11th Conference on Broadband Dielectric Spectroscopy and its applications

PROGRAM & BOOK OF ABSTRACTS

Under the patronage of the International Dielectric Society

Donostia-San Sebastian, Spain

September 2022

ACKNOWLEDGEMENTS

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We also thank Karmela Alonso (DIPC) for providing all the support for organizing this meeting.

The organization of BDS2022 would not have been possible without the patronage of the International Dielectric Society and the scientific contribution of all the participants to this meeting.

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PREFACE

Welcome to the 11th Conference on Broadband Dielectric Spectroscopy and its Applications (BDS2022), organized under the International Dielectric Society's (IDS) patronage.

We are proud to organize this edition, the first in-person meeting of the dielectric community after four years. We have had a hard time with the pandemic and mobility restrictions to travel and meet. Still, finally, we are here not only to share knowledge, experiences, and science but also because we are inspired when we are together.

Broadband dielectric spectroscopy (BDS) is a well-established and powerful experimental technique permitting the investigation of the molecular dynamics of polar (and nonpolar) materials over a wide frequency range covering up to 16 decades at different temperatures and pressures. BDS finds a considerable number of applications in various fields of science and technology.

The BDS2022 meeting in Donostia-San Sebastian will provide a platform for exchanging knowledge related to dielectric spectroscopy: from historical backgrounds to the most recent advances in the experiment and simulations. The meeting in San Sebastian is also open to researchers outside the dielectric community whose research could start new synergies at both experimental and theoretical levels.

As traditionally, the first day of our meeting starts with a tutorial session that introduces a selection of fields to young researchers.

We hope your stay at San Sebastian will be tremendously productive and that you will enjoy the program of the BDS2022 conference.

R. Richert

Silvina Cerveny

Chair of BDS2022

Ranko Richert

President of IDS

PROGRAM

Sunday	Monday	Tuesday	Wednesday	Thursday	Friday
	Opening Session 8:40 – 11:00	Polymer Dynamics (1) 08:30-10:45	Glassy Dynamics (2) 08:30-11:15	Young Researcher Session 08:30-11:10	Polymer Dynamics (3) 09:30-11:15
	Coffee Break 11:00-11:30	Coffee Break 10:45-11:15	Coffee Break 11:15-11:45	Coffee Break 11:10-11:40	Coffee Break 11:15-11:45
	Water and H-Bonded Systems (1) 11:30 – 13:00	Water and H-Bonded Systems (2) 11:15 – 12:45	Soft Matter (2) 17:00 – 18:30	Confinement Effects 11:40-12:55	Glassy Dynamics (3) 11:45-13:15
	Lunch 13:00 – 14:45	Lunch 12:45-14:45	Lunch 13:30-15:00	Lunch 13:00-14:45	Lunch 13:15-15:30
REGISTRATION 14:00 – 19:00	Glassy Dynamics (1) 14:45 – 16:30	Industrial Application 14:45-17:30	Charge Transport 15:00-16:30	Soft Matter (3) 17:00 – 18:30	
TUTORIAL SESSION 15:30-18:30	Coffee Break 16:30-17:00	POSTER SESSION with Beer and “Pintxos” 17:30 – 19:00	POSTER SESSION with Beer and “Pintxos” 16:30 – 18:00	Coffee Break 11:00-11:30	
	Soft Matter (1) 17:00 – 18:30			Polymer Dynamics (2) 15:30-17:15	
WELCOME DRINK 18:30-20:00			IDS Meeting 17:30 -20:00	Conference Dinner, 20:30 Debye, YRS and poster prizes	

Tutorial session

Sunday, September 4, 2022

SUNDAY - 4th September 2022		
	TUTORIAL SESSION **Chair: Daniele Cangialosi**	
15:30 – 16:30	**Simone Napolitano** Université libre de Bruxelles	Mobility gradients, immobilization phenomena, perturbations in local order and way more: analysis of relaxation spectra based on the dielectric strength
16:30 – 17:30	**Martina Havenith** Ruhr University Bochum	Introduction to Terahertz (THz) Spectroscopy and THz Calorimetry
17:30 – 18:30	**Michael Vogel** Technische Universität Darmstadt	Similarities and differences of NMR and BDS dynamic susceptibilities
18:30 – 20:00	**Welcome Drink**	

	MONDAY - 5th September 2022	
	Opening Session **Chair: George Floudas**	
8:40 -9:00	**Welcome**	
9:00 – 9:30	**Angel Alegria**	Segmental dynamics in polymer blends: from BDS results to DSC data and the other way around
9:30 – 10:00	**Ranko Richert**	Unusual Dielectric Saturation Behavior in Liquid Glycerol
10:00 – 10:30	**Karolina Adrjanowicz**	Stereo-regulation, molecular weight, and dispersity control of various poly-acrylates via free-radical polymerization supported by the external high electric field
10:30 – 11:00	**Simone Napolitano**	Slow dynamics facilitates equilibration of liquids and glasses
11:00 – 11:30	**Coffee Break**	
	Water and Hydrogen Bonded Systems (1) **Chair: Michael Vogel**	
11:30 – 12:00	**Martina Havenith**	Probing local solvation dynamics
12:00 – 12:15	**Jorge Melillo**	Dynamics of aqueous peptide solutions in folded and disordered states
12:15 – 12:30	**Martin Tress**	When molecular heterogeneities matter: thermal expansion and relaxation time in polyalcohols
12:30 – 13:00	**C. Alba-Simionesco**	Out-of-equilibrium liquids in water glycerol solutions at low temperatures
13:00 – 14:45	**Lunch**	
	Glassy Dynamics (1) **Chair**: **Karolina Adrjanowicz**	
14:45 – 15:15	**Birte Riechers**	Predicting nonlinear physical aging of glasses from equilibrium relaxation via the material time
15:15 – 15:45	**Josep Lluís Tamarit**	Double primary relaxation in anisotropic oriental glass-formers with translational order
15:45 – 16:00	**Farnaz Emamverdi**	Molecular mobility and gas transport properties of high-performance mixed matrix membranes based on PIM-1 and porous covalent organic frameworks
16:00 – 16: 15	**Steven Kooi**	Segmental Relaxation Dynamics by BDS: Insights into High-Strain-Rate Micro-particle Impact Response of Elastomers
16:15 – 16:30	**Tom Fielitz**	Variability in Polymer Fragility Measurements
16:30 – 17:00	**Coffee Break**	
	SOFT MATTER (1) **Chair: Michael Wübbenhorst**	
17:00 – 17:30	**Roberto Macovez**	Plasticizing effects and conformational dynamics in binary mixtures and polymer dispersions of pharmaceuticals
17:30 – 17:45	**Josu Martinez-Perdiguero**	Dielectric and polar properties of the ferroelectric nematic phase
17:45 – 18:00	**Paulina Szymoniak**	Molecular dynamics of nanophase-separated superglassy polymers by neutron scattering, dielectric spectroscopy, and fast scanning calorimetry
18:00 – 18:30	**Aurora Nogales**	Dielectric spectroscopy in Polyvinylidene Difluoride based ferroelectric systems

	TUESDAY - 6th September 2022	
	POLYMER DYNAMICS (1) **Chair: Tiberio Ezquerra**	
8:30 – 9:00	**George Floudas**	How macromolecules and ions penetrate narrow pores
9:00 – 9:30	**Caroline Genix**	Interfacial properties of polymer nano-composites studied by dielectric spectroscopy and small-angle scattering
9:30 – 10:00	**Apostolos Kyritsis**	Semi-crystalline amphiphilic block copolymers in the form of molecular brushes: thermal transitions and molecular mobility
10:00 – 10:15	**Alejandro Miccio**	From monomer´s chemical structure to polymer dynamics by combining artificial neural networks and ECNLE theory
10:15 –10:45	**Alexei P. Sokolov**	Viscoelasticity of Polymers with Dynamic Bonds
10:45 – 11:15	**Coffee Break**	
	Water and Hydrogen Bonded Systems (1) **Chair: Christiane Alba-Simionesco**	
11:15 – 11:45	**Jan Swenson**	Influence of Confinements and Partial Crystallization on the Glass Transition and Dynamic of Water.
11:45 – 12:15	**Cindy J. Galindo**	Cole-Cole broadening in microwave dielectric relaxation of univalent and bivalent electrolytes.
12:15 – 12:30	**Bence Kutus**	Ion association equilibria and kinetics of dimethyl phosphate in aqueous salt solutions.
12:30 – 12:45	**Yang Yao**	State of water in lipidic mesophase.
13:00 – 14:45	**Lunch**	
	INDUSTRIAL APPLICATIONS **Chair: Marian Paluch**	
14:45 – 15:15	**W. H. Hunter Woodward**	The Stewardship of Dielectric Spectroscopy Data: A Case Study
15:15 – 15:45	**Clemens Sill**	Polymer chain dynamics in simplified industrial nanocomposites: a multi-scale study
15:45 – 16:00	**Sébastien Pruvost**	Dielectric properties and high voltage conductivity of epoxy-liquid ionic networks
16:00 – 16:15	**Emmanuel Logakis**	Sustainable materials based on dynamic covalent crosslinks for applications in the electrical industry
16:15 – 16:30	**Bienvenu ATAWA**	In-Situ electromechanical coupling: an original approach for the investigation of conductive elastomeric composites
16:30 – 16:45	**Yaw S. Obeng**	Broadband Dielectric Spectroscopic Studies of Material Reliability in Integrated Systems
16:45 – 17:00	**Silvia Soreto**	Flash technology applied in porcelain sintering
17:00 – 17:30	**Anatoli Shergei**	Universal relationship between the electro-magnetic interference shielding effectiveness of composite materials and their electrical properties
17:30 – 19:00	**POSTER SESSION WITH PINTXOS AND BEER**	

	WEDNESDAY - 7th September 2022	
	GLASSY DYNAMICS (2) Chair: **Thomas Blochowicz**	
8:30 – 9:00	**Marian Paluch**	Role of dipole moment in the dielectric response of glass forming liquids
9:00 – 9:30	**Tina Hecksher**	Time scales and spectral shapes of supercooled molecular liquids
9:30 – 9:45	**Florian Pabst**	Understanding the relaxation spectra of ionic liquids – Comparison of dielectric spectroscopy and light scattering
9:45 – 10:00	**Federico Caporaletti**	Experimental evidence of mosaic structure in strongly supercooled molecular liquids
10:00 – 10:15	**Jan P. Gabriel**	The Dielectric and Rheological Responses of Strongly Asymmetric Mixtures of Glycerol/Propanol
10:15 - 10:45	**Ryusuke Nozaki**	Dielectric α relaxation process in the glass transition temperature region.
10:45 – 11:15	**Kristine Niss**	From isochrones to isomorphs.
11:15 – 11:45	**Coffee Break**	
	SOFT MATTER (2) **Chair: Aurora Nogales**	
11:45 – 12:15	**Friedrich Kremer**	Steps towards an atomistic understanding of dielectric relaxation processes
12:15 – 12:30	**Zaneta Wojnarowska**	Liquid-liquid phase transition in a family of ionic liquids. Dielectric studies at ambient and elevated pressure
12:30 – 12:45	**M.A. Kolmangadi**	Side chain length dependent dynamics and conductivity in self assembled ion channels
12:45 – 13:00	**Emeline Dudognon**	Probing dynamics of an amorphous drug by Dielectric Relaxation spectroscopy and MD Simulations: effect of low concentration strongly hydrogen-bonded water
13:00 – 13:30	**Andreas Schönhals**	Multiple glassy dynamics of a homologous series of triphenylene-based columnar liquid crystals – A study by broadband dielectric spectroscopy and advanced calorimetry
13:30 – 15:00	**Lunch**	
	CHARGE TRANSPORT **Chair: Alexei Sokolov**	
15:00 – 15:30	**Maria Madalena Dionísio**	Conductivity mechanisms in 2-picolinium ionic liquid salts with different alkyl chain length
15:30 – 15:45	**Achilleas Pipertzis**	Ion Transport in Polymerized Ionic Liquids
15:45 – 16:00	**Radu Andrei**	Polymerized ionic liquids: Correlation of ionic conductivity with nanoscale morphology and counter-ion volume
16:00 – 16: 30	**Shinian Cheng**	High-pressure dielectric studies as a key for understanding the dynamics of ionic glass-formers
16:30 – 18:00	**POSTER SESSION WITH PINTXOS AND BEER**	
	IDS Board Meeting (17:30 – 20:00)	

	THURSDAY - 8th September 2022	
	YOUNG RESEARCHER SESSION **Chair: Simone Napolitano**	
8:30 – 8:42	**Alaa Hassan**	Towards dynamics measurements of individualized macromolecules
8:42 – 8:54	**Vijayakumar Balachandar**	Dynamic behaviour of heavy water inside and outside of poly(N-isopropylacrylamide) microgel using broadband dielectric spectroscopy
8:54 – 9:06	**Yael Beilinson**	The nature of the low temperature crossover of water in hard confinement
9:06 – 9:18	**Claudia Borredon**	Quantitative Structure–Property Relationship approach to estimate the α-relaxation dynamics of molecular glass-formers
9:18 – 9:30	**Panagiotis Kardasis**	Effect of star architecture on the dynamics of 1,4-cis-polyisoprene under nanometer confinement
9:30 – 9:42	**Mathias Mikkelsen**	Subtle Influence of Hydrogen-Bonded Structures in Phenylalcohols
9:42 – 9:54	**Wing Kit Or**	Towards experimental detection of crystallization in individualized polymer chains
9:54 – 10:06	**Matteo Sanviti**	Dielectric relaxation processes in semicrystalline polymeric thin films
10:06 – 10:18	**Arthur Schulz**	Broadband dielectric spectroscopy on lithium-salt-based and choline-chloride-based deep eutectic solvents
10:18 – 10:30	**Spyridakou Marianna**	Effects of Nanometer Confinement on the Self-assembly and Dynamics of Poly(γ-Benzyl-L-Glutamate) and its Copolymer with Poly(isobutylene)
10:30 – 10:42	**Jules Trubert**	Pressure dependence of structural relaxation parameters in thermoplastic amorphous polymers
10:42 – 10:54	**Beibei Yao**	Ion dynamics of trihexyltetradecylphosphonium -based ionic liquids with big anions at ambient and elevated pressure
10:54 – 11:06	**Francesco Coin**	Broadband dielectric spectroscopy of pectin-based hydrogels
11:10 – 11:40	**Coffee Break**	
	CONFINEMENT EFFECTS **Chair: Jan Swenson**	
11:40 – 12:10	**Michael Vogel**	Liquid Dynamics in Confinements and Mixtures: Combined BDS, NMR and MD Simulation Approaches
12:10 – 12:25	**Katarzyna Chat**	Influence of polymer chain length on non-equilibrium phenomena in cylindrical nanopores.
12:25 – 12:55	**Natalia T. Correia**	Dynamic Disorder in a Nano-Sized Channel-Shaped Pharmaceutical Cocrystal Architecture
13:00 – 14:45	**Lunch**	
	SOFT MATTER (3) **Chair: Madalena Dionisio**	
14:45 – 15:15	**Paul Ben Ishai**	A New Approach to an Old Idea. Understanding the Fröhlich B(T) Function
15:15 – 15:30	**M. Jasiurkowska-Delaporte**	Studies of molecular dynamics in electrospun polymer/pharmaceutical drug fibers.

