoparticles of three various concentrations. The complex dielectric permittivity is investigated in the frequency range from 20 Hz up to 100 kHz. An LCR meter was used to measure the dielectric spectra and the liquid samples were sandwiched between two disks (electrodes) of a modular rheometer. The spectra are studied at equilibrium and under the shear rates of 10 s⁻¹, 100 s⁻¹, 500 s⁻¹, and 1000 s⁻¹. It was found that the low-frequency dielectric spectra of the nanofluids exhibit a remarkable conductivity contribution. This contribution and the whole dielectric spectra are independent of the applied shear rates. Any permittivity changes are within an experimental error. The finding applies to measurements at temperatures of 293 K, 313 K, and 333 K. Based on the conducted experiment one can also conclude that there are no shear-induced structural changes in the nanofluids, so indicating the stable physical properties of the nanofluid under the shear flow.

Acknowledgments

This research was funded by Slovak Research and Development Agency under the contract No. APVV-22-0115, APVV-18-0160 and The Slovak Academy of Sciences and The Ministry of Education, Research, Development and Youth of the Slovak Republic in the framework of project VEGA 2/0029/24.

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High-resolution TGA combined with BDS: a new tool to investigate the effect of water on the electrical conductivity of concrete

Mohamad Barzegar^{1*}, Guido Goracci¹, Pavel Martauz², and Jorge S. Dolado^{1,3*}

¹ *Centro de Física de Materiales, CSIC-UPV/EHU, Paseo Manuel de Lardizábal 5, 20018 Donostia-San Sebastián, Spain*

² *Považská Cementáreň Cement Plant (PCLA), Ulica Janka Kráľa, 01863 Ladce, Slovakia*

³ *Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 Donostia-San Sebastián, Spain*

Email: * mohamad.barzegar@ehu.eus, j.dolado@ehu.eus

This study investigates the impact of water on the electrical conductivity of concrete using high-resolution thermogravimetry (HR-TGA) combined with Broadband Dielectric Spectroscopy (BDS). Electrical conductivity is crucial for smart concrete applications and is influenced by the cement type, aggregates, and water content. Two types of cement binders, ordinary Portland cement (OPC) and Geopolymer binders, with and without TiO₂ and graphite additives were examined.

HR-TGA characterized water distribution, while BDS assessed dielectric properties. Results showed distinct water distributions and dielectric responses for OPC and Geopolymer. TiO₂ increased total water content, while TiO₂ with graphite reduced it. However, despite the change in total water amount, our study showed that the change in different water distributions can result in different dielectric responses. Furthermore, the electrical conductivity of geopolymer was more sensitive to the addition of aggregates and change in water distribution compared to OPC.

For OPC, adding TiO₂ powder decreased the critical first water population significantly, reducing the samples' electrical conductivity. TiO₂ increased this water population in Geopolymer, causing a major conductivity drop upon drying. Graphite addition mitigated TiO₂'s effect and enhanced the enhancing conductivity.

This research highlights HR-TGA and BDS as effective tools for understanding water's role in the electrical properties of concrete, aiding smart material development.

Isotopic Study on the Dynamics of High-Density-Amorphous Ice Under High Pressure

Kaito Sasaki*, Yoshiharu Suzuki, Rio Kita and Naoki Shinyashiki

Department of Physics, Tokai University, Kitakaname 4-1-1, Hiratsuka, Kanagawa 259-1292, Japan

Email: * sasaki.kaito.w@tokai.ac.jp

When ice Ih is compressed to above 1 GPa at sufficiently low temperatures, it transforms into High Density Amorphous Ice: HDA. The molecular motion of HDA of H₂O under high pressure and that of the HDA of H₂O, D₂O, and H₂¹⁸O at 1 atm have been studied through dielectric spectroscopy measurements [1-3]. It has been reported that the molecular motion of HDA at 1 atm shows a significant hydrogen isotope effect (the difference in glass transition temperature, $\Delta T_{g,1atm} = 12$ K) [2,3], but no such report exists under high pressure. This study reports that the hydrogen isotope effect on the molecular motion of HDA under high pressure is not as significant as that at 1 atm.

The samples used were H₂O (Milli-Q, with a resistivity of 18.2 M Ω ·cm), D₂O (Wako Pure Chemical Industries, 99.75 atom% of D), and H₂¹⁸O (Taiyo Nippon Sanso, 99.5 atom% of ¹⁸O). Pure HDA was prepared by amorphizing ice Ih by pressurizing it to 1.5 GPa at 77 K. Dielectric spectroscopy measurements were performed using a Solartron impedance analyzer (SI1260) in the frequency range of 10 mHz to 10 MHz. A homemade parallel plate electrode was used as the probe. The measurement temperature range was 135-150 K, and the measurement pressure was 1 GPa.

All samples showed a single relaxation process. Figure 1 shows the reciprocal temperature dependence of the dielectric relaxation time, τ , of H₂O and D₂O HDA at 1 GPa. The τ of H₂O and D₂O HDA showed a linear dependence on the temperature reciprocal with almost the same slope, although their absolute values differed.

On the other hand, no significant difference was observed in the τ of H₂O and H₂¹⁸O HDA.

We defined the glass transition temperature, T_g , as the temperature at which τ reaches 100 s.

Using linear fitting with the least squares method, the T_g was estimated to be 123 K for H₂O and H₂¹⁸O HDA and 128 K for D₂O HDA at 1 GPa, yielding a hydrogen isotope effect of $\Delta T_{g,1GPa} = 5$ K. The fact that $\Delta T_{g,1GPa}$ is smaller than the reported $\Delta T_{g,1atm} = 12$ K at 1 atm [2] indicates that the isotope effect on τ of HDA decreases under high pressure. Furthermore, the lack of a significant difference in the τ of H₂O and H₂¹⁸O HDA strongly suggests that the mechanism of the dielectric relaxation of HDA is reorientation of water molecules.

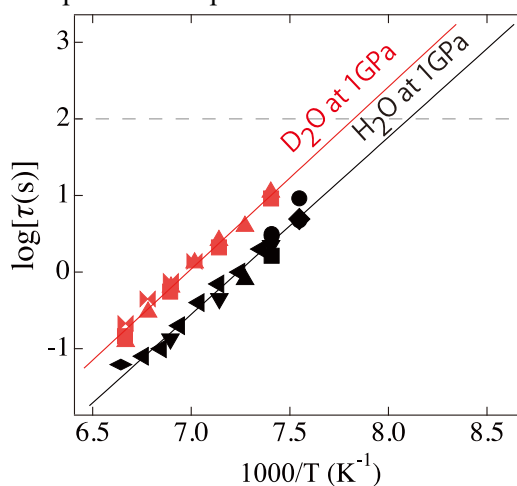


Figure 1. Reciprocal temperature dependence of the relaxation time of HDA at 1 GPa. The horizontal dashed line indicates $\tau=100$ s. Solid lines are obtained by least square fits.

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The Molecular Nature behind the Dielectric Spectra in the Gigahertz Domain

Kang Hu^{1*}, Hiroaki Matsuura¹, Junkai Zhang¹ and Ryo Shirakashi^{1*}

¹ Institute of Industrial Science, The University of Tokyo, Japan

Email: * kang.hu@univ-ciffel.fr; aa21150@iis.u-tokyo.ac.jp

The dielectric spectroscopy technique has been widely employed to characterize different food products. For instance, previous work found that the deterioration rate of lactose dehydrogenase (LDH) in solution has the power-law relationships with the dielectric relaxation times of water in the solution, particularly sensitive to the γ relaxation time (~ 20 GHz) [1]. This finding suggests that controlling and evaluating water dynamics (e.g., this γ relaxation time) leads to managing the deterioration of biomolecules, which might be a potentially useful method for screening the bioprotective agents in the long-term preservation of pharmaceutical proteins. To this end, molecular dynamics (MD) simulations were carried out for aqueous lysozyme solutions and bioprotective sugar solutions with various concentrations for a better understanding of the molecular origin of this dielectric time constant.

The rotational relaxation time of individual water molecules and the corresponding probability density function for protein solutions and sugar solutions were first obtained by MD simulations. It was found that the dielectric loss spectra calculated from the probability distribution of water relaxation time could be approximated by the Debye function. Upon increasing the solute solutions, the dielectric loss spectrum was gradually distorted from the Debye curve due to the broader non-Gaussian distribution of water rotational relaxation time. The dielectric relaxation time calculated from this probability function is nearly identical to the γ relaxation time measured by broadband dielectric spectroscopy (BDS). The excellent agreement for the protein solutions and saccharides solutions studied here unambiguously proves that the dielectric relaxation in this gigahertz domain originates from the collective effect of the rotational self-correlation of water molecules only. This original finding associates the molecular water behavior with the macroscopic dielectric measurements.

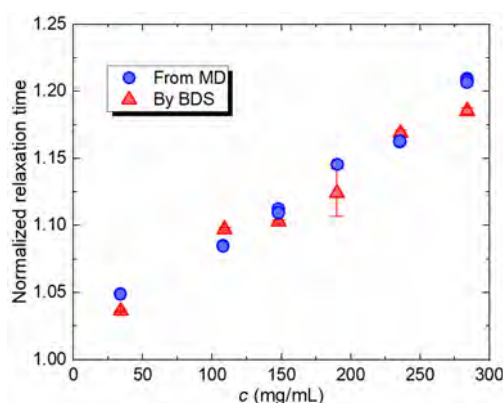


Figure 1. Normalized relaxation time of various concentrations of lysozyme solutions [2].