	POLYMER DYNAMICS (2) **Chair: Friedrich Kremer**	
15:30– 16:00	**Simone Cappacioli**	TBD
16:00 – 16:30	**Laurent Delbreilh**	How can dielectric spectroscopy be used to investigate molecular mobility in amorphous and semi-crystalline biobased polyesters? From defective to improved applicative biopolymers…
16:30 – 16:45	**Aurélien Roggero**	Analyzing the α-relaxation of epoxy in immersion: crossover from VFT to Arrhenius dependence of the relaxation times
16:45 – 17:15	**Tiberio Ezquerra**	Is the sub-glass temperature relaxation of furan-based polymers related to their high gas barrier properties?
17:15 – 17:45	**Coffee Break**	
20:30	**CONFERENCE DINNER – DEBYE PRIZE Awarding Ceremony**	

	FRIDAY - 9th September 2022	
	POLYMER DYNAMICS (3)	
9:30 – 10:00	**Michelina Soccio**	Dielectric spectroscopy as an effective tool to unveil the origin of the outstanding functional properties in biopolymers
10:00 – 10:30	**Michael Wübbenhorst**	VFT-type cooperative dynamics in “simple” supercooled liquids, liquid crystals and plastic crystals
10:30 – 11:00	**Koji Fukao**	A hidden relaxation process under DC conductivity in poly(2-vinylpyridine) and nano-composites
11:00 -11:30	**Coffee Break**	
	GLASSY DYNAMICS (3) **Chair: Ranko Richert**	
11:30 – 12:00	**Ernst Rossler**	NMR relaxometry: catching up with dielectric spectroscopy accessing the relaxation spectra in glass forming liquids
12:00 – 12:15	**Kevin Moch**	Dielectric spectroscopy reveals the structural relaxation of tributyl phosphate
12:15 – 12:30	**Till Böhmer**	The material time of physical aging: dynamic light-scattering vs. dielectric spectroscopy
12:30 – 13:00	**Thomas Blochowicz**	The Generic Line shape of Glassy Dynamics: Experimental Conditions for its Visibility
13:00 – 15:30	**Lunch and Farewell**	

ORAL contributions

Segmental dynamics in polymer blends: from BDS results to DSC data and the other way around

Angel Alegría[1,2]

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The segmental dynamics in polymer mixtures is in general heterogeneous and it is nowadays well established that this heterogeneity arise from the combination of two major effects: the thermally driven concentration fluctuations (TCF) and the self-concentration (SC) originated mainly in chain connectivity.

During last years, we have been using these ideas to establish a minimal model able to describe the dielectric relaxation results in polymer blends starting from the corresponding information of the neat components of the mixture. This modelling has also allowed us to connect the dielectric relaxation results in the mixtures with the mechanical behavior just above T_g, accessing in this way to frequencies much higher than those that can be reached experimentally in the mechanical characterization (1). In addition, the values of the model parameters can be connected with the TCF as determined by small angle neutron scattering by considering that the relevant length for the segmental dynamics is a few nanometers (2). More recently, we have applied a similar approach for the quantitative connection between the dielectric α-relaxation of the polymer blends and the calorimetric traces at the glass transition range (3).

In this talk I will summarized all these previous results and illustrate how based in this approach the dielectric relaxation behavior of polymer blends could be anticipated starting from the DSC traces of the blends, with the dielectric relaxation and DSC data of the neat components as single additional input.

1. Modeling the high frequency mechanical relaxation of simplified industrial polymer mixtures using dielectric relaxation results. Gambino, T.; Alegria, A. ; Arbe, A. ; Colmenero, J. ; Malicki, N. ; Dronet, S.. Polymer 187 (2020) 122051.

2. Concentration fluctuations ad nano-segregation in a simplified industrial blend with large dynamic asymmetry. Gambino, T.; Shafqat, N.; Alegria, A.; Malicki, N.; Dronet, S.; Radulescu, A.; Nemkovski, K.; Arbe, A.; Colmenero, J.. Macromolecules 53 (2020) 7150-7160.

3. Reproducing the calorimetric glass transition trace of simplified industrial polymer mixtures from the modeling of dielectric relaxation and the input of small angle neutron scattering. Shafqat, N.; Alegria, A.; Arbe, A.; Malicki, N.; Dronet, S.; Porcar L.; Colmenero, J. Macromolecules (submitted).

Unusual Dielectric Saturation Behavior in Liquid Glycerol

Ranko Richert[1], Erik Thoms[1], Dmitry V. Matyushov[1,2]

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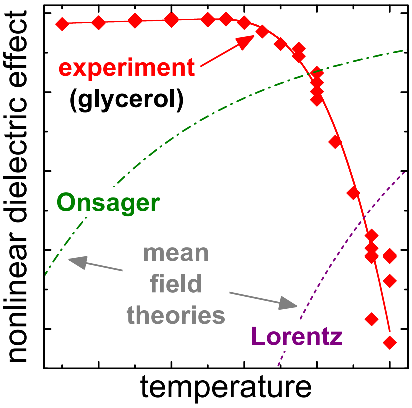
Many new nonlinear dielectric results have been published in recent years, but much of their focus is on the supercooled regime of molecular glass-formers, because that is where the strongest and most interesting nonlinear effects are expected [1]. Moreover, it is assumed that the dependence of the static dielectric constant on the electric field is governed by the inevitable effect of saturation, usually quantified by the Piekara factor a. As a result, there is little expectation that saturation data provide new insight into a liquid.

Here, we present results on the nonlinear dielectric behavior of the static dielectric constant, for which the available data is scarce and even contradictory [2]. The measurements are based on a recently developed technique for high ac field dielectric measurements in the static limit [3], and the interpretation employs the proper relation between Piekara factor a and nonlinear susceptibility χ_3 [4]. The field dependence of the static permittivity, ε_s, was determined over a wide temperature range, from 230 to 320 K. We observe that the temperature dependence of the Piekara factor $a = \partial\varepsilon_s/\partial E^2$ changes drastically around the melting point at 290 K, from $\partial a/\partial T = +1.4$ to -130 in units of 10^{-18} V^2 m^{-2} K^{-1} [5]. No analogous feature can be found in the corresponding low field data. These unexpectedly high values of $|a|$ indicate more pronounced dielectric nonlinearity with increasing temperature as well as a concomitant temperature driven increase in higher order orientational dipole correlations and considerable correction terms with respect to the central limit theorem. As indicated in the Figure, mean field theories fail qualitatively in explaining these observations.



[1] R. Richert, "Nonlinear dielectric effects in liquids: a guided tour," J. Phys.: Condens. Matter 29, 363001 (2017).

[2] Y. Marcus and G. Hefter, "On the pressure and electric field dependencies of the relative permittivity of liquids," J. Solution Chem. 28, 575–592 (1999).

[3] E. Thoms and R. Richert, "New experimental approach to nonlinear dielectric effects in the static limit," J. Mol. Liq. 340, 117107 (2021).

[4] R. Richert and D. V. Matyushov, "Quantifying dielectric permittivities in the nonlinear regime," J. Phys.: Condens. Matter 33, 385101 (2021).

[5] E. Thoms, D. V. Matyushov, and R. Richert, "Communication: Strong increase of correlations in liquid glycerol observed by nonlinear dielectric techniques," J. Chem. Phys. (in press).

Stereoregulation, molecular weight, and dispersity control of various poly-acrylates via free-radical polymerization supported by the external high electric field

Katarzyna Chat,[1,2,] Paulina Maksym,[2,3] Wenkang Tu,[4] Kamil Kaminski,[1,2] **Karolina Adrjanowicz[1,2]**

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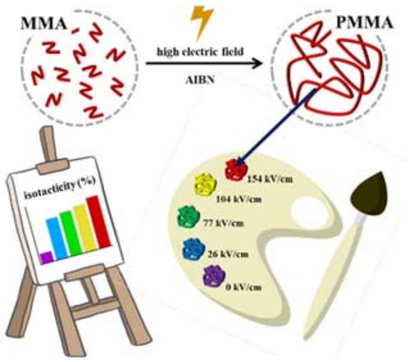
[4] Institute of Materials Engineering, University of Silesia, 75 Pulku Piechoty 1a, 41-500 Chorzow, Poland

Here, we present a robust synthetic protocol in which the high electric field supports the thermally-induced free-radical polymerization of various acrylates (MMA, HEMA, IBA). The reaction conditions are very simple, and the process does not require catalysts or solvents (AIBN was only used as the initiator). The electric field magnitudes used in this study ranged from 0 kV/cm up to 154 kV/cm. By combining dielectric spectroscopy, nuclear magnetic resonance spectroscopy, exclusion chromatography, and differential scanning calorimetry, we have demonstrated the remarkable effect of external electric field (both ac and dc) on polymerization progress and products characteristics. Changing the field frequency or magnitude makes it possible to control the molecular weight, dispersity, and stereochemistry of produced polymers. Isotactic-rich structures seem to be more preferred at high electric fields. This approach provides a unique opportunity to produce macromolecules of well-designed compositions, topologies, and micro- and macro-structures. It is much simpler, "green" and does not involve complicated intermediate steps or synthesis procedures.



Slow dynamics facilitates equilibration of liquids and glasses

Simone Simon Napolitano, Zijian Song, Cristian Rodríguez-Tinoco, Allen Mathew

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

The rate at which a nonequilibrium system decreases its free energy is commonly ascribed to molecular relaxation processes, arising from spontaneous rearrangements at the microscopic scale. While equilibration of liquids usually requires density fluctuations at timescales quickly diverging upon cooling –known as the α-, structural (segmental) modes–, growing experimental evidence indicates the presence of different alternative pathways of weaker temperature dependence. Such equilibration processes exhibit a temperature-invariant activation energy on the order of 100 kJ mol^{-1}. Based on a large series of molecular dynamics and equilibration experiments, we identified the underlying molecular process responsible for this class of Arrhenius equilibration mechanisms with a slow mode (SAP), universally present in the liquid dynamics [1]. While in bulk samples the SAP can be masked by conductivity and electrode polarization, measurements in thin films permitted us to directly access the relaxation spectra of these slow modes.

Within experimental uncertainties, the SAP can be associated to the spectral response of a molecular mechanism with a single relaxation time, corresponding to a simple exponential decay in the time domain. By analyzing polymer chains of different molecular weight (from 43 to 6000 kg mol^{-1}) and films of different thickness (7 nm – 100 μm), we verified that this process is present also in bulk melts and that the activation energy and the characteristic molecular time of the SAP are not affected by either the macromolecular or the sample size. This feature permitted us to discriminate between possible classes of relaxation mechanisms and discard diffusion-limited, nucleation-driven processes and polymer specific (Rouse) modes whose characteristic time would, instead, increase change with film thickness and molecular weight. Furthermore, as the position of the SAP peaks is invariant with sample size even in those cases where the α–process shifts upon confinement, we conclude the slow Arrhenius processes is related to a genuine molecular mechanism, totally decoupled from segmental motion in proximity of the glass transition.

The SAP, which we show is intimately connected to high temperature flow, can efficiently drive melts and glasses towards more stable, less energetic states. Our results show that measurements of liquid dynamics can be used to predict the equilibration rate in the glassy state. Finally, we emphasize that our discussion does not invoke the macromolecular nature of polymers –SAPs have been observed, both via dielectric and mechanical spectroscopy, in small molecules– and we anticipate that the intimate relationship between equilibration and SAP holds independently on the chemical nature of the nonequilibrium system.