Acknowledgments

This work was supported by JSPS (KAKENHI), grant number 21K18684.

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Early detection of Xylella-related plant disease via Broadband Dielectric Spectroscopy

Marianna Ambrico^{1*}, Antony Surano², Paolo F. Ambrico¹, Angelantonio Minafra², Pasquale Saldarelli², Maria Saponari² and Donato Boscia²

¹ CNR-ISTP, Institute for Plasma Science and Technology, Via Amendola 122/D I-70125 BARI (ITALY)

² CNR-IPSP, Institute for Sustainable Plant Protection, Bari Branch, Via Amendola 122/D I-70125
Email: *marianna.ambrico@cnr.it

In Southern Italy, we face the infection of *Xylella fastidiosa*, a Gram- negative bacterium destroying millions of olive trees. Thus, the early detection is vital for fighting the disease. The *X. fastidiosa* induces a xylem-limited disease that appears as a blockage of the water in the xylem vessels due to the a defense responses in the plants. However, such defense mechanisms do not hinder the bacterium and the occlusion of the vascular tissue, making the symptoms even worse, thud compromising the plant life till to its death.

The ionic charge composition of xylem sap makes Broadband Dielectric Spectroscopy a viable, label-free tool, and easy alternative for plant health diagnosis, *in vivo*, on-field and, in the laboratory on xylem sap extracts.[1,2] Then, we introduce this technique in the study of well- changes when plant health is affected by *Xylella*., have been tested *in vivo*, in both healthy and pre-symptomatic states.

In-vivo results on two different cultivars, LECCINO and OGLIAROLA showed that that they respond differently to *Xylella*, having a lesser impact on LECCINO compared to OGLIAROLA consistent with visual observations made on symptomatic plants, but a considerable time after infection (12 to 14 months).

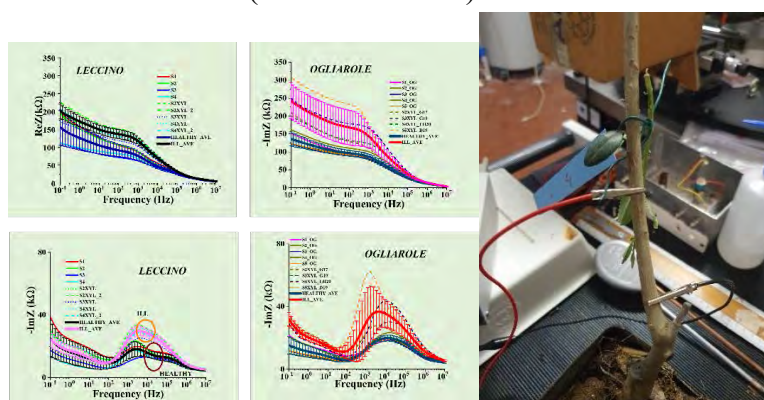


Figure 1. In vivo read outs of the impedances (Z) of two olive species (LECCINO and Ogliarola) in healthy and Xylella affected status. The experimental configuration is on the right. The spectra of the affected plants appear modified although symptoms are not yet present. Differences in the magnitude of modification is observed due to the higher resistance of LECCINO with respect to OGLIAROLA.

Acknowledgments (10 pt, bold)

The authors acknowledge the project REACH-XY (Research actions for reducing the impact on agricultural and natural ecosystems of the harmful plant pathogen *Xylella fastidiosa*)

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Effect of Hard Confinement (in Nanopores) on the Phase State and Dynamics of 1-propanol/water mixtures

Vasileios Moschos^{1*}, and George Floudas^{1,2,3}

¹ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

² Max Planck Institute for Polymer Research, 55128 Mainz, Germany

³ University Research Centre of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina, Greece

Email: * v.moschos@uoi.gr

1-propanol/water mixtures, investigated over the whole composition range, are shown to be structurally and dynamically heterogeneous [1]. By combining thermodynamic (DSC), structural (XRD) and dynamical probes (Dielectric Spectroscopy), the pertinent phase diagram of the binary system is established, consisting of liquid 1-propanol, liquid water, hexagonal ice and different hydrates. It can be discussed in terms of four regimes, all having in common a droplet arrangement of the minority component (Regimes I-IV). When water droplets are strongly confined by 1-propanol (Regime I), the crystallization of water is fully suppressed and the dynamics are reminiscent to the ultra-viscous water state known as high-density liquid (HDL). Moderately confined water droplets (Regime II) crystallize homogeneously, well within “No Man’s Land”. On the other hand, when 1-propanol is the minority component, the dynamics are interface-dominated and hydrate formation ensues. Here we report the simultaneous application of hard confinement in the mixtures within nanoporous alumina (AAO) [2]. Hard confinement alters the phase diagram of the binary system, resulting in the suppression of the crystallization within Regime II. Within Regimes III and IV, water crystallization strongly resembles that of pure water within AAO [3]. The hydrophobic/hydrophilic interaction between water and 1-propanol within AAO, is qualified by calculating the Hamaker constants of the three-component system. The only marginal speeding of the dynamics of the main relaxation process in the solution, the Debye-like process, indicates the relaxation of fewer repeat units.

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786.

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Nanoconfined Ionic Liquid Crystals as Hybrid Materials with Improved Conductivity Properties

Andreia F. M. Santos^{1*}, M. Teresa Viciosa², Inês Matos¹, João C. Sotomayor¹, João L. Figueirinhas³, Maria H. Godinho⁴, Luis C. Branco¹, C. J. Dias¹ and Madalena Dionísio¹

¹ LAQV-REQUIMTE, Department of Chemistry, and ⁴ i3N/CENIMAT, Department of Materials Science, NOVA School of Science and Technology, NOVA University of Lisbon, Caparica, Portugal

² Centro de Química Estrutural, and ³ CeFEMA and Department of Physics, Instituto Superior Técnico, University of Lisbon, Lisbon, Portugal
Email: *afm.santos@fct.unl.pt

Ionic liquids (ILs) are low melting organic salts, whose properties can be tuned by the wise pairing of the cation and anion. In this context, it is also possible to incorporate liquid crystalline features, being the final salt called ionic liquid crystal (ILC). Herein, a series of ILs having bromide as anion and 2-picolinium with different alkyl side chains as cation ($[C_n\text{-}2\text{-Pic}][\text{Br}]$ ($n = 6, 12$ and 16) were synthesised and characterised in terms of their phase transformations and conductivity properties, revealing thermomesomorphic behaviour for C_{12} and C_{16} [1]. In these two ILCs, it was possible to distinguish different conductivity mechanisms that varies with the physical state, being chain length dependent (crystalline phase) and independent (liquid crystalline phase) [1,2]. Moreover, it was also found that $[C_{16}\text{-}2\text{-Pic}][\text{Br}]$ undergoes several polymorphic conversions with a concomitant variation of the underlying charge migration process, turning its conductivity mechanism unpredictable over a large T -range. Aiming to solve this issue, hybrid solid-like materials with improved performance at RT relative to the bulk were developed by incorporating this ILC into an SBA-15 silica matrix with ~ 6.8 nm in pore diameter [3]. Three composites were prepared at guest-host fractions of $\sim 40, 60$ and 80% (w/w) and investigated by a sum of structural, thermal and dielectric techniques. For $C_{16}\text{@SBA}_{60\%}$, that stood out from the others and from the neat C_{16} , the amorphisation of the guest allowed to obtain a cost-efficient material to operate mainly between -20 to 20°C , taking advantage of its long-term stability, as well as higher σ_{dc} conductivity in a wider temperature window, being less affected by electrode polarisation.

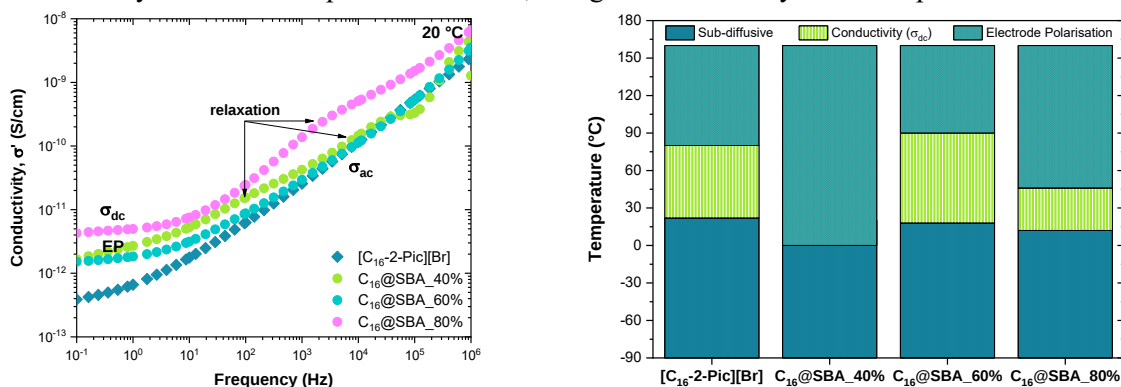


Figure 1. Comparison between the real conductivity spectra at 20°C for $[C_{16}\text{-}2\text{-Pic}][\text{Br}]$ and the three composites, which is also schematised over a wide T -range on the right-side plot.

Acknowledgments: This work was supported by LAQV (UIDP/50006/2020), i3N (UIDP/50025/2020), CQE (UIDP/00100/2020) and CeFEMA (UIDP/04540/2020), which are financed by national funds from FCT-MCTES.