[1] Song *et al.*, Science Advances **8**, eabm7154 (2022)
[2] Mandanici *et al.*, The Journal of Chemical Physics **128**, 124505 (2008)

Probing local solvation dynamics

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Terahertz (THz) spectroscopy is a most sensitive tool to probe any changes in the intermolecular interaction between water molecules. Since water is the most important solvent on earth, as it is involved in all biological reactions as well as in most chemical reactions, such as supramolecular chemistry and electrocatalysis, the contribution of the solvent to the total free energy of a reaction is crucial, yet an experimental challenging parameter to probe experimentally as well as theoretically. While initially, the broad band absorption of water was considered as a source of trouble experimentally, systematic spectroscopic studies revealed, that the THz frequency range provides a fingerprint spectrum of any changes in respect to hydrogen bond strength, tetrahedrality, dynamics, which are all of major importance to rationalize and predict the outcome of a reaction. Even small changes in hydration of proteins and ions causes significant changes in the spectrum and could be investigated in detail [1]. While the individual changes might be small, the large number of solvent moelcules involved makes this contribution into a major driving force for fundamental reactions. These changes can be quantified by THz spectroscopy and recorded during protein folding and upon introducing local mutations. More recent studies revealed that these spectroscopic signatures of hydration can be directly correlated to enthalpic and entropic changes of the solvent, ΔH and ΔS, which determine the reaction path and reaction rates [2]. The outcome of a reaction is determined by the free enery $\Delta G = \Delta H - T\Delta S$. A reduction in G is necessary for a reaction to be spontaneous at constant pressure and temperature. Typically, for biological reactions, there is a subtle balance between a favourable enthalpy and an unfavourable entropic term, which almost cancel, thus allowing to fine tune reactions by temperature. THz spectroscopy now allows to map local water changes and allow to investigate whether these changes are more a cause or a consequence of fundamental biological reactions, such as enzymatic catalysis or protein aggregation.

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Dynamics of aqueous peptide solutions in folded and disordered states

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The interaction of water with biological materials is one of the most exciting topics in science: life is impossible without water. Fundamental biological processes take place in aqueous environments, but generally in confinement: proteins work in cells surrounded by a few layers of water molecules. Thus, studies of the dynamical properties of water in solutions of biological matter at supercooled temperatures can help to gain fundamental understanding of the interaction between water and bio-systems. However, bulk water unavoidably crystallizes in the temperature range from 150 to 235 K (“no man’s land”)[1]. This is why many low temperature experiments are usually performed in hydrated powders[2,3] and not in biologically realistic water solutions.

In this work, we used different solutions of ε-poly(lysine) (ε-PLL), a peptide consisting of a chain of 32 lysines. ε-PLL in water solution has two different conformations: pure β-sheet at pH = 10 and a more disordered conformation at pH = 7[4]. For solutions at pH = 10, it is possible to reach water concentrations up to 40% without the presence of ice. For these reasons, we consider that ε-PLL aqueous solutions can be treated as a biological model system. Here, we were able to determine the dynamics of ε-PLL in water solution at pH = 10 and p = 7 by broadband dielectric spectroscopy (BDS)[5]. We found three main relaxations: the fast-water relaxation, the relaxation of the solute affected by water (α-relaxation) and a water relaxation affected by the solute (slow-water relaxation). We were able to determine that the dynamic of the peptide in folded state is slower than the one in disordered state. This comparison opens a route for the comprehension and characterization of intrinsically disordered proteins.

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When molecular heterogeneities matter: thermal expansion and relaxation time in polyalcohols

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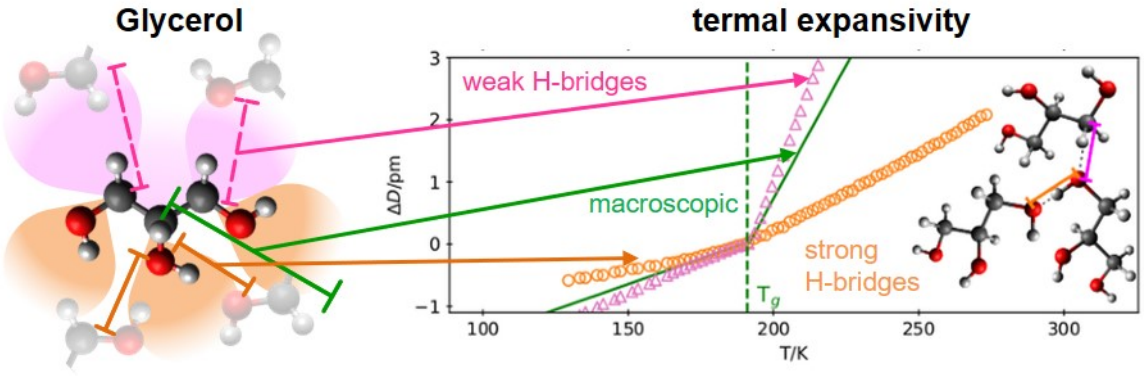
In the present study, we focus on the structural relaxation in liquids which is considered to be directly dependent on the available free volume around each molecule. Many theoretical concepts of liquid dynamics and the glass transition approximate this molecular quantity using changes of the macroscopic density. However, particularly hydrogen bonding liquids defy a proper description by these approaches (e.g. the failure of density-scaling in such materials). To investigate densification on the molecular scale, we carried out infrared spectroscopy on a series of polyalcohols. By analyzing specific molecular vibrations and correlating them with interatomic bond lengths, the thermal expansion of intramolecular covalent bonds and strong intermolecular hydrogen bridges is quantified. Pronounced differences between intra- and intermolecular expansion verify the dominance of the latter. Surprisingly, the overall thermal expansion (i.e. the cube root of inverse density) is even bigger than that of the strong hydrogen bridges. To exclude a failure of this method, we confirmed its validity by successfully describing the density of water based on the extracted hydrogen bridge lengths. This suggests that weak hydrogen bridges dominate thermal expansion while the strong hydrogen bridges clearly control the glass transition. These results demonstrate that inhomogeneities on intra- and intermolecular scale can play distinct roles in densification and orientational relaxation and require a careful consideration in a comprehensive theoretical description.

Gabriel, Tress, Kossack, Popp, Kremer *J Chem Phys 154* (2021) 024503



Out-of-equilibrium liquids in water glycerol solutions at low temperatures

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The proneness of water to crystallize is a major obstacle to understanding its putative exotic behavior in the supercooled state. It also represents a strong practical limitation to cryopreservation of biological systems. Adding some concentration of glycerol, which has a cryoprotective effect preventing, to some degree, water crystallization, has been proposed as a possible way out, provided the concentration is small enough for water to retain some of its bulk character and/or for limiting the damage caused by glycerol on living organisms. Through a time-resolved polarized neutron scattering investigation, and by considering a nano-segregated water-glycerol solution, we were able to characterize the key parameters of ice formation at temperatures near and below the calorimetric glass transition of the solution. Thanks to this analysis and by combining several spectroscopic techniques (dielectrics (1), neuron spin echo, NMR), we identify the nature of the out-of-equilibrium liquid phases appearing below the melting temperature in these solutions for molar fractions between 0.15 and 0.5, including the eutectic point, providing more arguments against the presence of an iso-compositional liquid-liquid transition (2). Finally, we propose a rule-of-thumb to estimate the lower temperature limit below which water crystallization does not occur in a broad range of aqueous solutions(3).

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Predicting nonlinear physical aging of glasses from equilibrium relaxation via the material time

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Physical aging deals with small property changes resulting from structural rearrangements. The understanding of this type of aging is crucial for non-crystalline materials like oxide glasses, polymers, and metallic glasses: only if material standards can be guaranteed, applications may benefit from the outstanding properties of these materials. Describing and predicting physical aging has thus been a focus of materials science for many years, but the subject still presents fundamental challenges [1].

We here address the concept of a material-time controlled aging, which was proposed by Narayanaswamy in 1971 [2]. While the material-time concept rationalizes several striking aging phenomena [2, 3, 4, 5], the existence of a material time has never been validated in direct, temperature-driven experiments. We do this here by long-time dielectric experiments on two glass-forming molecular liquids, demonstrating with the fundamental material-time prediction that linear-response aging data determine the nonlinear aging behavior.

An ideal aging experiment involves a temperature jump that starts from a state of thermal equilibrium, changes temperature rapidly compared to the response time scale of the material and monitors the system's gradual approach to equilibrium at the new temperature [6]. Doing this requires a setup allowing for fast temperature changes and precise temperature control with minimal long-time drift. This was realized a by Peltier element with direct contact to the thin-sample plane-plate capacitor allowing for well-controlled temperature jumps from few Millikelvin up to some Kelvin in amplitude. Moreover, highly accurate measurements are needed because the long-time tail of physical aging and the entire aging response to a small temperature step involve minute changes of material properties. These were thus tracked with an Andeen-Hagerling ultra-precision capacitance bridge allowing for measuring capacitive changes down into the Attofarad range. We performed temperature-jump experiments around a reference temperature with experiments spanning a total of 52 weeks on a single sample, including single temperature jumps, double jumps similar to Kovacs' cross-over protocol [7], and multi jumps resembling a sinusoidal temperature modulation.

Remarkably, even complex nonlinear aging responses are predictable in fine detail from the linear response data collected from single-jump experiments by means of the material-time concept. And not only experimental linear relaxation data holds this predictive power: we demonstrate on a set of simulations that equilibrium fluctuations can be used as a basis for the prediction of the nonlinear aging response, emphasizing the role of linear responses for physical aging beyond the linear regime.

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Double primary relaxation in anisotropic oriententional glass-formers with translational order

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Plastic crystal denotes a crystalline arrangement of weakly interacting molecular entities showing translational long-range (high-symmetry) order with dynamical orientational disorder, with three-dimensional thermal reorientational fluctuactions.[1] When cooled down, plastic crystals show both specific heat and dynamic anomalies characteristic of the glass transitions, in such a way that below the glass transition temperature, the dynamical orientational disordered becomes arrested and an orienational glass (OG) is obtained, in a similar way to a structural glass (SG) obtained when cooling down an orientational and translational disordered system. Despite OGs are systems with fewer degrees of freedom than estructural glasses SGs, the main dynamical fingerprints (as main cooperative α-relaxation, secondary Johari-Goldstein relaxation) are virtually the same.

Some recent works concerning systems with low-dimensional, highly anisotropic disorder involving quasi-planar hexasubstituted benzene derivatives have revealed, contrary to what might be expected from a decrease in disorder, a greater complexity of the dynamics: the low-dimensional glass-former actually exhibits a richer landscape, with two distinct whole-molecule (primary) α- and α'-relaxations.[2,3]

Pentachlorobenzene (PCNB, $C_6Cl_5NO_2$), displays a layered structure with rhombohedral symmetry in which molecules are siting in parallel planes. The molecules can rotate around a sixfold-axis parallel to the ***c*** rhombohedral axis. In addition to the in-plane dipole reorientations, giving rise to the main α-relaxation, a (small) out-of-plane component of the molecular dipole (due to the tilt of the NO_2 group with respect to the plane of the benzene ring) could account for an additional cooperative α'-relaxation. This gives rise to two reorientational dynamical processes, associated with reorientational motions of the larger dipole (in-plane) component within the (001) planes of the hexagonal structure and with the small (out-of-plane) dipole component fluctuations around the ***c*** hexagonal axis.

Nevertheless, molecular dynamic (MD) simulations reveal that dynamics of in-plane dipole-dipole correlations consist of two-single processes that can account for both α- and α'-relaxations. In addition, MD simulations evidence that out-of-plane dipole-dipole correlations do not decay appreciably, i.e., there is a negligible tilting motion of their rotation axis. Guided by these simulations, the relaxation dynamics of some other quasi-planar hexasubstituted benzene derivatives as 1,2-dichloro-tetramethyl-benzene and 1,3-dichloro-tetramethyl-benzene, has been studied. It should be noted that the chosen systems are *pure* planar molecules with dipole moment lying exclusively in the plane of the benzene ring and, consequently, any of the two distinct whole-molecule (primary) α- and α'-relaxations can be rationally attributed to an out-of-plane dipole-dipole correlation. Experimental broadband dielectric experiments will be presented for these low-dimensional orientational disordered Systems.

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Segmental Relaxation Dynamics by BDS: Insights into High-Strain-Rate Microparticle Impact Response of Elastomers

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Laser-induced projectile impact testing (LIPIT), an optically driven microscale mechanical testing platform, is used to study[1,2] the dynamic deformation response of a series of elastomers including model poly(urethane urea) elastomers (PUU). LIPIT measurements provide time resolved imaging of the impact of individual micro-projectiles, with velocities in the 10 to 2000 m/s range, with selected target materials. Visualization of the impact event yields the depth of penetration and the extent of rebound of the micro-projectiles. The ratio of the rebound velocity to the initial velocity is termed the coefficient of restitution and is used to estimate the amount of energy absorbed by the sample during impact. Coefficient of restitution data as a function of the impact strain rate is used to elucidate high-rate deformation induced glass transitions (Tg).

In conjuction with dynamic mechanical analysis and solid state nuclear magnetic resonance (NMR) measurements, broadband dielectric loss spectroscopy (BDS) has become an important technique employed to understand the possible molecular relaxation mechanisms responsible for strain rate dependent glass transitions. Dynamic Tg data extacted from broadband dielectric relaxation measurements predict glass transitions at impact strain rates that correspond nicely with experimentally observed changes in coefficient of restitution in the LIPIT experiments. BDS is also used to characterize the segmental relaxation dynamics in our model elastomers.

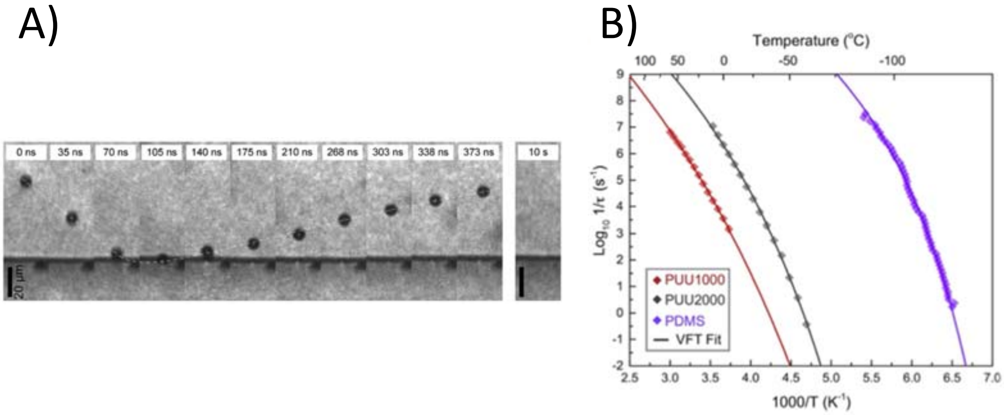

Figure 1: A) Typical sequence of images recorded in a LIPIT experiment using a high-speed camera with 3-ns exposure time showing particle impact on modified PUU sample, B) Arrhenius plot of segmental mobility (1/τ) obtained by BDS for modified PUUs (PUU1000, PUU2000) and PDMS; solid lines are fits to a Vogel Fulcher Tammann (VFT) equation[3].

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Molecular mobility and gas transport properties of high-performance mixed matrix membranes based on PIM-1 and porous covalent organic frameworks

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Especially now in times of the energy revolution, the demand for energy-efficient separation processes promotes the advancement of new high-performance materials for use as highly selective separation membranes. Polymers with intrinsic microporosity (PIMs) are of high interest in the field of gas separation membranes. Currently the application of PIMs for membrane technology is still restrained by their strong tendency to physical aging involving a significant loss of their good gas separation properties. Physical aging phenomenon is related to the molecular mobility of PIMs which was investigated by broadband dielectric spectroscopy (BDS) previously [1]. In this work, covalent phosphinine-based framework (Eto-CPSF) was used as a nanofiller (0-10 wt %) in a PIM-1 matrix to potentially enhance the gas transport properties and prevent physical aging. Since molecular mobility is a fundamental parameter determining gas transport as well as physical aging in such a material, our study includes dielectric investigations by BDS of pure PIM-1 and PIM-1/Eto-CPSF mixed matrix membranes to establish a correlation between molecular mobility and gas transport properties. In addition, gas permeability was determined by the time-lag method (0-10 bar pressure) at 35 °C for N_2, O_2, CH_4 and CO_2 for all MMMs.

The dielectric behavior of the polymeric films and their response upon heating were measured by isothermal frequency scans during different heating/cooling cycles in a broad temperature range up to 250 °C. Multiple dielectric processes following Arrhenius behavior were observed. Local fluctuations, Maxwell-Wagner-Sillars (MWS) polarization and structural relaxations were discussed correlating to structural-properties of PIM-1. As main result for MMMs, the permeability of PIM-1 for CH_4 and CO_2 gases were increased significantly with only 5 wt% of nanofiller within the polymer matrix. However, this is not observed for Eto-CPSF concentrations higher than ca. 7 wt% probably due to a microphase separated morphology of the nanocomposite system. Furthermore, the permselectivity of membranes for pair gases O_2/N_2 and CO_2/N_2 show enhancement up to a concentration of about 7 wt% Eto-CPSF filler.

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Variability in Polymer Fragility Measurements

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Relaxation rates of glass-forming materials undergo significant changes as they cool, particularly as the material approaches its glass transition.[1] This rate of change at the glass transition is defined as the fragility, a measured parameter that varies significantly between materials and even across different techniques or research laboratories for the same material. Examples of this variability include the fragility of polystyrene (110-150),[2] polycarbonate (100-280),[3] and polyvinyl acetate (70-130)[4] despite excellent fits to the Vogel-Fulcher-Tammann equation for most of these studies!

In a recent work,[4] we showed that fragility can be derived from a novel derivative approach to linearize the relaxation data. This has the unique advantages of both normalizing the abscissa for comparison across materials and for direct extraction of the fragility as a function of the glass transition temperature. This allowed us to speculate on the role of experimental variables, measurement techniques, and glass transition on the overall uncertainty of fragility estimates and how they could perhaps explain differences observed between different laboratories, but without concrete data to test these speculations.

This talk presents new data on our study of polystyrene using broadband dielectric spectroscopy, fast scanning calorimetry, and ellipsometry on the same spun-cast films. Using the same film with the same sample origin, operator, and environmental effects allows us to separate effects of the sample preparation from the precision of each individual measurement. A combined approach allowed us to assess intrinsic differences between the techniques, while a study across multiple films, prepared on different days by different operators, enabled assessment of the repeatability that may be expected in different laboratories. These data were ultimately used to perform a Gage R&R assessment,[5] wherein the application of statistics tests allows for the identification of key variability sources.

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Plasticizing effects and conformational dynamics in binary mixtures and polymer dispersions of pharmaceuticals

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I will present the results of dielectric spectroscopy characterization on amorphous active pharmaceutical ingredients, either mixed with other small-molecule organic compounds or dispersed in biopolymer matrices. Differential scanning calorimetry is used as complementray characterization tool to investigate the equilibrium and non-equilibrium phase properties.

In my talk I will focus on three aspects of these binary systems:

- the plasticizing *vs* antiplasticizing effect of each component, as observed both in the glass transition temperature and the structural relaxation (α) time of the mixtures;
- the existence of one, or more, Johari-Goldstein (β) relaxations;
- the relaxation time and activation energy of conformational intramolecular secondary (γ) relaxations.

I will show that dielectric spectroscopy is a powerful tool to investigate temperature-dependent or relaxation-mode-dependent plasticization effects, and present unexpected results concerning the antiplasticizing effect of some small-molecule additives.
Our spectroscopy data indicate that while binary mixtures of small-molecule compounds exhibit a single Johari-Goldstein relaxation, homogeneous asymmetric binary dispersions of drugs in biopolymers may show two such relaxations, despite the existence of only a single structural relaxation.

Finally, I will demonstrate that comparative studies of dielectric relaxations in binary glassy mixtures involving molecules with only few torsional degrees of freedom are not only useful as they allow identifying them as Johari-Goldstein or intramolecular processes, but may also serve to build a database of temperature-dependent conformational relaxation times of specific functional groups or molecular rings occurring in similar molecules.

Dielectric and polar properties of the ferroelectric nematic phase

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Liquid crystal materials presenting polar nematic phases have been long-time predicted, but have only been experimentally realized recently. The discovery of ferroelectric nematic phases [1-4] represents a major development and a milestone in liquid crystal research with deep implications in both fundamental and applied science. The large values of the dielectric constants ($>10^5$) and spontaneous polarizations of ~ 6 uC/cm2 reported ask for detailed and systematic studies of the dielectric and polar properties of such materials.

In this contribution we present a thorough broadband dielectric spectroscopy study of RM734 in the 10^{-1}-10^8 Hz range which shows pretransitional effects in the normal nematic phase and complex behavior in the ferroelectric phase. A quantitative analysis of the relaxation processes has also been carried out.

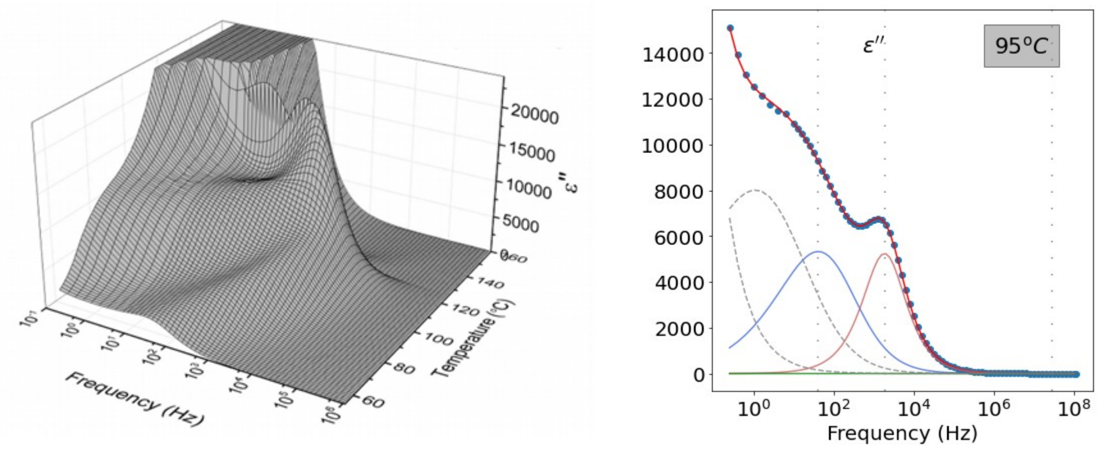

Figure: Left: 3D plot of the imaginary part of the electric permittivity of RM734 showing the nematic and ferroelectric phases in the anaylized frequency and temperature ranges. Right: Deconvolution of the spectrum at 95ºC (ferroelectric phase) in two main Havriliak-Negami relaxation modes plus spurious conductivity effects.

N.S. and A.M. acknowledge financial support from ARRS (P1-0192) and RJM from UK Research and Innovation (UKRI).

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Molecular dynamics of nanophase-separated superglassy polymers by neutron scattering, dielectric spectroscopy, and fast scanning calorimetry

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Janus polytricyclononenes (PTCN) with rigid backbones and flexible n-alkyl (n = propyl, butyl, hexyl, octyl, decyl) are novel, innovative materials that show potential in separating hydrocarbons. These superglassy polymers were designed to show an enhanced and controllable gas permeability via flexible alkyl side chains that promote mass transport, as opposed to conventional microporous polymers, where permeability is a function of the free-volume entities.

PTCNs, investigated by small angle X-ray scattering (SAXS), show nanophase separation between the n-alkyl side chains and the backbones. The size of the nanodomains increases with the length of the n-alkyl side groups. In addition, for the alkyl chain-rich nanodomains a distinct α-relaxation was found by means of broadband dielectric spectroscopy (BDS) and temperature modulated DSC (TMDSC). The glass transition of the backbone-rich domains, which is beyond or near to the degradation of the materials, was evidenced by fast scanning calorimetry (FSC) by decoupling it from decomposition, employing high heating rates up to 10^4 K/s [1].

Further, Janus PTCNs were studied by quasielastic neutron scattering (QENS) employing the backscattering IN16B (ILL, Grenoble) and time of flight FOCUS (PSI, Villigen) instruments. For an overview of dynamic processes setting in at different temperatures, inelastic (IFWS) and elastic fixed window scans (EFWS) were conducted. IFWS showed that the segmental motions of alkyl-rich nanodomains shift to higher temperatures with increasing alkyl chain length, which agrees with SAXS and BDS findings. For the lowest side chain lengths an additional low temperature relaxation process was found, assigned to methyl group rotations.

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Dielectric spectroscopy in Polyvinylidene Difluoride based ferroelectric systems

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Electroactive polymers like Poly(vinylidene fluoride) (PVDF) and its copolymers have attracted interest for long time, due to their ability to convert mechanical strain into electrical energy and vice versa [Wang et al. *ACS Applied Energy Materials* **2021**, *4* (10), 11133–11143]. Piezo and ferroelectric properties of PVDF based materials are central to that conversion. The large difference in electronegativity between fluorine atoms and hydrogen and carbon atoms produces a strong electric dipole in PVDF monomer, perpendicular to the main chain. These monomer dipoles, upon crystallization, can produce arrangements that give rise an overall dipolar contribution per unit cell, leading to ferroelectricity. However, whereas PVDF copolymers with Trifluoroethylene (PVDF-TrFE) crystallize at room temperature into an intrinsically ferroelectric phase, PVDF homopolymer can crystallize into several crystalline phases, although not all of them are polar or ferroelectrically active (FEA). The chain conformation is different in each of these phases, and subsequently, the arrangement of the chain dipoles is different. The most common crystalline phase obtained from melt processing, the non-polar α–phase, presents a TGTG' conformation, with dipole cancelation. A route to obtain ferroelectric phases in PVDF is processing by solution in polar solvents [Ma, W et al. *Journal of Macromolecular Science, Part B* **2008**, *47* (3), 434–449]. Also, ferrolectric PVDF can be obtained under confined conditions like, for example, when processing to form nanoparticles (Figure 1) or into nanotubes. In this talk we will discuss the molecular dynamics of ferroelectric PVDF phases and compare them with that of PVDF-TrFE ferroelectric copolymers.

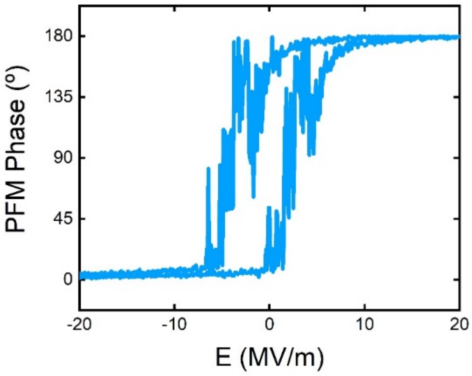

Figure 1: Ferroelectric response (by Piezoelectric Force Microscopy, PFM) of PVDF nanoparticles prepared by nanoprecipitation from solution.