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Phase Behavior, Relaxation Dynamics and Ionic Conductivity in Mixtures of Protic Ionic Liquids

Achilleas Pipertzis¹, Nicole Abdour² Anna Martinelli² Jan Swenson*

¹Department of Physics, Chalmers University of Technology, 41296, Gothenburg, Sweden

²Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 41296, Gothenburg, Sweden

Email: *jan.swenson@chalmers.se

The mixing of protic ionic liquids is a promising way for the design of amorphous liquid electrolytes with high ionic conductivities [1]. The protic ionic liquids (PILs) can be synthesized via the stoichiometric neutralization reaction of certain Brønsted acids and Brønsted bases and they are advantageous over the aprotic analogues with respect to synthesis procedure and cost [2],[3]. Herein, the phase behavior, the relaxation dynamics, and the ionic conductivity have been studied in a mixtures of two protic ionic liquids based on 1-ethylimidazolium bis(trifluoromethylsulfonyl)imide $[C_2HIm][TFSI]$ and 1-ethylimidazolium nitrate $[C_2HIm][NO_3]$ doped with 0.2 M LiTFSI salt. The mixture of protic ILs seems to distinctly decrease the degree of crystallinity, shift the melting transition to lower temperatures and yield a glass transition temperature and local relaxation dynamics in between the two parent PILs. Moreover, the doping with Li salt suppresses the crystallinity of the PILs, yielding completely amorphous liquid electrolytes, exhibiting a Vogel-Fulcher-Tammann (VFT) temperature dependence of the dc-conductivity and a high ionic conductivity at ambient temperature, as shown in Figure 1(a,b). Furthermore, by a combination of the three experimental techniques; TM-DSC, dielectric spectroscopy, and viscometry, it is evident that the σ -process is coupled to the structural relaxation process (*i.e.* T_g -related), as depicted in Figure 1(c). Overall, the extended temperature range of the liquid state in Li-salt doped mixtures of PILs emerge new promising routes for their application as liquid electrolytes or as a liquid phase in heterogeneous electrolytes in energy storage devices (*i.e.* Li-ion batteries, structural batteries, supercapacitors, etc) distinctly extending their operating temperature.

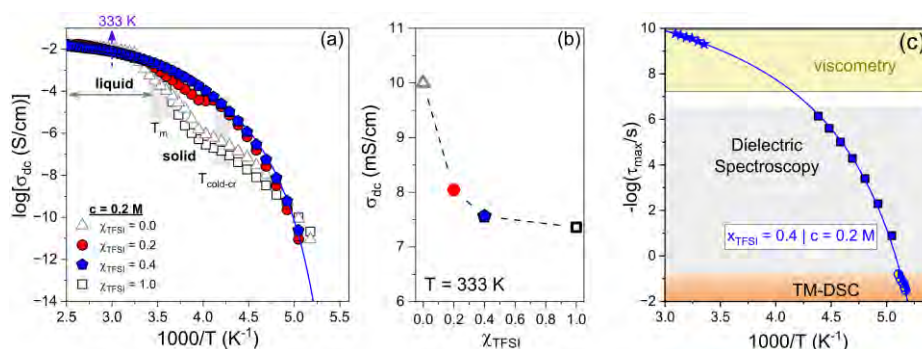


Figure 1. (a) Temperature dependence of dc-conductivity for the mixtures of PILs doped with LiTFSI (filled symbols) and their parent PILs (open symbols). (b) Dc-conductivity as a function of mole fraction. (c) Arrhenius relaxation map depicting the σ -process (squares), extracted from dielectric spectroscopy and the structural α -process, extracted from TM-DSC (circles) and viscometry (stars).

Acknowledgments: This work was financially supported by a grant from the Area of Advance Materials Science at Chalmers University of Technology.

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Enhanced decoupling of conductivity relaxation from structural relaxation in non-stoichiometric protic ionic liquids

Jinhai You¹ and Michael Wübbenhorst^{1*}

¹ Laboratory for Soft Matter and Biophysics, Department of Physics and Astronomy, KU Leuven, Leuven 3001, Belgium.

Email: * michael.wubbenhorst@kuleuven.be

As a subset of ILs, protic ionic liquids (PILs) have gained significant research attention due to their distinct qualities compared to traditional solvents [1], [2]. Non-stoichiometric PILs result from an excess of the precursor Brønsted acid or base and may potentially demonstrate outstanding physicochemical properties, such as enhanced conductivity [3], [4].

In this work, we investigate the charge motion and molecular dynamics of non-stoichiometric PILs (utilizing aminoethyl sulfate triflate ([Ahs][TfO])) through broadband dielectric spectroscopy (BDS), building upon our earlier findings [5]. Specifically, the ratios between the base (Ahs) and the acid (TfOH) are systematically varied to 5:5, 4:6, 3:7, 2:8, and 1:9, corresponding to the designations of AT-55, AT-46, AT-37, AT-28, and AT-19, respectively. The findings reveal a significant enhancement of the DC conductivity upon addition of acid, accompanied by a substantial decrease in the glass transition temperature, T_g . Careful fitting of the dielectric spectra shows that non-stoichiometric PILs with higher acid content exhibit an increasing decoupling between the conductivity relaxation and the structural relaxation, which is also supported by the modulus analysis including a modified KWW approach. It turns out that the temperature dependence of the KWW exponent β correlates well with the temperature dependence of the decoupling index. Based on these findings, a physical picture emerges that assumes nano-phase separation in the non-stoichiometric systems having a moderate acid fraction.

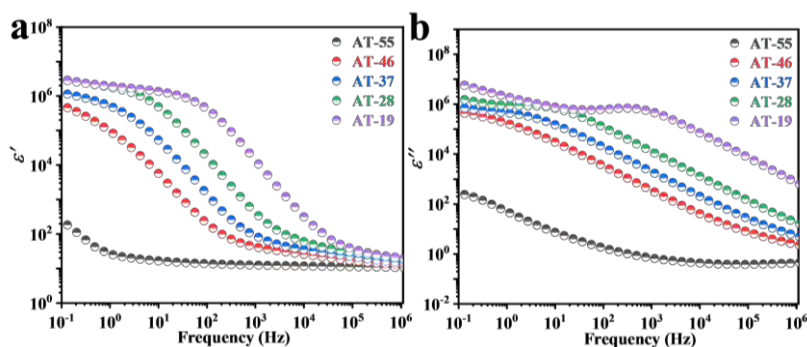


Figure 1. The a) real part and b) imaginary part of permittivity spectra of AT-55, AT-46, AT-37, AT-28 and AT-19 at -40°C.

Acknowledgments

J. H. You acknowledges the China Scholarship Council (CSC) for a doctoral scholarship (Grant No. 202006310030).

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Demixing of Polymerized Ionic Liquid/Ionic Liquid Mixtures by Infiltration in Nanopores

Yun Dong¹, Martin Steinhart² and Hans-Jürgen Butt¹, George Floudas^{1,3,4*}

¹ Max Planck Institute for Polymer Research, 55128 Mainz, Germany

² Institut für Chemie neuer Materialien, Universität Osnabrück, D-49069 Osnabrück, Germany

³ Department of Physics, University of Ioannina, 45110 Ioannina, Greece

⁴ University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina, Greece

Email: *gfloudas@uoi.gr

Ion transport through membrane nanopores is pertinent to several applications including water desalination and energy harvesting. We synthesized a series of polymerized ionic liquids (PILs) based on the 1-butyl-3-vinylimidazolium cation ($[\text{BVIM}]^+$ with three different anions ($[\text{X}]^-$: $[\text{TFSI}]^-$, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$)^[1] to explore how mixtures of the PIL with the corresponding IL (poly $[\text{BVIM}]^+[\text{X}]^-$ /[BMIM]⁺[X]⁻) penetrate nanopores.

For this purpose we employ ex situ reflection optical microscopy of the evolution of the imbibition length and *in situ* conductivity measurements by nanodielectric spectroscopy. The latter provides details of ion motion during and following imbibition. In the bulk, symmetric poly $[\text{BVIM}]^+[\text{X}]^-$ /[BMIM]⁺[X]⁻ mixtures are locally heterogeneous composed of nearly pure IL domains and mixed PIL/IL domains. When the mixture is placed on top self-ordered nanoporous aluminum oxide templates (AAO) the ionic liquid is dragged by capillary action into the pores. During imbibition the two components partially demix. At the end of the filling process the pores contain an excess of the IL and a minority of PIL chains. Subsequently we explored the effect of polymer adsorption^[2] and surface functionality on the kinetics of ion transport. The results suggest the possibility to separate a mixture of ionic compounds (IL and PIL in this case) by the difference in the imbibition kinetics of its constituent components. Applications of AAOs as separation membranes for ionic systems are discussed.

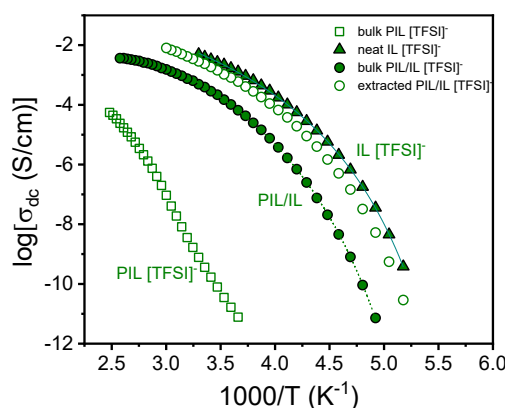


Figure 1. Ionic conductivity of the material extracted from AAO nanopores of 65 nm in diameter following the *in situ* nDS (open circles). The conductivity data are compared with the neat IL (filled triangles), the bulk PIL (open squares) and the bulk PIL/IL blend (spheres).

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Rheo-combined Dielectric Spectroscopy to Monitor Isothermal Crystallization of Poly(butylene succinate) (PBS)

Hyeong Yong Song^{1*} and Manfred Wilhelm¹

¹ *Institute of Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology, 76131, Karlsruhe, Germany*

Email: * hyeongyong.song@kit.edu

Recently, aliphatic polyesters have received much attention regarding their biodegradability, particularly from an ecological point of view. Poly(butylene succinate) (PBS) is one of the interesting biodegradable polymers. It has been utilized in packaging film, bags, flushable hygienic products, and mulching film. PBS exhibits excellent characteristics including susceptibility to biodegradation, thermoplastic behavior, reasonably balanced thermo-mechanical properties, and processibility with conventional equipment for plastics [1], [2]. Mechanical and processing properties of PBS are affected by crystallinity and crystallization rate as well as amorphous chain characteristics. For instance, high crystallinity of PBS slows down degradation rate and deteriorates barrier properties. Thus, it is important to understand crystallization kinetics of PBS for processing aspect [3]. To this end, this study utilized a rheo-dielectric set-up for in-situ measurements of isothermal crystallization. By doing so, rheological modulus developments were recorded simultaneously with dielectric permittivity changes. Considering the similarity between crystallizing polymers and polymer nanocomposites, we applied the modulus decomposition approach to rheological modulus of crystallizing PBS. Using this approach, two characteristic times were defined: rheological induction time and gelation time. The dielectric permittivity data were more sensitive to presence of crystals. The crystalline formation was indicated by the Maxwell-Wagner-Sillars (MWS) polarization, which occurs due to charge build-up created by contact between amorphous supercooled melt and crystalline surface. Finally, we proposed how to obtain consistent crystallinity results from dielectric properties and showed a crystallinity-bulk modulus plot.

Acknowledgments

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Using Dielectric-Resonance Spectroscopy to Study the Dielectric Behaviors of Polymer-Based Ferroelectrets

Peng Fang¹, Xingchen Ma² and Xiaoqing Zhang^{2*}

¹ Shenzhen Institute of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055, China

² Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China

Email: * x.zhang@tongji.edu.cn

Ferroelectrets, also called piezoelectrets, are kind of polymer-based cellular electrets with strong ferroelectric effects [1]. Their ferroelectricity originates from a combination of the internally stored quasi-permanent charges, which is the intrinsic nature of electrets, and the heterogeneous cellular structures. Ferroelectrets exhibit a number of advantages like large piezoelectric d_{33} coefficient, low acoustic impedance, flexibility, etc., enabling a variety of applications. Dielectric-resonance spectroscopy (DRS) is a powerful technique to investigate ferroelectrets [2]. It has the advantage of yielding several essential parameters in a single measurement by least-squares fit, including relative permittivity ϵ_{33} , complex electromechanical coupling factor k_t , elastic modulus c_{33} , and d_{33} . In addition, recording spectra at elevated temperatures can acquire the temperature-dependent properties of ferroelectrets.

In our work, we fabricated two types of ferroelectret samples, i.e., the traditional foam-structure ferroelectrets from polyethylene naphthalate (PEN) and the compound layer-structure ferroelectrets by combining cellular polypropylene (PP) and solid polytetrafluoroethylene (PTFE) films. Clear dielectric-resonance spectra demonstrate the performances of samples, and the parameters achieved by fitting of spectra are in agreement with those by other techniques. All samples show strong piezoelectricity with d_{33} as high as a few hundred pC/N, and the anti-resonance frequency f_{res} is around 500 and 90 kHz for the foam- and layer-structure ferroelectrets, respectively. More applications of DRS on ferroelectret study are also suggested.

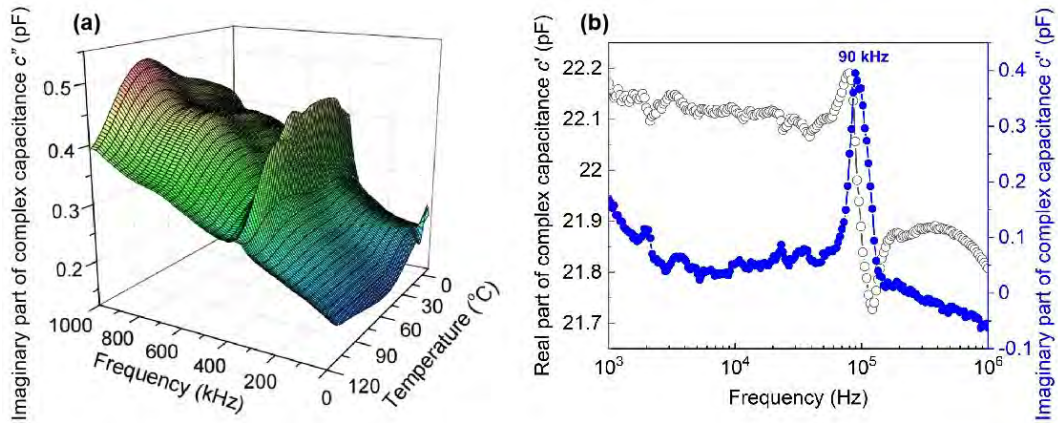


Figure 1. Dielectric-resonance spectroscopy: (a) Frequency-temperature map of c'' for a foam-structure ferroelectret and (b) c' and c'' for a layer-structure ferroelectret.

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Advanced PVDF-TiO₂ Composites for Efficient Energy Storage

Carlos Figueiras¹, Luiza-Izabela Jinga², Filipe Amaral^{1,3} and Silvia Soreto^{1*}

¹ i3N and Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal

² National Institute for Laser, Plasma and Radiation Physics, RO-077125 Magurele, ROMANIA

³ Polytechnic Institute of Coimbra, Coimbra Health School (ESTeSC), 3046-854 Coimbra, Portugal

Email: * silvia.soreto@ua.pt

Interest in renewable energy has spurred the development of novel materials for high-power energy storage, such as capacitors. Flexible polymer composites are key advancements with potential uses in electronics and healthcare [1].

In this research, PVDF composites with rutile TiO₂ filler, codoped with niobium and magnesium, were created with the primary aim of enhancing their dielectric properties. The rutile codoped ceramic powder (Mg_{1/2}Nb_{1/2})_xTi_{1-x}O₂, with x=5%, was synthesized via solid-state reaction and ball-milled for particle size homogenization. This composition was chosen for its high dielectric constant ($\epsilon' > 10^4$). The PVDF composites were fabricated using the simple solution mixing technique, with extra steps for proper particle dispersion.

X-ray diffraction, X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy analysed the structural properties of the powders and composites. Scanning electron microscopy with EDS assessed morphological aspects, especially filler dispersion. Impedance spectroscopy evaluates the dielectric properties and the effect of the codoped filler across a wide temperature range (150-370 K) and frequency range (10²-10⁶ Hz).

All composites exhibited enhanced dielectric properties compared to neat PVDF ($\epsilon' = 10.46$, $\tan \delta = 0.062$), with the 21 wt% filler composite showing the best performance ($\epsilon' = 15.58$, $\tan \delta = 0.041$).

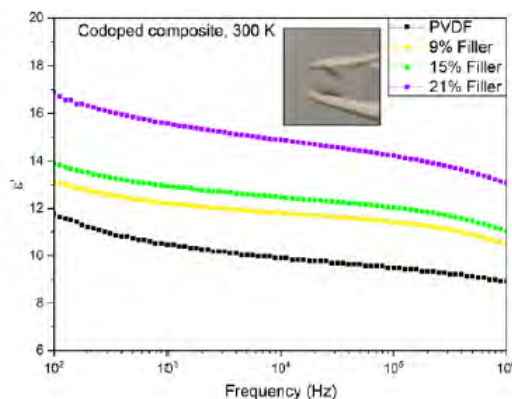


Figure 1. Dependence of the real part of the permittivity (ϵ') with the frequency, for composites with different contents of codoped TiO₂, at 300 K.

Acknowledgments

The authors acknowledge the support of FCT-Fundação para a Ciência e a Tecnologia, I.P., in the scope of the projects LA/P/0037/2020, UIDP/50025/2020 and UIDB/50025/2020 of the Associate Laboratory Institute of Nanostructures, Nanomodelling, and Nanofabrication-i3N.

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Dielectric behaviour of BFO ceramics

Subir Majumder*, Gilad Orr, Paul Ben Ishai

Dept. of Physics, Ariel University, Kiryat Hamada 3, Ariel, Israel.

*Email: subirm@ariel.ac.il

Recently, BFO (BiFeO_3) has gained renewed attention for its multiferroic properties, enabling simultaneous ferroelectric and ferromagnetic ordering at room temperature. Its magneto-electric coupling between electric and magnetic polarizations makes it suitable for various applications. BFO is stable between 767°C and its peritectic temperature of 930°C . However, the high volatility of bismuth in this range complicates obtaining the desired phase. Additionally, two stable phases, $\text{Bi}_2\text{Fe}_4\text{O}_9$ (mullite-like) and $\text{Bi}_{25}\text{FeO}_{40}$ (sillenite-like), also influence the material's dielectric properties.