How macromolecules and ions penetrate narrow pores

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Understanding that way that polymers penetrate in narrow pores is important for applications including separation of proteins with relevance e.g. in cell biology. In general, placing macromolecules close to interfaces alter their conformational and dynamic properties. Much of this behavior stems from polymer-substrate interactions. Taming the strength of interfacial interactions especially under non-equilibrium conditions (e.g. during flow), may enable the design of polymer interfaces with controlled physical properties (viscosity, glass temperature as well as wettability and adhesion) of importance in applications. Herein we follow the polymer dynamics *in situ* at the chain length scale by studying the evolution of normal modes in the type A polymer (according to Stockmayer's classification) polyisoprene (PI) during imbibition in nanopores. The specific scientific question we address is, *if* and *how*, adsorption affects the imbibition kinetics of polymers. We follow the details of polymer imbibition *in situ* by employing the *nanofluidic* method.[1] The latter provides simultaneous access to (i) the kinetics of imbibition, (ii) the molecular dynamics and (iii) the viscosity experienced by the polymer during flow.[2-4] In another area, we investigate *if* and *how* the ionic conductivity and chain mobility of a polymer electrolyte is affected during imbibition and following imbibition in nanopores. To this end, the archetypal polymer electrolyte poly(ethylene oxide) (PEO)/LiTFSI is employed. By following the evolution of dc-conductivity during flow within nanoporous alumina templates, we find that ion mobility is strongly affected by polymer adsorption.[5]

The work is supported by the Hellenic Foundation for Research and Innovation (H.F.R.I.) under the "First Call for H.F.R.I. Research Projects to support Faculty members and Researchers and the procurement of high-cost research equipment grant" (Project Number: 183).

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Interfacial properties of polymer nanocomposites studied by dielectric spectroscopy and small-angle scattering

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Polymer nanocomposites (PNCs) are made by the dispersion of hard fillers into polymer melts. These materials display striking structural and dynamical properties, which depend in a subtle way on the interactions between the polymer chains and the particle surfaces. For strongly interacting systems such as poly(2-vinylpyridine) mixed with silica nanoparticles (NPs), broadband dielectric spectroscopy (BDS) evidenced the existence of slow-down polymer layers surrounding the NPs. First, the effect of chain mass [1] and blending of short and long chains [2] on the segmental dynamics and elastic properties of the interfacial layers will be discussed. In the latter case, we used the combination of isotopic labeling and small-angle neutron scattering to determine the influence of the NP surfaces on the polymer structure. [3] Different degrees of spatial segregation could be identified, including a peculiar, “fish-shaped” interfacial gradient characterized by reverse Monte Carlo (RMC) simulations.

In a second part, recent BDS results on the effect of NP surface modification will be presented, showing that the suppression of the attractive NP-polymer interactions has a strong impact on the dynamics of the interphase. It significantly reduces the slow-down effect of NPs without changing the interfacial layer thickness. In parallel, grafting induces stronger interparticle attractions, thereby modifying the NP dispersion as followed by small-angle X-ray scattering and RMC simulations, this time of the NP configuration.

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Semi-crystalline amphiphilic block copolymers in the form of molecular brushes: thermal transitions and molecular mobility

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Amphiphilic block copolymers (AmBCs) consist of at least two blocks of distinct chemical nature that undergo nanophase separation as a result of chain association in solvents that selectively dissolve one of the blocks. It is well established that the ability of the AmBCs to react in environmental changes by alterations in morphology depends mainly on the degrees of polymerization of the two blocks, the hydrophobic character of the insoluble block and the molecular architecture of the copolymers. On the other hand, molecular brushes (MBs), i.e., graft copolymers with a backbone and side chains, are interesting macromolecular building blocks for nanomaterial fabrication exhibiting interesting chain association and phase separation properties.

In this work we employ, mainly, differential scanning calorimetry, DSC, and broadband dielectric spectroscopy, BDS, techniques to investigate thermal transitions and molecular mobility in a series of recently synthesized AmBCs, in the form of hetero-MBs, that comprise a hydrophilic pendent block, poly(oligoethylene glycol methacrylate), POEGMA, and different water-insoluble blocks of the family of n-alkyl methacrylates as the hydrophobic pendent side group. More specifically, poly(hydroxyl propyl methacrylate), PHPMA, poly(lauril methacrylate), PLMA and poly(stearic methacrylate), PSMA, short side chains are combined with POEGMA at various compositions leading to the synthesis of hetero-MBs with one or two crystallizable side chains.

The research interest in this work focuses on the investigation of the intermolecular interactions established between the two different side chains - blocks that control the miscibility of the two blocks and the morphology of the copolymers in the dry state of the AmBCs. The study of the molecular mobility in both, local and segmental length scale, provides valuable information in this respect. The crystallization behavior of the hetero-MBs and the impact of the crystallinity on the molecular mobility of the copolymers are also discussed in details.

FROM MONOMER’S CHEMICAL STRUCTURE TO POLYMER DYNAMICS BY COMBINING ARTIFICIAL NEURAL NETWORKS AND ECNLE THEORY

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The analysis of structural relaxation dynamics of polymers gives an insight into their mechanical properties, whose characterization is used to qualify a given material for its practical scope. The dynamics is usually expressed in terms of the temperature dependence of the relaxation time, which is available through experimental measurements (broadband dielectric spectroscopy, dynamical mechanical analysis, among others) following the polymer synthesis. In this work, we propose a combined approach of artificial neural networks and the elastically collective nonlinear Langevin equation (ECNLE) to estimate the temperature dependence of the main structural relaxation time of polymers (see Figure 1) based only on the knowledge of the chemical structure of the corresponding monomer[1-4].

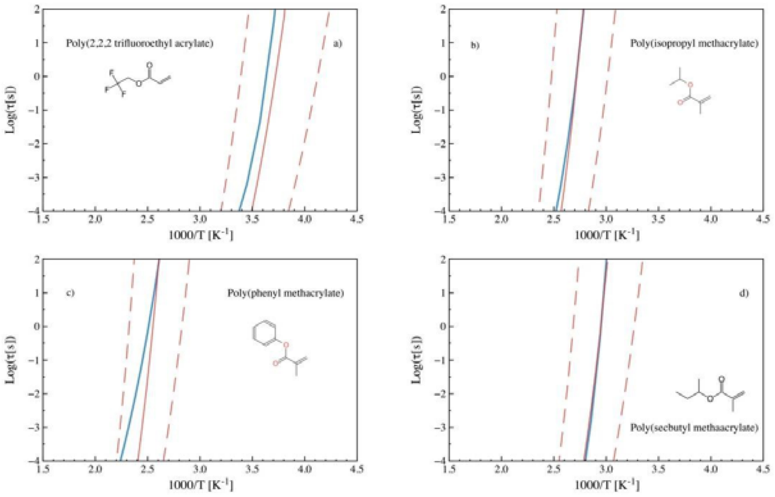

Figure 1. Experimental (blue) and predicted (red) relaxation times (obtained from ECNLE theory) vs 1000/T. The corresponding monomeric chemical structure is presented on the left side of the image. Dashed lines stand for the confidence interval corresponding to the typical deviation in the ANN prediction (10% relative error): a) Poly (2, 2, 2 trifluoroethyl acrylate), b) Poly (isopropyl methacrylate). c) Poly (phenyl methacry-late), and d) Poly (secbutyl methacrylate).

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Viscoelasticity of Polymers with Dynamic Bonds

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It is well-recognized now that the enormous volume of polymers produced in recent decades and their low recyclability create ecological problems. One of the potential solution to improve their recyclability is a substitution of some covalent bonds in these materials by dynamic (reversible) bonds, such as hydrogen, ionic or dynamic covalent (e.g. vitrimers) bonds. This makes polymer-based materials not only recyclable, but also enables unique properties such as self-healing, shape memory, time programmable and also extreme toughness. The talk will overview studies of dynamics and viscoelastic properties of model polymers with dynamic bonds using Broadband Dielectric Spectroscopy and rheology. We demonstrate that dynamic bonds introduce multiple relaxation processes controlling different aspects of structural rearrangements [1-3]. Our analysis reveals [2] that relationship between bond dissociation time and stress relaxation time follows well the predictions of bond lifetime renormalization model. However, the most interesting behavior appears when dynamic bonds aggregate in microphase separated clusters. We demonstrate that the relaxation in these clusters, and not the polymer backbone, controls viscosity of these materials [1,3,4]. Moreover, these materials can exhibit extremely long rubbery plateau with the level almost approaching glassy modulus [3]. Based on broad range of experimental data we propose a general model describing unique viscoelastic behavior of polymers with clusters of dynamic bonds [4]. At the end, we emphasize great perspectives of polymers with dynamic as materials for sustainable future [5].

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From fundamentals to the device, microwave sensor for express in-vitro characterization of biological fluids

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Whenever water molecules interact with either dipolar or charged systems, the main water dielectric relaxation peak broadens. If a solute is dipolar in nature, new solute-water clusters are created due to dipole-dipole interactions. It leads to the "red shift" of the dielectric loss maximum frequency. In the case of ionic solutions, another cluster structure develops, due to dipole-charge interactions and a "blue shift "is observed. In the general case when a solute molecule has both charged and dipole groups, the dielectric loss maximum demonstrates a "red" or "blue" shift, depending on the entity concentration. In all aqueous solutions, the water-solute interactions can be considered as dipole-matrix interactions in which water is the dipole subsystem. The phenomenological 3D trajectories approach was applied to the results of isothermal dielectric measurements of different concentrations of the following aqueous solutions: Hydrocarbons, NaCl and KCl, AMP and ATP, Amino Acids and proteins [1-5]. The parameters of the main water peak define a trajectory that can clarify the nature and rate, at which water interacts with the solute. This paper extends this approach from comparatively simple solutions to the complexity of Red Blood Cells (RBC) suspensions by monitoring the RBC cytoplasm under different external conditions [6,7]. Dielectric measurements of RBC suspensions in the frequency region of 100 MHz to 50 GHz as a function of aging or external glucose concentration also reveal a distinct time point or glucose concentration, after which the spectra are radically changed. We conclude that the microwave dielectric response of the cytoplasm is due to the water therein and its interaction with physiological active components in the cytoplasm. Based on a microwave sensor, we presented an approach and the miniaturized device for screening and testing biological fluids (blood, milk, sperm, etc.). This technology allows quick quantitative measurement of numerous characteristics of bodily fluids in a labeling-free manner. This technology can be used for a wide range of applications, including the analysis of various deviations in patient states expressed in changes in the composition of the blood or erythrocyte cytosol.

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Cole-Cole broadening in microwave dielectric relaxation of univalent and bivalent electrolytes

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The extensive studies of water are linked to its significant role in life. One of the most important features of water is its well-known strong polarity [1]. Water molecules can establish an elastic hydrogen-bonded (H-bonded) network[2], in which H-bonds are relatively weak(compared to ice) due to thermal fluctuations. H-bonds break and form on a picoseconds time scale, a short lifetime that characterizes the dynamical flexibility of liquid water [3]. The main consequence is the remarkable ability of water to respond to changing molecular structures. Hence, whenever water interacts with any solute of ionic or non-ionic nature, the formation of hydration shells causes a structural and dynamic modification of the H-network [4, 5]. Further, the nature of the perturbations strongly depends on the identity and concentration of the ions, giving rise to subtle differences that can play key roles in different biological processes including the selectivity of membrane ion channels and pumps to Na^+, K^+, $Mg^{2+,}$ and Ca^{2+}. A clear understanding of these differences is of great interest to several fields such as biology, food sciences, and electrochemistry.

Microwave dielectric spectroscopy (MDS) is a powerful technique to evaluate the microwave dielectric response of bulk water in the systems, also known as γ-dispersion. MDS allows measuring the complex dielectric permittivity as a function of the frequency of different aqueous solutions and gives relevant information regarding molecular interactions and arrangements[3]. In the microwave frequency range, pure distilled water at 20 C shows a maximum loss peak at around 18 GHz [3]. If any solute with ionic nature interacts with water, some specific changes are observed in the complex dielectric spectrum: reduction of static permittivity, shift and broadening of the main relaxation peak, and appearance of conductivity tail [4]. These notable changes can be correlated with the variations in the H-bond network caused by the coulombic forces originated by the ions [5].

In this work, the microwave dielectric response of aqueous solutions of univalent NaCl and KCl and bivalent $CaCl_2$ and $MgCl_2$ electrolytes at different concentrations has been measured between 500 MHz and 40 GHz. The complex permittivity spectra are represented by a Cole-Cole (CC) relaxation time distribution. The behavior of the CC parameters including the dielectric strength ($\Delta\varepsilon$), the relaxation time (τ), and the broadening (α) is used to build a 3D phase space that describes the dynamic and structural properties of the studied systems [6]. Using the phenomenological approach of the 3D trajectories and the idea that the mechanism of the dielectric relaxation of water is the migration of orientational defects, we present an accurate comparison between univalent and bivalent electrolytes in terms of minimum water cluster size and their relaxation time. Moreover, the average number of perturbed water molecules in each electrolyte solution has been calculated. The results of this research will contribute to the enhancement of the current knowledge on the interactions of water with ions at the molecular level.

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Ion association equilibria and kinetics of dimethyl phosphate in aqueous salt solutions

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Cations accumulate around nucleic acids, due to their negatively charged phosphate backbone, giving rise to the formation of an ion atmosphere in solution. Such interaction of cations with phosphate groups is essential for stabilizing the tertiary structure of these bio-macromolecules. Dimethyl phosphate ($DMP^–$) is a simple and widely used model to specifically study such ion-phosphate interactions, which can be largely elucidated in terms of ion pairing. However, despite numerous experimental and simulation studies, the nature and stability of ion-pairs as well as the associated ion pairing kinetics have remained elusive.

In this work, we study the ion association between $DMP^–$ and Na^+, Mg^{2+}, or Ca^{2+} ions using dielectric relaxation and nuclear magnetic resonance spectroscopies. We find that in $DMP^–$ is weakly hydrated, i.e. the dynamics of anion-bound solvent molecules are very similar to those in the bulk. Further, in solutions of NaDMP, $DMP^–$ is mostly present as non-associated anion in gauche-gauche conformation. Addition of NaCl, $MgCl_2$ or $CaCl_2$ to a 0.2 M NaDMP solution gives rise to notable ion-pair formation, with 20–27% of all $DMP^–$ ions being paired to Mg^{2+}/Ca^{2+} ions at a twofold excess of $MgCl_2/CaCl_2$. Expectedly, Na^+ forms weaker ion-pairs owing to its lower charge density; the maximum degree of ion association is ~11% in the 0.2–2 M concentration range of NaCl.