The dielectric permittivity of a sintered ceramic pellet with 62.81% BiFeO_3 , 36.53% $\text{Bi}_2\text{Fe}_4\text{O}_9$, and 0.66% $\text{Bi}_{25}\text{FeO}_{40}$ was studied from -120°C to 200°C . The pellet was prepared via a solid-state reaction using analytical grade Bi_2O_3 and Fe_2O_3 powders in a 55:45 (mol%) ratio, sintered at 815°C for 2 hours. X-ray diffraction (XRD) peaks identified the phase composition, while SEM micrographs confirmed multiple phases, including nano-crystallites, amorphous regions, and a porous structure.

The dielectric response below 0°C shows three relaxation processes due to dipole reorientation or charge carrier movement. As temperature rises, dielectric properties change significantly, leading to breakdown at higher temperatures and low frequencies. SEM images reveal a porous structure indicating conduction pathways. This presentation will discuss the impact of these pathways and the presence of water on the dielectric behaviour of these ceramics. It is noted also that activation energy of the observed relaxation processes is similar to that of ice, suggesting the behaviour is due to trapped water molecules in the pores. This is supported by mass loss after dielectric measurements, confirming water escape as temperature rises. Understanding this relationship is crucial for improving material performance and stability.

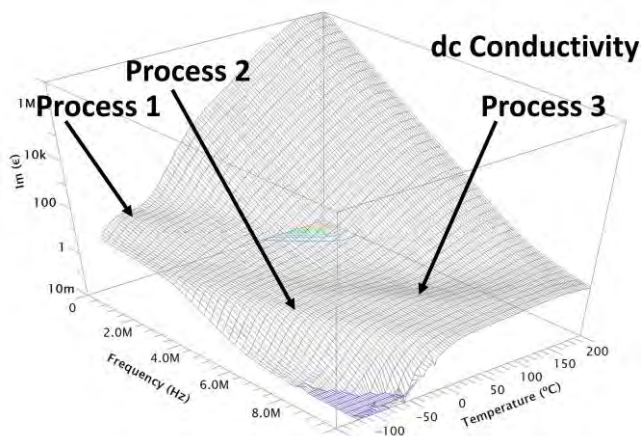


Figure 1. Relaxation landscapes and dc conductivity phenomenon observed in BFO ceramic pellet

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Thermal expansion of inter-molecular H-bonds

Martin Tress^{1*}, Robin Horstmann², Friedrich Kremer¹ and Jan P. Gabriel^{3*}

¹ Peter Debye Institute for Soft Matter Research, Leipzig University, 04103 Leipzig, Germany

² Institute for Condensed Matter Physics, Technical University Darmstadt, 64289 Darmstadt, Germany

³ Institute of Materials Physics in Space, German Aerospace Center, 51170 Köln, Germany

* Martin.Tress@uni-leipzig.de

Understanding the glass transition has been a challenge for decades, yet no comprehensive explanation exists. Besides its key-feature, a tremendous increase of structural relaxation time upon cooling, the temperature dependent changes in the specific volume are often used to describe and characterize this phenomenon. Recently, even a rather direct connection between thermal expansion and fragility has been discovered [1]. However, acknowledging that the structural relaxation is an event on molecular scale, it may be too simplistic to consider a macroscopic and averaged thermal expansion.

Here we analyze infrared spectroscopy (IR) data of hydrogen (H) bond stretching vibrations in several H-bonding liquids quantitatively to extract inter-molecular H-bond lengths in wide temperature ranges of the liquid and glassy state. For water, the extracted expansivity of this H-bond differs strongly from that of the average nearest neighbor distance of oxygen atoms obtained through a common conversion of mass density which is easily assigned to the considerable structural reorganization in the water network [2]. Comparing the thermal expansion coefficient of these two (inter-molecular H-bonds and specific volume) reveals that the most compact molecular arrangement is formed in the range ~316-331 K (i.e. well above the density maximum). This is close to the temperature of several pressure-related anomalies which confirms this characteristic point in the supra-molecular arrangement. These results confirm our earlier approach to deduce inter-molecular H-bond lengths via IR in polyalcohols [3] quantitatively and open a new alley to investigate the role of inter-molecular expansion as a precursor of structural relaxation on a bond-specific level.

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Temperature Based Study of Dielectric Permittivity and Dielectric Susceptibility in the Binary Mixture of Polar Liquids

V. P. Pawar* and Shagufta Tabassum

Department of Physics & Electronics, Maharashtra Udayagiri Mahavidyalaya Udgir, India

Email: *pawar_vyankat@yahoo.com

The interaction of electromagnetic radiation with a dielectric material gives a complex quantity. The real part indicates dielectric permittivity or dielectric gain and the imaginary part is the magnetic susceptibility or dielectric loss. This complex study of polar liquids in a binary mixture gives information regarding frequency dispersion in dielectric permittivity and dielectric loss. The static dielectric indicates that the electric charge distribution in the material can be distorted or polarized by applying an electric field. An alternating electric field of appropriate frequency gives rise to dielectric dispersion; the characteristic orientation motions of the dipoles result in a frequency variation of the dielectric constant and the appearance of dielectric loss over a broadband of frequencies.

Acknowledgments

The department of Science and Technology, New Delhi is grateful acknowledged (Project no. SR/S2/LOP-25/2007) for laboratory facility. We are thankful to the A. C. Kumbharkhane for providing TDR facility and Dr. S. C. Mehrotra, Ramanujan Chair Professor, Department of Computer Science and IT, Dr. B.A.M. University, Aurangabad for their valuable discussion and suggestions.

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Dielectric evidence of high kinetic stability in vapour-deposited binary glasses with large T_g contrast

Erik Thoms*, Zijian Song, Kai Wang & Simone Simon Napolitano

Laboratory of Polymer and Soft Matter Dynamics, Experimental Soft Matter and Thermal Physics (EST),
Université libre de Bruxelles (ULB), Brussels 1050, Belgium

*current address: School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287, USA,
Email: ethoms@asu.edu

Irreversible adsorption of polymer chains is a non-equilibrium process with significant influence on the properties of thin films and coatings. Direct measurements of the adsorption rate, ν , require a considerable experimental effort, while a theoretical model predicting this relevant quantity is missing at the state of the art. We show that the adsorption rate can be predicted solely by measurement of the dielectric Slow Arrhenius Process (SAP) [1], exploiting the fundamental connection between the two processes [2].

Our simple model is based on the hypothesis that each time the SAP relaxes, a constant number of molecules adsorbs. ν then depends linearly on the SAP relaxation rate, $f_{\text{SAP}}(T)$, scaled with the density and degree of polymerization, with an efficiency factor Y independent of the temperature of the experiment or the material. On flat substrates, we find that the rate at which chains adsorb does not depend on the particular chemical composition of the polymer, but on the SAP rate only. Consequently, ν can be obtained without any direct adsorption measurements: predictions can be achieved based on fast dielectric measurements alone, or, exploiting the compensation law of the SAP [3], based on the activation energy of any other equilibration process facilitated by the SAP.

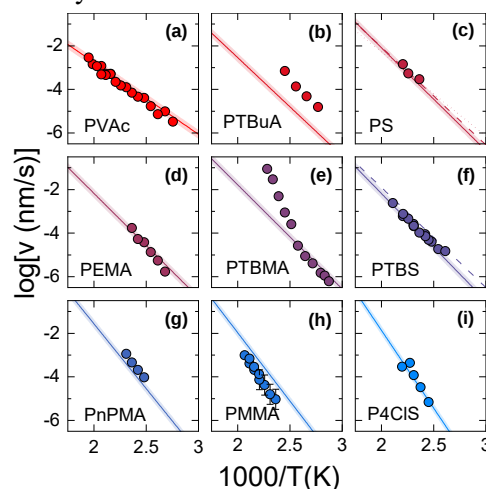


Figure: Measured (symbols) and predicted (lines, shaded area indicates one standard deviation) ν for nine polymers as a function of the inverse temperature. Dashed and dotted lines show predictions of the adsorption rate based on E_{SAP} -values obtained through aging and dewetting, respectively.

Acknowledgments

This work was supported by Fonds de la Recherche Scientifique FNRS under grant T.0184.20 “EXOTICAGE”; Action de Recherche Concertée—ULB under grant ARC 20061 “SADI”

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Conductive P3HT Nanostructures: Structure/Property Relationship and Applications

Lucas Leveque*, Laurent David, Guillaume Sudre, Anatoli Serghei

IMP Laboratoty – Université Lyon 1

*lucas.leveque@etu.univ-lyon1.fr

Email : * lucas.leveque@etu.univ-lyon1.fr

Semiconducting polymer nanostructures, including nanotubes, nanowires, and nanopillars, have been extensively employed in applications such as organic photovoltaic cells [1] and field-effect transistors [2]. Their unique morphological and physical characteristics hold significant promise for advancements, particularly in the realm of particle detection. In this study, we fabricated polymer nanotubes made of poly(3-hexylthiophene) (P3HT) and polystyrene (PS) using a template method employing nanoporous aluminum oxide (AAO) membranes. The goal was to maintain the superior electrical properties of P3HT nanotubes while enhancing stability against high voltage and morphological changes. The confinement induced by AAO membranes influences the electrical and structural properties of P3HT, thereby enhancing its performance in various devices.

We measured the electrical conductivity and phase transitions of both P3HT nanostructures and bulk P3HT using Broadband Dielectric Spectroscopy (BDS). The crystalline properties were investigated through Wide-Angle X-ray Scattering (WAXS) analysis conducted at the European Synchrotron Radiation Facility (ESRF). Our findings indicate that the nanotubes exhibit significantly higher electrical conductivity compared to the bulk material. This enhancement is attributed to the confinement effects, which promote the alignment of polymer chains to facilitate efficient charge transport. Moreover, the interactions between the nanopore walls and the nanostructures play a crucial role in determining the crystallinity and conductive properties, with thicker nanotubes demonstrating superior conductivity compared to nanowires. By combining the conductive properties of P3HT with the stability of PS, we achieved a nanostructure that not only retains high electrical performance but also shows improved resistance to high voltage and morphological stability, making it suitable for advanced electronic applications.

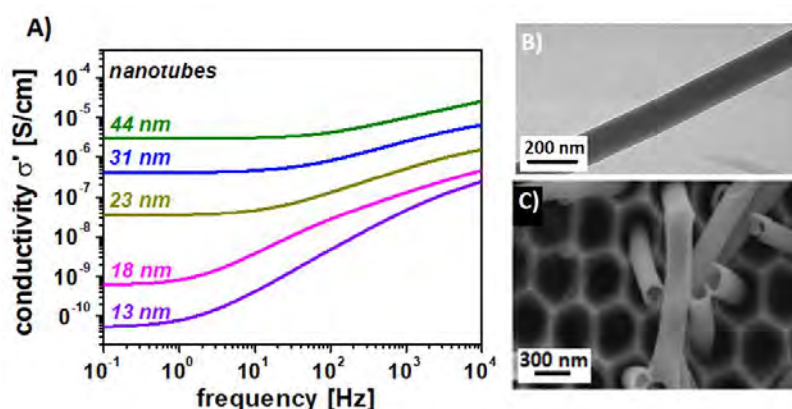


Figure 1 : A) Conductivity of P3HT nanotubes vs frequency for several nanotubes thickness, B) TEM image of P3HT nanotube, C) SEM image of P3HT nanotubes

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Dynamics of a Confined Drug from Complementary Perspectives: Experiments vs MD Simulations

Teresa Cordeiro¹, M. Teresa Viciosa², Madalena Dionísio¹, Frédéric Affouard³ and Natália T. Correia^{*3}

¹Department LAQV-REQUIMTE, Universidade Nova de Lisboa, Portugal

²Centro de Química Estrutural, Universidade de Lisboa, Portugal

³Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207, UMET, Unité Matériaux et Transformations, F-59650 Villeneuve d'Ascq, France

Email : *natalia.correia@univ-lille.fr

This study investigates the physical state and molecular mobility of simvastatin (SIM), a cholesterol-lowering and almost water insoluble drug, confined into a 3.5 nm pore diameter MCM-41 silica matrix, using calorimetric and spectroscopic techniques complemented by molecular dynamics (MD) simulations [1].

X-ray diffraction, infrared spectroscopy (ATR-FTIR) and Differential Scanning Calorimetry demonstrated that SIM is fully amorphous upon loading, however, the distribution of SIM within the pores is uneven. Thermogravimetric and ATR-FTIR results indicated the presence of strong guest-host interactions and a high thermal resistant population, which is consistent with the findings of MD simulations. These investigations provide evidence that the majority of SIM molecules tend to accumulate near the inner pore wall being strongly anchored by three to five hydrogen bonds (Figure 1).

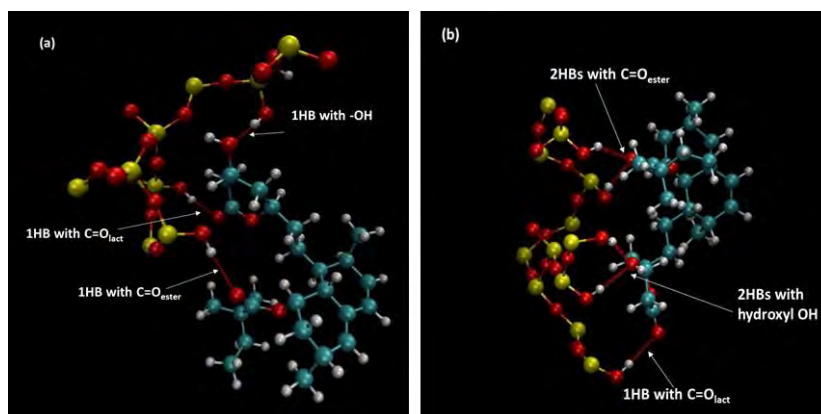


Figure 1. Snapshots by MD simulations of SIM confined in a cylindrical pore of 3.5 nm diameter that mimics MCM-41 mesoporous materials, illustrating the interaction with the silanol groups of the MCM matrix through a) three hydrogen bonds and (b) five hydrogen bonds identified by the white arrows.

The multiplicity of binding sites renders the surface layer molecules dynamically rigid, resulting in the absence of a calorimetric signature and of a surface relaxation process resolved by Broadband Dielectric Spectroscopy.

Furthermore, MD simulations indicated the presence of a pore-core molecular fraction in agreement with a calorimetric low- T_g , which is a manifestation of true confining effects. In addition, MD simulations show that the orientation of the dipoles in the pores is different from that observed in the bulk, resulting in the cancellation of the total dipole moment and the failure to detect an α -fast dielectric relaxation and the corresponding Johari-Goldstein β -process.

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Imbibition Kinetics of Poly(ethylene oxide) in Nanopores by *In Situ* Nanodielectric Spectroscopy

Panagiotis Kardasis,¹ * George Floudas^{1,2,3}

¹*Department of Physics, University of Ioannina, 45110 Ioannina, Greece*

²*University Research Center of Ioannina (URCI) - Institute of Materials Science and Computing, 45110 Ioannina, Greece*

³*Max Planck Institute for Polymer Research, 55128 Mainz, Germany*

Email: * p.kardasis@uoi.gr

Understanding how polymers move through nanopores is important for both academic research and technological applications.[1] By using confinement within nanoscopic cylindrical pores we have recently shown that a semicrystalline polymer (PEO) can flow at temperatures below the melting point. [2] This time we employed *in situ* nanodielectric spectroscopy (*nDS*), [3,4] and study the imbibition kinetics of PEO in anodic aluminum oxide nanopores (AAO) by following the evolution of the dielectric loss curves at a temperature above the melting point ($T = T_m + 5\text{K}$). Interestingly, a new dynamic process (X-process) appears at the early stages of the imbibition process. A previous study of PEO in nanofilms has shown that the melting transition is accompanied by the appearance of a Slow Arrhenius process (SAP).[5] By performing simulations, we predict the dielectric function's time evolution and we show that the origin of the X-process is not due to the air influence. This process was found to be dominant under nanometer confinement as it presents high dielectric strength ($\Delta\epsilon_X / \Delta\epsilon_a \sim 10^3$) and a peculiar T -dependence. At higher temperatures, a correlation between the temperature dependence of the X-process and the terminal relaxation (obtained from rheology) is shown. Lastly, we demonstrate the effect of pore size and molar mass on the position and dielectric strength of the X-process.

Acknowledgments

This research was supported by the ReBond Project, funded from Horizon Europe Programme (MARIE SKŁODOWSKA-CURIE ACTIONS) of the Marie-Sklodowska Curie Doctoral Network (HORIZON-MSCA-2022-DN-01) under ReBond REA Grant Agreement N°101119786. P.K. was supported by the Hellenic Foundation for Research and Innovation (HFRI) under the 4th Call for HFRI Ph.D. Fellowships (Fellowship Number: 9360).

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Dynamics of polylactic acid under ultrafine nanoconfinement: the collective interface effect and the spatial gradient

Shiwang Cheng*, Juncheng Zheng and David Kogut

Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, MI, United States of America
Email: * chengsh9@msu.edu

Polymers under nanoconfinement can exhibit large alterations in dynamics from their bulk values due to an interface effect. However, understanding the interface effect remains a challenge, especially in the ultrafine nanoconfinement region. In this contribution [1], we prepare new geometries with ultrafine nanoconfinement ~ 10 nm through controlled distributions of the crystalline phases and the amorphous phases of a model semi-crystalline polymer, i.e., the polylactic acid. Broadband dielectric spectroscopy measurements show that ultrafine nanoconfinement leads to a large elevation in glass transition temperature and a strong increment in polymer fragility index. Moreover, new relaxation time profile analyses demonstrate a spatial gradient that can be well described by either a single-exponential decay or a double-exponential decay functional form near the middle of the film with a collective interface effect. However, the dynamics at the 1-2 nanometers vicinity of the interface exhibit a power-law decay different from the single-exponential decay or double-exponential decay functional forms as predicted by theories. These results thus call for further investigations of the interface effect on polymer dynamics, especially for interfaces with perturbed chain packing.