A quantitative analysis of the dielectric and NMR data suggests that contact ion-pairs dominate for Mg^{2+} and Ca^{2+}, whereas solvent-shared ion-pairs prevail for Na^+. Comparison of our speciation model to previous studies on RNA suggests that cation binding to $DMP^–$ can be used to predict condensation of Mg^{2+} ions to the phosphate backbone of RNA, reinforcing that $DMP^–$ is a reasonable proxy for studying ion-phosphate interactions of nucleic acids.

The concentration dependence of the solute relaxation times can largely be explained by a cation metathesis reaction in addition to ion-pair self-dissociation. We find the lifetimes of these ion-pairs to follow the trend $Mg^{2+} >> Ca^{2+} > Na^+$, which help narrowing down the so far broad ranges of ion-pair lifetimes reported in the literature.

State of water in lipidic mesophase

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Water is the most ubiquitous and essential liquid on earth, and it is fundamental to the existence of life. Many biological processes take place in crowded aqueous surroundings and water in living cells can be considered as confined water.[1] However, water behaves differently under confinement with respect to the crystallization and dynamics compared to those in the bulk.[1,2,3] Especially in biological systems, the role of confined water is of crucial importance though still far from fully understood. Here, I will present the state of water under soft confining media provided by lipidic mesophase (LMP). An unfrozen lipid formerly synthesized in our group opens the gate for the study of water in LMPs at subzero temperatures.[4] Yet, the complex synthetic procedure with low yields narrows the large-scale application. We will present here our recent discovery of a commercially available lipid, phytantiol, that gives the access to the liquid water in LMPs at subzero temperatures.[5] The comprehensive understanding on the crystallization and dynamics of water confined in the lamellar phase were obtained from differential scanning calorimetry and broadband dielectric spectroscopy. Two dynamically different fractions of water were observed that are assigned to a slower bound water close to the head group of the lipid and a faster interstitial water inner the lamellar channel. I will also present the evidence for the application of the cryogenic liquid water in LMPs on cryo-enzymatic reactions. In the end, I will discuss the recent understanding on the state of water during the phase transition in LMPs from the cubic to the reverse hexagonal phase.[6]

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Influence of Confinements and Partial Crystallization on the Glass Transition and Dynamic of Water

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The dynamics of water is commonly studied in both hard confinements and different types of aqueous solutions. There are two main reasons for such studies of interfacial water: Firstly, because the dynamical properties of interfacial water is essential to determine in order to understand its role for life. Secondly, geometrical confinements and mixing with another soft component can prevent crystallization and enable studies of water in the so-called no man's land (the approximate temperature range 150-230 K) where bulk water rapidly crystallizes. Here, we apply broadband dielectric spectroscopy combined with calorimetric measurements to elucidate the dynamics of water in such systems, where all the water is fully amorpous or partly crystalline. Furthermore, we make comparisons with similar studies on amorpous bulk ice [1,2] to determine the relevance of our findings for the dynamical properties of bulk water.

The results from the dielectric relaxation measurements show that the main water relaxation below 150 K is similar for bulk water and water in hard confinements and aqueous solutions at high water contents. This finding suggests that the results obtained for interfacial water may be of more relevance for supercooled and glassy bulk water than previously thought [3]. It also questions whether the main relaxation of amorpous bulk ice should be interpreted as be the glass transition related □-relaxation, since it appears as a secondary □-relaxation in aqueous solutions [3].

For partially crystalline aqueous solutions it was found that the amorphous water dynamics and glass transition temperature were affected by the crystallinity, but that these effects can almost completely be explained by freeze concentration of the solution. Thus, the water dynamics of the partially crystalline sample becomes the same as for a fully amorphous sample with the same water concentration as the amorphous part of the partially crystalline solution [4]. This also implies that the dynamic crossover of the water relaxation from a high temperature non-Arrhenius behavior to a low temperature Arrhenius dependence is unaffected by the partial crystallization and still occurs as a single crossover at the calorimetric glass transition of the solution [4].

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The Stewardship of Dielectric Spectroscopy Data: A Case Study

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This talk will present an overview of an R&D project involving the stewardship of broadband dielectric spectroscopy data. Previously, this data in its raw form was not easily readable by humans or computers and first needed to be converted into a common ASCII-based table format. Data analysis was then performed via several repetitive steps in proprietary spreadsheet software. Here, by implementing open-source tools to rapidly visualize and analyze dielectric spectroscopy data (Figure 1), a more collaborative project was achieved. With this power the team was able to streamline experimental planning and achieve measurement optimization. Finally, this same software would save both the raw data and the empirical fit parameters in a tidy data format such that it is readily accessible by both humans and computers for several (software) generations to come. This case study provides a single example of how rapid data visualization and centralized tidy data storage can benefit a myriad of analytical techniques.

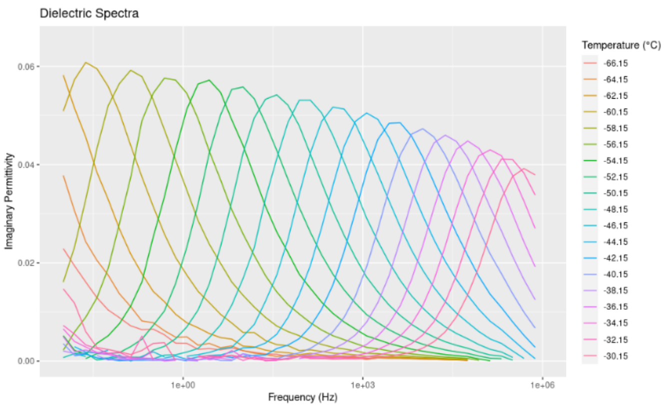

Figure 1. *Dielectric loss of DC 704 from −66 to −30 °C as rapidly visualized via a custom script in the programming language R.*

Polymer chain dynamics in simplified industrial nanocomposites: a multi-scale study

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The dynamics of long polymer chains, in presence of nanoparticles, have been investigated. The nanocomposites were inspired by tire industry-like rubber materials and were made of entangled polyisoprene linear chains filled with chemically treated silica nanoparticles. Combining rheology, dielectric and neutron spin echo (NSE) measurements, we determined the modification of the polymer chain dynamics from unfilled state to high filler concentration over a broad range of time and length scales.

We found that nano-fillers do not modify the time-temperature-superposition shift of dynamic behavior upon temperature changes of any of the investigated relaxation mechanisms. However, they do slow down the dynamics at time and length scales below the entanglement regime. This impact on the polymer chain dynamics was found to be more pronounced with increasing filler concentration up to 30% in volume fraction.

The polymer dynamics probed by NSE was found to reflect a mix of dynamical contributions without allowing to straightforfardly discriminate among them. Conversely, rheology and dielectric spectroscopy, as they probe very specific relaxation mechanisms, showed a more pronounced slowing down effect induced by the presence of the fillers. In particular, we showed that the α-relaxation was strongly impacted by the presence of fillers, which was unexpected based on our literature research [1, 2]. One obvious difference between commonly investigated compounds and the present study is that we exclusively characterized non-crosslinked samples.

In addition, we explained the broadening of the peak of the α-relaxation by the stretching of the distribution of relaxation times. This occurs concomitantly with the increase of the part of non-soluble polymer with increasing filler concentration. We thus performed additional NSE measurements with labelled, protonated polyisoprene chains bound to the fillers and embedded in a fully deuterated matrix to specifically study the dynamic behavior of localized polymer chains. We proved that, even at a small concentration of filler, the polyisoprene chains bound to the filler surface via the silane agent do not show any dynamics in the investigated Fourier timescale. We thus demonstrated the existence of a population of localized polymer chains whose dynamics are profoundly altered as compared to the free polymer chains within the bulk. This is in line with the full-chain relaxation observed by dielectric normal mode, which does not show a clear trend with filler concentration. Together with the labelled NSE study, we interpret these results in the way that the full-chain relaxation of the localized polymer at the filler surface is suppressed and only the normal mode of the free polymer is observed.

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Dielectric properties and high voltage conductivity of epoxy-liquid ionic networks

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In recent years, ionic liquids (ILs) have attracted great interest in the materials field, due to their low vapor pressure, good chemical and thermal stability, infinite number of cation-anion combinations, high ionic conductivity and ability to dissolve polymers. In addition, their low melting point allows them to be compatible with the polymer process temperature. These characteristics make them attractive in a wide range of fields, such as electrolytes, lubricants, plasticizers and material additives.

Recently, several authors have demonstrated the reactivity of ionic liquids towards epoxy to form new epoxy-based networks. In 2012, the initiation of homopolymerization of an epoxy system by an imidazolium-based IL was demonstrated [2]. A few years later, the same team extended the study to pyridinium- and phosphonium-based ILs and pointed out that they also have the ability to form new epoxy networks without the aid of a conventional hardener [3, 4]. These studies have highlighted the key role of ILs and their impact on the final properties of the material. Indeed, thermal stability, glass transition and hydrophobicity can be increased due to the presence of ILs incorporated in the epoxy network. However, many questions remain open, including the network formation and mechanisms induced by phosphonium-based ILs to the epoxy prepolymer.

The present study proposes to complete the knowledge on these new epoxy-ionic liquid networks, by providing the last building blocks for a complete understanding through molecular mobility [5]. The study of molecular relaxations observed by dielectric spectroscopy as well as characterizations by dynamic mechanical analysis have allowed to finely analyze the epoxy network formed by homopolymerization. Particular attention will be paid to the electrical conductivity and its dependence on the electric field and temperature.

Acknowledgments

This work was performed in collaboration with the SuperGrid Institute. This work was supported by a grant overseen by the French National Research Agency (ANR) as part of the "Investissements d'Avenir" Program (ANE-ITE-002-01).

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Sustainable materials based on dynamic covalent crosslinks for applications in the electrical industry

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Environmental performance has become a new important material selection criterion, added next to quality, technical performance, and cost. Environmental Product Declarations (EPD), based on thorough Life Cycle Assessments (LCA), emerged as the new standard to communicate meaningfully and effectively the environmental impacts of products. The choice of the input raw materials (thermoplastics, thermosets, metals) together with the energy spent during manufacturing, the losses during the use phase and the product's end-of-life are crucial for a favorable EPD.

In this talk, current research efforts for substituting traditional fossil-based plastics, utilized in ABB products (e.g. switches, circuit breakers, embedded poles, motors, generators) with sustainable/circular alternatives will be discussed and the associated environmental benefits will be highlighted. Special attention will be given to a new class of materials, introduced in 2011 by Leibler and co-workers, the vitrimers [1]. Vitrimers are permanent networks of polymer chains connected via dynamic covalent bonds, which allow the network to change its topology while maintaining a constant number of chemical bonds at all temperatures [2]. Thanks to this unique characteristic, they retain mechanical stability and solvent resistance, but can also flow when heated above the vitrimer transition temperature (T_v) bridging the gap between thermoplastics and thermosets.

Studies on the electrical/dielectric properties of a vitrimer system based on exchangeable imine-linked chemical bonds will be presented by employing AC dielectric breakdown strength and broadband dielectric spectroscopy (BDS) measurements. The dielectric response at various temperatures will be analysed to shed light in the structure-property relationships of this novel material class. Finally, the environmental benefits in terms of recyclability (end-of-life solvolysis), reusability (re-integration of manufacturing scrap) as well as welding and repairability will be demonstrated.

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In-Situ electromechanical coupling: an original approach for the investigation of conductive elastomeric composites

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Conductive polymers composites are widely used since they possess electrical properties, high fatigue strength, high resistance to corrosion and low weight[1]. In their daily use, these materials are submitted to various external solicitations such as temperature variation, mechanical deformation, external electrical field that can influence their functional properties. The developpement of experimental approaches that considered these external solicitations are needed to fully understand the evolution the material properties and predicts its life time.

In this work, we investigated the in-situ coupled electrical/mechanical properties of carbon black filled thermoplastic polyurethane CB/TPU and Polyethylene CB/PE under uniaxial tensile test. Moreover, the evolution of the electrical properties of CB/TPU submitted to thermomechanical treatment was evaluated. It was proven that the thermomechanical treatment induces strong structural changes in TPU matrix that influenced the interpenetration of the CB fillers and thus their state of electrical conductivity. In the case of the CB/PE, the electrical properties were determined under uniaxial tensile test in both parallel and perpendicular to the stretching direction as schematized in figure 1.

We developed an original in-situ coupled electromechanical approach to predict the evolution of the electrical properties upon uniaxial stretching in the direction perpendicular to the stretching without any direct contact between the sample and the electrodes. This authentic approach is based on the scaling laws of the Maxwell-Wagner-Sillars interfacial polarization of a bilayer system between an insulator air gap and a conductive polymer composite[2], CB filled polyethylene (CB/PE). Determining the evolution of conductivity in the parallel and perpendicular to stretching direction helps to deeply understand the interconnections within the conductive fillers and their interaction with the polymer matrix.

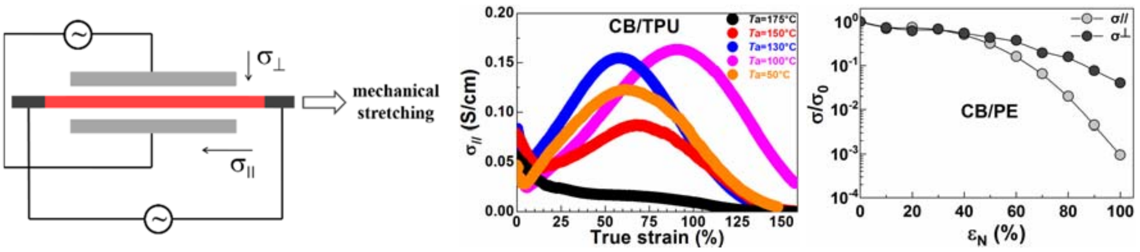

Fig. 1: (left) Schematic illustratration of the electromechanical set up. (middle) conductivity evolution in the stretching direction as function of the strain magnitude at different annealing temperature. (right) evolution of the normalized conductivity as function of the strain magnitude in both parallel and perdirection.