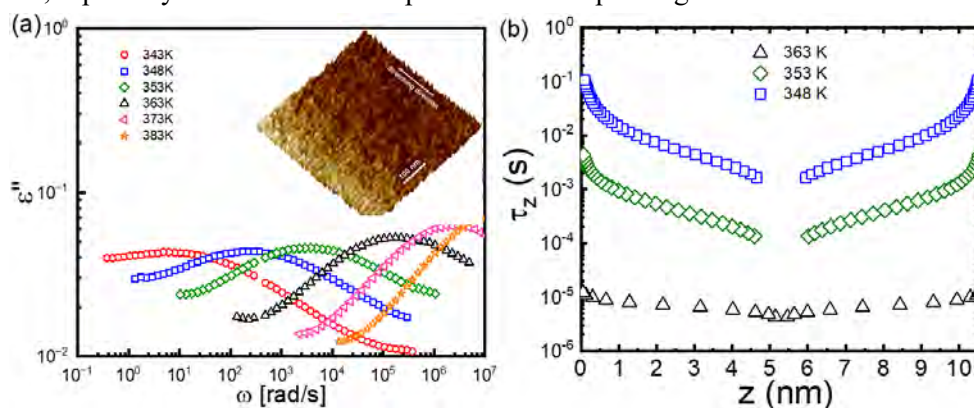


Figure 1. (a) Dielectric loss spectra of the polylactic acid (PLA) under ultrafine nanoconfinement of 10 nm at different testing temperatures. The inset gives an atomic force microscopy measurements of the microstructure of the polylactic acid where the bright ridges represent the crystalline phase and the dark valleys are the confined amorphous PLA. (b) Representative analyses of the gradient of the dynamics at the interface from the dielectric spectra.

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This work was supported by National Science Foundation under an Award number NSF-DMR 2211573.

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Glassy Dynamics from First-Principles Simulations

Florian Pabst^{1,*}, Stefano Baroni¹

¹ *Scuola Internazionale Superiore di Studi Avanzati, Trieste, Italy*

Email: * fpabst@sissa.it

The microscopic understanding of the dramatic increase in viscosity of liquids when cooled towards the glass transition temperature is a major unresolved issue in condensed matter physics. Here, we use machine learning methods to accelerate molecular dynamics simulations with first-principles accuracy for the glass-former toluene. We demonstrate that we are able to reach the time and temperature ranges where all features of glassy dynamics, such as the non-Arrhenius behavior of viscosity, relaxation stretching, and physical aging, can be observed. Importantly, we show that the strong increase in viscosity upon cooling is intimately linked to the increasing number of dynamically correlated molecules N^* in a simple way: the apparent activation energy, taken as the slope of the temperature-dependent viscosity in the Arrhenius plot, is proportional to the number of dynamically correlated molecules N^* . This finding is in accordance with experimental results from non-linear dielectric spectroscopy on four different structural glass formers [1], but is at variance with the idea that the energy of local barriers determines the change in activation energy [2]. Moreover, N^* is also shown to govern physical aging, as the evolution of N^* after a temperature jump closely resembles the evolution of the system's density. On the other hand, the stretched exponential shape of relaxation functions is found to be independent of N^* , despite the widespread notion that increasing dynamic heterogeneity should lead to a higher degree of stretching. Instead, it is in line with the experimental observation that relaxation stretching has a generic shape for various liquids [3].

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Universal relationship between the electromagnetic interference shielding effectiveness of composite materials and their electrical properties

Anatoli SERGHEI, C. Retailleau, H. Lecocq, V. Bounor-Legaré, P. Cassagnau

University Claude Bernard Lyon 1, Ingénierie des Matériaux Polymères,
CNRS, Villeurbanne, France

Email: * anatoli.serghei@univ-lyon1.fr

With the tremendous technological developments related to the accelerated growth in the field of telecommunications, our contemporary society is increasingly facing the problem of electromagnetic pollution. Developing technological solutions and materials for protecting instruments and systems from electromagnetic interference phenomena becomes thus a major challenge in our society. In the current work, the electromagnetic interference shielding properties and the electrical properties of poly (methylmethacrylate) based composite materials prepared using different types of fillers (carbon nanotubes, carbon black, silver coated glass microfibers) have been investigated in a broad frequency range. By combining a theoretical and an experimental analysis we show that, irrespective of the nature of the conductive material (carbon based or metallic), the correlation between the electromagnetic shielding effectiveness, electrical conductivity and sample thickness follows a universal behavior, all experimental points falling onto a single universal curve predicted by our theoretical analysis. This is demonstrated not only for our own experimental results, but also for numerous experimental data reported in the scientific literature where other types of polymer matrices and other types of fillers have been investigated. The universal relationship found in our study opens the perspective of a precise predictive determination of the electromagnetic interference shielding effectiveness of composite materials based exclusively on their electrical properties.

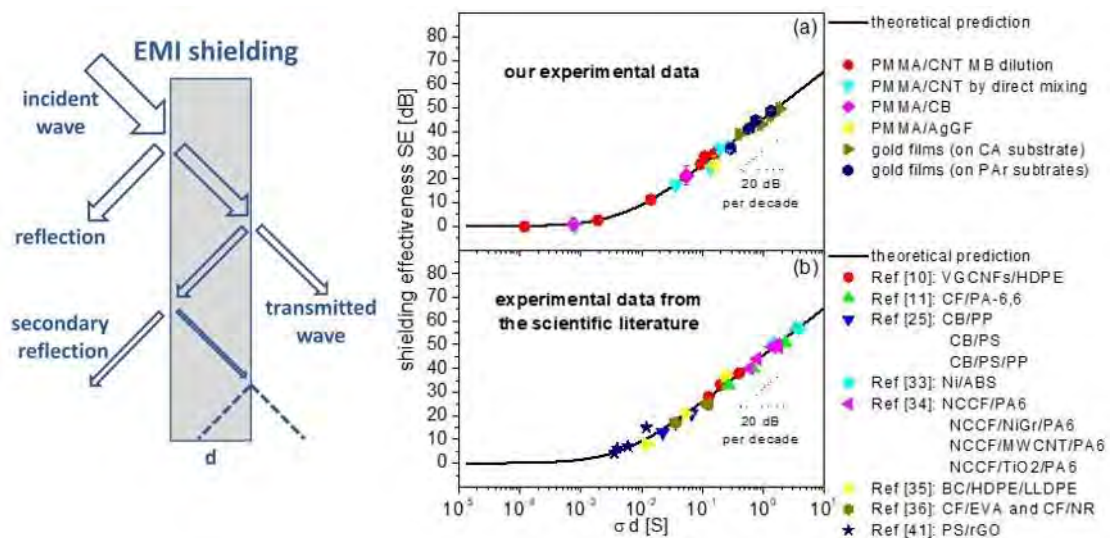


Figure 1. (left) schematic representation of electromagnetic shielding mechanisms. (right) electromagnetic shielding effectiveness of different composite materials as a function of the product between the material conductivity and the sample thickness.

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Materials electrical characterization: from DC to microwave frequencies

Luís Cadillon Costa^{1,*}, François Henry²

¹ *I3N and Physics Department, University of Aveiro, 3810-193 Aveiro, Portugal*

² *C.N.R.S., 94320 Thiais, France*

Email: * kady@ua.pt

DC electrical conductivity, as a function of temperature, gives crucial information about the transport processes in materials.

Impedance spectroscopy is a powerful tool to understand the relaxation processes that can be present in dielectrics.

In this work, the characterization methods, from DC to microwave frequencies, will be presented. From the point of view of applications, and due to its potential applications in industry, the Positive Temperature Coefficient of Resistivity effect will be discussed. In particular, it can be used in auto controlled heaters, temperature sensors, protection circuits and in security systems for power electronic circuits. Polymer composites with performant dielectric properties, at microwave frequencies, will be presented, which can be used in microwave ovens, to avoid the electromagnetic leakage.

Comprehensive Electrical and Biological Analysis of Bioglass in Bulk and Pressed Powder Forms

S.R. Gavinho¹, A.C. Gonçalves¹, J.S. Regadas¹, M.A. Valente¹, M.P.F. Graça^{1,*}

i3N and Physics Department, Aveiro University, 3800-193 Aveiro, Portugal

*e-mail: mpfg@ua.pt

Bioglasses have been utilized since the last century as biomaterials in the field of bone regeneration. The most well-known bioglass, Bioglass[®], developed by Larry Hench and colleagues, is noted for its high bioactivity [1]. Bioglasses are being investigated for their use in drug delivery systems, where their porous structure can be utilized to encapsulate and release pharmaceuticals in a controlled manner, promising localized treatment of infections and chronic conditions [2]. Another emerging application is in dental repair and regeneration, where bioglasses can aid in the repair of dental tissues and the regeneration of enamel and dentin [3]. Additionally, the bioglass surface can store electrical charge, which can further accelerate the osseointegration process, promoting the long-term success of an implant [4]. These diverse applications underscore the versatility and potential of bioglasses in various biomedical fields [5]. In this study, Bioglass 45S5 was produced using the melt-quenching method to create bulk samples. These initial specimens were then ground into finer particles and subsequently milled for varying durations to achieve different particle sizes. Specifically, a group of samples was prepared by systematically altering the total ball milling time, ranging from 1 hour to 24 hours, to observe the impact of milling duration on the material's properties. The finely milled powder obtained from this process was then used to fabricate pellets through compression.

Both the bulk and pellet samples underwent an electrical polarization process utilizing a corona triode system. This system applies a high-voltage electric field to induce polarization in the materials. The primary objective of these procedures was to thoroughly analyze and understand the effects of the modified electrical characteristics on the biological response of the bioglass. This comprehensive analysis aimed to provide insights into how the electrical properties influence cellular interactions and overall bioactivity, potentially leading to improved applications in biomedical fields.

The electrical studies were conducted using Thermally Stimulated Depolarization Current (TSDC) and Broadband Dielectric Spectroscopy, while the biological analysis was performed through bioactivity tests.