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Broadband Dielectric Spectroscopic Studies of Material Reliability in Integrated Systems

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Recent technological advances and materials innovations have shifted the architecture of integrated circuits from planar two-dimensional to three dimensional (3D) systems, as in stacked integrated circuit chips (3D-ICs). However, the performance demands of these 3D-IC devices seem to be at odds with the reliability needs because while the emerging devices are expected to operate at higher current densities, they have lower voltage tolerances at higher electric fields. With these changes, the reliability of the electronic circuitry has shifted from being transistor-dominated to interconnect-dominated, along with new materials related challenges such as stress induced unexplained early failures, electromigration, etc. Unfortunately, traditional metrology has been unable to adequately address the measurement needed to in-situ characterize the underlying failure mechanism. We have successfully demonstrated the application of broadband dielectric spectroscopy (BDS)-based metrology in addressing some of these metrology gaps. In this talk, we will revisit our applications of BDS to understanding of failure mechanisms due to material aging, and application as an early warning system in emerging 3D integrated electronic devices.

Flash technology applied in porcelain sintering

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The ceramic manufacturing industry is now focused on reducing greenhouse gas emissions, a difficult mission since the sintering process requires high temperatures. Porcelanas da Costa Verde SA, is a ceramic company from Portugal, that intends to investigate, develop and validate the use of an alternative, innovative and environmentally more sustainable technology for porcelain sintering during the first firing/biscuit process – FLASH technology, through the FLASHPOR project.

FLASH is a Field Assisted Sintering Technique that allows the densification of ceramics at a significantly lower temperature and time (less than 60s). The sintering temperature and time decrease have high impacts on the sustainability as well as on the production rate. Nevertheless, FLASH sintering is not easily implemented in the industry and cannot be used for all types of ceramics. Therefore, it is essential to establish and define the FLASH sintering conditions for each case. In this work, the electrical properties were analysed and FLASH processing was mapped for porcelain, evaluating the effects of the electric field and current on the densification and microstructure development.

Universal relationship between the electromagnetic interference shielding effectiveness of composite materials and and their electrical properties

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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.

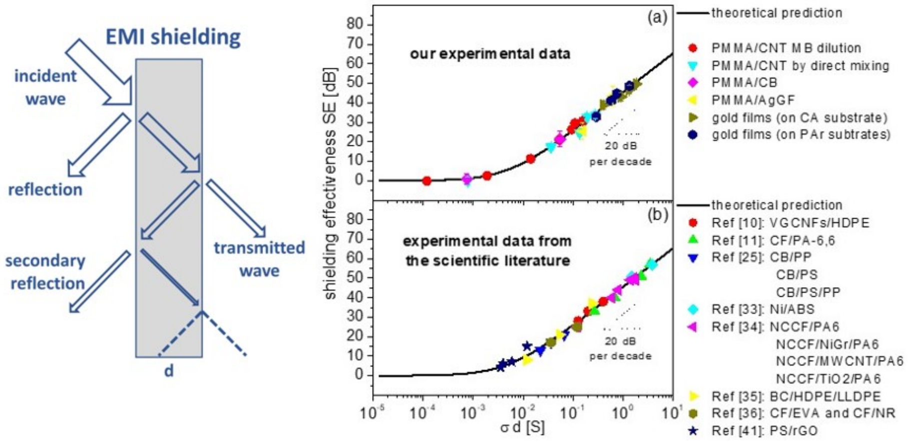

Fig. 1: (left) schematic representation of electromagnetic shielding mechanisms. (right) electromagnetic shielding effectiveness of different composite materials as a function of the product between the material conductivity and the sample thickness.

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Role of dipole moment in the dielectric response of glass forming liquids

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From the view point of dielectric spectroscopy studies of the reorientation dynamics of glass-forming liquid, the molecular polarity is a key physical quantity. It results from the fact that only molecules possessing a permanent dipole moment can contribute to the orientational correlation function probed by dielectric spectroscopy. Apart from that, the dipole moment value itself determines the number of relaxation properties of glass-forming liquids. One of them is the shape of the dielectric response function of the α-relaxation. In the first step, we will discuss the correlation between molecular polarity and the width of the α-relaxation peak determined from broadband dielectric spectroscopy measurements. In this discussion, we will be referring to the recent interpretation of the spectral shape of the dielectric response proposed by Blochowicz and co-workers. Their interpretation is based on the assumption that experimentally obtained dielectric loss peak of polar materials contains two modes with slightly different relaxation rates: faster, corresponding to the self-term of the dipole-dipole correlation function, and slower mode being related to the cross-correlation term. Therefore, as a next step we will verify this assumption using molecular dynamics simulations of both polar and non-polar systems.

Time scales and spectral shapes of supercooled molecular liquids

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Broadband dielectric spectroscopy is a powerful tool to investigate the two hallmark dynamic features of supercooled liquids: non-exponential relaxation and non-Arrhenius temperature dependence of the relaxation time, due to its ramarkable bandwidth and resolution. The question is, if there is a generic relaxation shape and in what sense [1]? In general, dielectric spectra display a wealth of different behaviors. Still there is a prevalence for a “square-root t” relaxation [2,3]. Through combining dielectric spectroscopy with complementary spectroscopic techniques, there is a emerging understanding of how to disentangle different dynamic features [4,5] and how different time scales are related [6,7,8]. Our group focuses on comparisons of dielectric, dynamic shear and bulk moduli, heat capacity and thermal expansion [2-4,6-8]. The talk gives an overview of our findings and how recent results fits into the general picture.

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Understanding the relaxation spectra of ionic liquids – Comparison of dielectric spectroscopy and light scattering

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Dielectric spectra of ionic liquids are notoriously difficult to interpret regarding the microscopic origin of different relaxational processes. This is due, on the one hand, to the DC conductivity or electrode polarization overshadowing them and, on the other hand, to the multitude of possible dynamic processes that are active. Among them are conductivity relaxation, dipolar reorientation and in cases of cations equipped with long alkyl-chains, also dynamics of supramolecular aggregates are discussed in the literature.[1] We show how depolarized light scattering, which is only sensitive to reorientational motions of the molecules, can help to disentangle the different dynamic processes seen in dielectric spectra. Thereby, it got clear that the reorientational time scale of cations and anions become separated if both ion species notably differ in size.[2] In such cases also the conductivity relaxation separates from the dipolar reorientation of the cations, leading to bimodal dielectric spectra. The dynamics of aggregates, on the other hand, are only seen in some special cases in the light scattering spectrum and are not visible in the dielectric data of any of the ionic liquids under investigation. The latter is confirmed by high pressure measurements.[3]

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Experimental evidence of mosaic structure in strongly supercooled molecular liquids

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The dynamics of supercooled liquids is dominated by the structural relaxation, which becomes very slow on approaching the glass-transition temperature Tg, where its characteristic relaxation time becomes eventually of 100 s. At slightly elevated temperatures, however, (~1.2 Tg) a second faster process known as the Johari-Goldstein relaxation (βJG) [1], decouples from the structural one and remains active even below Tg. The β_{JG}-process is known to be a genuine feature of the glass-transition and strongly coupled to the α-relaxation [2], though its dedicated role in the glass-transition -whether of an actor or a spectator- remains under scrutiny. The lack of a firm microscopic theory of the glass-transition and the difficulty of experimental and numerical techniques to probe the spatial and the temporal properties of this process in the relevant dynamic range, leave this debate still open. Employing X-ray scattering time-domain interferometry (TDI) [3-6], a technique able to investigate microscopic density fluctuations in the 10ns-10us time-window, we here demonstrate that the molecules participating to the β_{JG}-relaxation are characterized, in the deep supercooled state, by two intriguing features [7]: (i) their mean-squared displacement satisfies the Lindemann criterion for structural instability and (ii) their number matches the threshold for site percolation. This suggests that the molecules participating to the β_{JG}-relaxation are very mobile and, on a timescale faster than the structural relaxation, escape the cages formed by the nearest neighbors. Furthermore these "uncaged" molecules form a percolating cluster pervading the whole sample and evolving on the timescale of the β_{JG}-process [7]. In other terms the β_{JG}-relaxation is related to the development of a mosaic structure in the supercooled phase, characterized by patches of less mobile molecules (i.e., those relaxing on the timescale of the structural relaxation) separated by a percolating, ever-changing network of more mobile ones [7] (see Fig. 1). The emergence of this infinite cluster clearly supports the idea that a dynamical transition takes place around ~1.2 T_g, in line with the basic concepts of the random first-order transition theory [8].

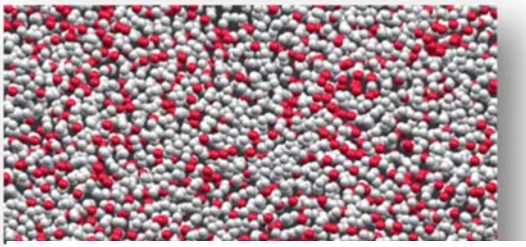

Figure 1: Sketch of the molecules undergoing the βJG – relaxation (red spheres) at a given time. They are highly mobile, perform larger spatial excursions than the rest of the molecules (white spheres) and are spatially connected in a percolating cluster

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The Dielectric and Rheological Responses of Strongly Asymmetric Mixtures of Glycerol/Propanol

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Significant progress has been made in recent years regarding the understanding of pure hydrogen-bonded systems. Currently, monohydroxy- and polyalcohols are considered to form transient hydrogen-bonded supramolecular structures in the form of chains, rings, and networks. As a consequence, complex dynamic behavior can be identified for network-forming glycerol [1] and chain-forming propanol [2] by combining dielectric and shear rheological spectra.

Now we transfer these concepts to study the combined dielectric and shear rheological spectral shape of glycerol/propanol mixtures. Although glycerol differs from propanol by only two additional hydroxy groups, the mixtures are strongly asymmetric ($\Delta T_{\text{melting}} = 291\text{K}-147\text{K} = 143\text{K}$, $\Delta T_{\text{glass}} = 190\text{K}-98\text{K} = 92\text{K}$). The strong asymmetry is manifested by the existence of two distinct glass transitions in calorimetric measurements at a concentration of 70mol% glycerol.

We discuss our findings of extremely broad spectral shapes compared to the neat liquids and assign molecular interpretations of the spectral features by performing comprehensive analyses of the three applied experimental techniques.

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Dielectric α-relaxation process in the glass transition temperature region

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If the glass transition phenomenon is purely thermodynamic relaxation origin such as deviation from the sub-equillibrium state, dielectric alpha process in the sub-equillibrium supercooled state should show no anomaly near the glass transition temperature Tg. In the last thiery years, there have been reports that the alpha process near Tg doesn't follow a curve (such as VFT or WLF equation) determined using data above Tg [1-4]. These experimental investigations have been performed for the sub-equillibrium supercooled liquids referring to Kovacs' volume recovery experiments [5,6]. However, some descrepancies are found in the features of anomaly described in these reports. On the other hand, most of such investigasions use polymeric materials such as atactic PVAc. Although, this is very good in keeping the sample amorphous, one is worried about unexpected effects due to entanglement and so on near Tg.

We have already published a report on sorbitol [2] and indicated that the temperature dependence of relaxation frequency of the alpha process shows anomaly near Tg. However, shape of the dielectric dispersion (directry connected to the distribution of relaxation times) doesn't show any anomaly in the same temperature region. This is quite different from the case of PVAc [1]. It is considered that liquids of small molecules such as sorbitol are more suitable in study of alpha process because molecular interaction essentially comes from hydrogen-bonding only. However, it is very difficult to follow the thermal history indicated by Kovacs [5] due to crystallization. Actually, dielectric measurements described in our report [2] have been performd in heating process after quench to a temperature far bellow thermal Tg.

This time, we would like to show a study of dielectric alpha process of some polyhydric liquid alcohols under the condistion of different thermal history. It has been suggested that cooling rate is very important to study temperature dependence of the alpha process from the view point of sub-equillibrium condition.

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From isochrones to isomorphs

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By using a high pressure cell designed for simultaneous dielectric spectroscopy and neutron scattering [1], we have studied the pressure and temperature dependent dynamics in a handful of different glass-forming liquids including van der Waals liquids, hydrogen bonding liquids and a room temperature ionic liquid [2-4]. Combining dielectric spectroscopy and quasielastic neutron scattering gives access to time scales from pico- to kilosecond and make it possible to follow the relaxation dynamics in the liquid from above the melting point and all the way down to the glass transition. Moreover, the neutron scattering data give information on the boson peak and fast relaxation in the deeply supercooled liquid. The data is analysed in view of the so-called isomorph theory which predicts the existence of lines in the temperature-pressure phase diagram where dynamics is invariant both in terms of time scale and spectral shape. Put in other words: density scaling and isochronal superposition are predicted by isomorph theory. Isomorph theory is only expected to hold in liquids without directional bonds, nevertheless the predictions hold to a very large extend in all the studied liquids, particularly in the high temperature / low pressure region.

Another prediction from isomorph theory is that the structure is invariant along the isomorph. With recent molecular dynamics and scattering experiments this prediction is also tested for an ionic liquid [4-5] and a van der Waals bonded liquid [6].