Acknowledgments

Acknowledgements: Work carried out with the support of the i3N, UIDB/50025/2020, UIDP/50025/2020 and LA/P/0037/2020 projects, as well as the following projects LISBOA-01-0247-FEDER-039985/POCI-01-0247-FEDER-039985.

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Dielectric properties of honey: application in botanical origin determination

Youssef Elamine^{*}, and Henrique Leonel Gomes

*Instituto de Telecomunicações, and Departamento de Engenharia Electrotécnica e de Computadores,
Universidade de Coimbra, 3030-290 Coimbra, Portugal*

Email: * youssef.elamine@co.it.pt

The analysis of natural products poses significant challenges due to their complex chemical compositions. Traditional methods require comprehensive chemical profiling, which is labor-intensive and time-consuming. However, the advancements of spectroscopic techniques offers promising solutions to these challenges, particularly in addressing food authenticity and quality issues.

In this study, we explored the complex chemical matrix of honey by probing its dielectric properties using Electrochemical Impedance Spectroscopy (EIS) in a broad frequency range from 60 Hz to 1 MHz. To validate our findings, we conducted a detailed mineral analysis, focusing on potassium due to its predominant concentration and role in influencing the electrical characteristics of honey.

The results showed that potassium significantly impacts the dielectric properties of honey, primarily shaping its electrical double layer at low frequencies and bulk conductivity at high frequencies. Modeling both honey and potassium solution revealed that the equivalent circuit employed delineates the electrical double layer (EDL) and bulk electrolyte conductivity, with distinct responses observed over the frequency range. At frequencies below 1 kHz, the impedance is predominantly influenced by the EDL, which is sensitive to ionizable species at the electrode/electrolyte interface, such as potassium. Above 10 kHz, the focus shifts to bulk conductivity, reflecting the overall mineral content. Besides the similar impedance profile, high correlation was established between potassium concentration in honey and the impedance.

In the honey market, the identification of botanical origin is determinant in shaping the consumer preferences and hence the pricing. Given that potassium constitutes a predominant species in honey composition, the EIS could be employed for rapid determination of the botanical origin of honey. The cost and time effectiveness of the technique promises an ideal approach for upscaling to industrial levels.

Acknowledgments

We acknowledge support from the FCT/MCTES, through national funds and when applicable co-funded EU funds by FEDER under the PT 2020 Partnership Agreement. The project contributing to this work was the institutional projects UIDB/EEA/50008/2020 (IT). Youssef Elamine was funded by the Instituto de Telecomunicações in the scope of the “CEEC Institucional” program funded by FCT (DOI 10.54499/CEECINST/00058/2021/CP2816/CT0001).

LIST OF PARTICIPANTS:

Achilleas A. Pipertzis	Sweden	Federico Caporaletti	Belgium
Adam Sieradzki	Poland	Florian Pabst	Italy
Aitor Erkoreka	Spain	Francesco Coin	Spain
Alexei Sokolov	USA	Francois Ladieu	France
Alfred Błażytko	Poland	Frederic Affouard	France
Alois Loidl	Germany	Friedrich Kremer	Germany
Ana R. E. Brás Würschig	Germany	Geoff Smith	UK
Ana Šantić	Croatia	George Floudas	Greece
Anatoli Serghei	France	Gustavo A. Schwartz	Spain
Andreas Schönhals	Germany	Henrique Leonel Gomes	Portugal
Andreia F. M. Santos	Portugal	Herbert Kliem	Germany
Anna Drzewicz	Poland	Hermínio Diogo	Portugal
Anne-Caroline Genix	France	Hiroaki Matsuura	Japan
Apostolos Kyritsis	Greece	Hyeong Yong Song	Germany
Aurélien Roggero	France	Ioannis Tzourtzouklis	Greece
Aurora Nogales	Spain	Jacob Gerasimov	Israel
Benjamin Malfait	France	Jan Swenson	Sweden
Bernard Roling	Germany	Jeppe Dyre	Denmark
Bruno Miguel Melo	Portugal	Jessica Mangialetto	Belgium
Carlos Mariano Dias	Portugal	Jiaxin Zhao	UK
Caroline Raepsaet	France	José L. Gómez Ribelles	Spain
Catalin Gainaru	USA	Joshua Sangoro	USA
Christiane Alba-Simionesco	France	Kaito Sasaki	Japan
Cindy Galindo	Israel	Kamil Kaminski	Poland
Daniele Cangialosi	Spain	Kang HU	Japan
Diogo Gomes	Portugal	Katarzyna Chat	Poland
Dirk Wilmer	Germany	Kaylie C. Glynn	USA
Dmitry V. Matyushov	USA	Kazunori Takahashi	Japan
Efrat Hochma	Israel	Keisuke Tominaga	Japan
Elisa Steinrücken	Germany	Kenneth Rojo	France
Emeline Dudognon	France	Kinga Łucak	Poland
Eric Dantras	France	Koji Fukao	Japan
Erik Thoms	USA	Kosei Kawai	Japan
Ernst Rössler	Germany	Kristine Niss	Denmark
Fabian Puga	France	Laurent Delbreilh	France

Lucas Leveque	France	Ralph Colby	USA
Luís Cadillon	Portugal	Ranko Richert	USA
Luka Pavic	Croatia	Roberto Macovez	Spain
Madalena Dionísio	Portugal	Rolf Zeissler	Germany
Magdalena Tarnacka	Poland	Ronald P. White	USA
Manuel Graça	Portugal	Ryo Shirakashi	Japan
Marceau Hénot	France	Sandra Krüger	Germany
Maria Lanca	Portugal	Sara Zimny	Poland
Maria Teresa V. Plaza	Portugal	Sébastien Pruvost	France
Marian Paluch	Poland	Senentxu Lancers-Mendéz	PT/Spain
Marianna Ambrico	Italy	Shiwang Cheng	USA
Marianna Spyridakou	Greece	Silvia Arrese-Igor	Spain
Martin Tress	Germany	Sílvia Gavinho	Portugal
Marzena Rams-Baron	Poland	Silvia Soreto Teixeira	Portugal
Maxwell Douglas C. Sparey	Austria	Silvina Cerveny	Spain
Men Guo	Israel	Simone Napolitano	Belgium
Michael Vogel	Germany	Sofia R. Mendes	Portugal
Michael Wübbenhorst	Belgium	Stavros X. Drakopoulos	USA
Michal Rajnak	Slovakia	Steven Kooi	USA
Michela Romanini	Spain	Subir Majumder	Israel
Mohamad Barzegar	Spain	Syed Tofail	Ireland
Morgan Lecouplet	Canada	Tatiana Starciuc	Sweden
Mustapha Raihane	Morocco	Thomas Blochowicz	Germany
Mydhil Varma	Israel	Thulasinath R. Venkatesan	Switzerland
Natália Correia	France	Tiberio Ezquerra	Spain
Nikolaos Fotaras	Greece	Tina Hecksher	Denmark
Panagiotis Kardasis	Greece	Torsten Granzow	Luxembourg
Paul Ben Ishai	Israel	V. P. Pawar	India
Paula Rodrigues	Portugal	Vasileios Moschos	Greece
Paula Vilarinho	Portugal	Yang Yao	Switzerland
Paulina Jesionek	Poland	Yasuaki Monnai	Japan
Paulina Szymoniak	Germany	Youssef Elamine	Portugal
Pedro Manuel Faia	Portugal	Yun Dong	Germany
Peng FANG	China	Yuri Feldman	Israel
Pierre-Michel Déjardin	France	Zaneta Wojnarowska	Poland
Raj Suryanarayanan	USA		

CONCLUDING REMARKS:

Dear participants,

We feel that the BDS2024 objectives were achieved thanks to the excellence of your contributions with truly impressive presentations, tutorials, talks and posters.

As **concluding remarks**, we would like to highlight **your enthusiasm**, the **lively discussions**, the **youth of many participants** who had the opportunity to share their works, many for the **first time**, the **friendly way** in which everyone welcomed those who were new to the field, the **inclusion of colleagues** who are not used to BDS conferences and who felt strongly motivated to participate in the future, the **out-of-the-box talks**, the introduction of a **dynamic** way of sharing results.

Concerning the young participants, we emphasize the **2024 IDS Debye Prize** and the **thirteen** more that were awarded: **seven** received honorable mentions with autographed books (Springer) and **six** received monetary prizes sponsored by the I3N laboratory, MDPI publisher and Crystals from MDPI (don't forget the open special [MDPI Topic](#) and Crystals [Special Issue](#)).

Finally, we would just like to add that the surplus from the meals in the rectory hall, invited speaker dinner and gala dinner were given to organizations supporting disadvantaged people, which included the “[Irmãzinhas dos Pobres](#)” and the “[Vale de Acór](#)” Foundation.

Now it's time to say goodbye to Lisbon and plan a trip to Leuven, Belgium in 2026.

Goodbye Lisbon, hello **Leuven!**

The BDS2024 Organizing Committee

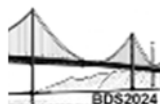
Natália Correia (Université de Lille) & Madalena Dionísio (FCT-NOVA),

Maria do Carmo Lança, Carlos J. Dias, Andreia F. M. Santos (FCT- NOVA),

Maria Teresa Viciosa, Hermínio Diogo (IST-UL)

Sílvia Soreto, Manuel Pedro Graça, Luís Cadillon (Universidade de Aveiro) and

Henrique Leonel Gomes (Universidade de Coimbra)



12th Conference on Broadband Dielectric Spectroscopy and its Applications

BDS2024



01 – 06 September 2024

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