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Steps towards an atomistic understanding of dielectric relaxation processes

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The theory of orientation polarization and dielectric relaxation was developed by P. Debye more than 100 years ago. It is based on the coarse grained approximation of a molecule by a sphere having one or more dipole moments. By that the specific intra- and inter-molecular interactions are explicitly *not* taken into consideration. In this talk the principal limitations of the Debye approximation are discussed. Experimental challenges and means will be presented to overcome these restrictions and to achieve an atomistic understanding of dielectric relaxation processes.

Liquid-liquid phase transition in a family of ionic liquids. Dielectric studies at ambient and elevated pressure

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When ionic liquid (IL) is cooled below the melting point, it usually enters into a supercooled state and subsequently into a non-equilibrium amorphous phase. The characteristic feature of this transformation is a continuous increase of density, accompanied by a slowing down of ions mobility. Alternatively, crystallization of IL can be observed at decreasing temperature. Recently, it has been shown that in addition to these two well-known transitions, selected ILs are capable of unique first-order liquid-liquid transformation (LLT).

The liquid-liquid phase transitions in a family of ionic liquids will be discussed in this talk. Using the dielectric spectroscopy we will examine the ion dynamics above and below the LLT. These data will be compared with mechanical and calorimetric measurements. Additionally, the isochronal character of liquid-glass and liquid-liquid transitions will be investigated at ambient and elevated pressure.

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Side chain length dependent dynamics and conductivity in self assembled ion channels

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We study the molecular mobility and electrical conductivity of a homologous series of linear shaped columnar ionic liquid crystals ILCn, (n = 8, 10, 12, 14, 16) using Broadband Dielectric Spectroscopy (BDS), Specific Heat Spectroscopy (SHS), and X-ray scattering. We aim to understand how the alkyl chain length influences the dynamics and electric conductivity in this system. Two dielectrically active relaxation modes are observed, the γ and the α_{core} process, that correspond to the localized relaxation of the alkyl chains, and cooperative motions of the aromatic core in the columns respectively. Both the γ relaxation and the α_{core} process slow down with increasing alkyl chain length. SHS reveals one relaxation process, the α_{alkyl} process that has similar temperature dependence as that of the α_{core} process for ILC12, 14, 16 but shifts to higher temperature for ILC8 and 10. For ILC12, 14, 16 the absolute values of DC conductivity increase by 4 orders of magnitude at the transition from the plastic crystalline to hexagonal columnar phase. For ILC8, 10 the DC conductivity behavior is similar to ionic liquids, where the conductivity is coupled with structural relaxation. Small-Angle X-ray (SAXS) investigations reveal that both the intercolumnar distance and disorder coherence length increase with alkyl chain length, conversely the DC conductivity decreases monotonically.

Probing dynamics of an amorphous drug by Dielectric Relaxation spectroscopy and MD Simulations: effect of low concentration strongly hydrogen-bonded water

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Active Pharmaceutical Ingredients (API) are usually formulated in the crystalline state but, over the years, the interest for the amorphous state has strongly developed. Indeed, the better bioavailuability of the glassy state appears as a way to circumvent the solubility issue encountered by the API of increasing complexity in the pipeline. However, the instability of this physical state can lead to the recrystallisation of the API, which is an obvious hindrance to its use. In order to limit this hurdle, it is important to control all parameters favoring this recrystallisation. Water is an important one since it is well-known for fastening the main mobility of amorphous compounds by lowering the glass transition. It can also influence, in the glassy state, more localized mobilities (plasticization or anti-plasticization) from which effects on sub-Tg recrystallisation is still an issue. It is all the more important to understand the mechanisms of action of water since environmental moisture can hardly be avoided and because it can impact the dynamics even at low water content such $1\%_w$. Moreover, even API that are poorly soluble in water in the crystalline state may be hygroscopic in the amorphous state and absorb water upon storage.

In the presented work, we investigate by means of complementary Dynamic Relaxation Spectroscopy (DRS) and Molecular Dynamics simulations (MD), the impact of a low water concentration on the dynamics of an amorphous API (of poor solubility in the crystalline state) and we focus in particular on localised intramolecular mobilities, the microscopic origin of which often remains unclear.

By DRS, we evidence that these residual water molecules give rise to a new secondary relaxation mode in the glassy state. It originates through the motion of water molecules hydrogen-bonded to API molecules and this dynamic is coupled the intramolecular motions of a flexible part of API molecules carrying functional groups. MD computations and analyses of the hydrogen bonding interaction (HB) allows to understand and rationalise these results. They establish that these water molecules can be divided in two categories:

- a majority of weakly or moderately HB water molecules to API which are easily removed from the system by usual drying process,
- a minority of much more highly HB water molecules strongly interacting with functional groups of the API molecules, creating some kind of bridges between drug molecules. These strongly HB water molecules localise themselves in small pockets in empty space existing between the API molecules due to the poor packing of the glassy state and are much more difficult to remove without a specific treatment.

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Multiple glassy dynamics of a homologous series of triphenylene-based columnar liquid crystals – A study by broadband dielectric spectroscopy and advanced calorimetry

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Hexakis(n-alkyloxy)triphenylene) (HATn) consisting of an aromatic triphenylene core and alkyl side chains are model discotic liquid crystal (DLC) systems forming a columnar mesophase. In the mesophase, the molecules of HATn self-assemble in columns, which has one-dimensional high charge carrier mobility along the columns. Here, a homologous series of HATn with different length of the alkyl chain (n=5,6,8,10,12) is investigated using differential scanning calorimetry (DSC), broadband dielectric spectroscopy (BDS) and advanced calorimetric techniques including fast scanning calorimetry (FSC) and specific heat spectroscopy (SHS). The investigation of the phase behavior was done utilizing DSC experiments and the influence of the alkyl chain length on the phase behavior was revealed. By the dielectric investigations probing the molecular mobility, a γ-relaxation due to localized fluctuations as well as two glassy dynamics the α_{core}- and α_{alkyl}-relaxation were observed in the temperature range of the plastic crystalline phase. Moreover, the observed glassy dynamics were further studied employing advanced calorimetry. All observed relaxation processes are attributed to the possible specific molecular fluctuations and discussed in detail. From the results a transition at around n=8 from a rigid constrained (n=5,6) to a softer system (n=10,12) on a molecular lenght scale was revealed with increasing alkyl chain length. A counterbalance of two competing effects of a polyethylene-like behavior of the alkyl chains in the intercolumnar domains and self-organized confinement is discussed in the context of a hindered glass transition.

Conductivity mechanisms in 2-picolinium ionic liquid salts with different alkyl chain length

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Ionic liquids (ILs) having bromide as anion and 2-picolinium with different alkyl side chains as cation ([C_n-2-Pic][Br] (*n* = 6 (hexyl), 12 (dodecyl) and 16 (hexadecyl)) were synthetized and characterized in respect to their phase transformations and conductivity behavior. While the lengthier ILs, [C_{12}-2-Pic][Br] and [C_{16}-2-Pic][Br], exhibit a smectic mesophase between the crystalline range and the isotropic liquid, being classified as ionic liquid crystals, the shortest [C_6-2-Pic][Br] vitrifies upon cooling, showing no liquid crystalline window. Therefore, the alkyl chain plays a role in determining the material's ordering and the correspondent conductivity mechanism of this attractive class of organic salts.[1] For [C_6-2-Pic][Br], when the glass transition temperature is crossed (below -60 °C), the dc conductivity plateau emerges due to long-range diffusive charge transport mechanism. This glass transition assisted hopping mechanism gives rise to conductivity values around 7 orders of magnitude higher than the homologous C_{12} and C_{16} ILs that, at sub-ambient temperatures, are in the crystalline state, however undergoing polymorphic transitions. While for the glass former, C_6, the dc conductivity evolves with the temperature increase according to a VFTH law, for the higher alkyl size chain ILs, an Arrhenius temperature dependence is found, revealing a temperature assisted charge transport mechanism, in which $\sigma'(T)$ trace is sensitive to the crystal-crystal and crystal-smectic transitions. Therefore, a correlation is established between each material phase and the respective conductivity mechanism. Moreover, Nyquist plots were constructed, appearing, at room temperature (24 °C), as semi-circles for [C_{12}-2-Pic][Br] and [C_{16}-2-Pic][Br], allowing to extract the respective RC parameters of the equivalent electric circuit. In the molten liquid state, the conductivity decreases with the lengthening of the alkyl chain owing to a viscosity increase.[2]

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Ion Transport in Polymerized Ionic Liquids

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Mixed ionic and electronic conductors are of great importance for Li-ion batteries.[1] Herein, the ion transport in imidazolium based Polymerized Ionic Liquids (PILs) bearing a π-conjugated polythiophene backbone with four different side-chain lengths [n = 4, 6, 8 and 10] and seven different counteranions ($[Br]^-$, $[BF_4]^-$, $[ClO_4]^-$, $[PF_6]^-$, $[Picrate]^-$, $[TFSI]^-$, and $[B(Ph)_4]^-$) were studied.[2] The combination of DFT calculations with X-ray scattering and dielectric measurements of ion conduction revealed that cation-anion complexation strongly influences the backbone dynamics (T_g) and the associated ionic conductivity. Pressure dependence of ionic conductivity showed that ion conduction is facilitated by local anion jumps and a simple "stick and jump" model can account for the enhanced ion conductivity for anions with intermediate size.

In the second part, diblock copolymer electrolytes based on a π-conjugated polyfluorene (PF) backbone were synthesized comprising nanodomains of a PIL and of a solid polymer electrolyte (SPE).[3] The former consists of an imidazolium PIL with a $[Br]^-$ counteranion and the latter of short EO chains doped with LiTFSI. The two nanophases support ionic conductivity, whereas the rigid PF backbone provides the required mechanical stability. Ionic conductivity measurements performed as a function of pressure identified local jumps of $[Li]^+$ and $[Br]^-$ ions in the respective SPE/PIL nanophases as responsible for the ionic conductivity. Between the two ions, it is $[Li]^+$ that has the major contribution to the ionic conductivity.

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Polymerized ionic liquids: Correlation of ionic conductivity with nanoscale morphology and counterion volume

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Polymerized ionic liquids (PILs) combine the attractive mechanical characteristics of polymers and unique physico-chemical properties of low molecular weight ionic liquids in the same material [1, 2, 3]. PILs have shown remarkable advantages when employed in electrochemical devices such as dye-sensitized solar cells and lithium batteries, among others. Understanding their ionic transport mechanism is the key for designing highly conductive PILs. In the current study, the correlation between morphology and charge transport in a homologous series of PILs with systematic variation of the anions is investigated using broadband dielectric spectroscopy, rheology, differential scanning calorimetry and X-ray scattering. As the volume of the counterions increases, the pedant-to-pedant separation increases, and ionic conductivity consequently decreases. The cations dominate structural dynamics since they are attached to the polymer chains, while the counterions are smaller and more mobile ionic species thereby controlling the ionic conductivity. Further interpretation of decoupling of ionic conductivity from the segmental relaxation enabled the correlation between polymer morphology and ionic conductivity. This study underscores the need for smaller counterions to obtain polymer electrolytes with higher ionic conductivity and decoupling index.

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High-pressure dielectric studies as a key for understanding the dynamics of ionic glass-formers*

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In this talk, the transport properties of several functionalized ionic glass formers are studied over an exceptionally wide temperature and pressure range by using ambient and high-pressure dielectric measurements. These studies enable us to address the fundamental problems regarding the effect of molecular packing on the transport properties of ionic systems in both liquid and glassy states. We established, in a wide thermodynamic space, a universal thermodynamic scaling behavior of entropy and conductivity in these systems with dominated electrostatic interactions, and a direct connection between thermodynamic and dynamic properties of ionic glass formers was found. Additionally, we found that the ion dynamics of polymerized ionic liquids at elevated pressure conditions can be understood through the free-volume theory. The proposed free-volume model is in good agreement with the experimental data. Finally, a pressure-induced liquid-liquid phase transition in a series of ionic liquids was presented. By monitoring the relaxation dynamics under high-pressure conditions, we addressed the long-standing questions regarding the effect of compression on the transition and density fluctuations at the transition temperature.

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Towards dynamics measurements of individualized macromolecules

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Detailed insight into the dynamics and other functionalities of synthetic polymers on the molecular level is highly desired in advancing nano-technology, however often it can be technically challenging. We investigate the dynamics in individualized polymeric chains by means of broadband dielectric spectroscopy. This method has revealed altered dynamics under conditions of spatial confinement in the past but there is no detailed information about the extent in which the properties of the material change as a result of individualizing the polymer chains. In order to address samples of such small scale, a nano-dielectric spectroscopy is developed by refining a nanostructured electrode setup combined with a procedure of chemical surface modification. The latter involves the deposition of a very regular pattern of gold nanoparticles (AuNPs) of well-controllable size and separation on the nanometer scale. These AuNPs act as anchors for the chemical grafting of end-functionalized polymers (e.g. thiol terminated PEO). To determine the (average) number and conformation of chains grafted to each AuNP, their volume and shape are characterized by AFM.

Dynamic behaviour of heavy water inside and outside of poly (*N*-isopropylacrylamide) microgel using broadband dielectric spectroscopy

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Aqueous suspension of non-ionic poly (*N*-isopropylacrylamide) microgel particles were prepared by one pot free radical precipitation polymerization technique. About 10 wt.% of PNIPAM microgels, dispersed in heavy water was used for the dielectric measurements in the frequency range of 0.1 GHz to 50 GHz and temperature between 288 K to 323 K. The relaxation process observed at around 16-18 GHz (h-process) was fitted well with single Debye equation, which corresponds to the overall rotational motion of the heavy water inclusive of that residing within and outside the microgel. Further, based on the assumption of the two water model and their contribution, heavy water outside the microgel (h1 with its relaxation time of $\square_{h1}$ fixed as relaxation time of heavy water) and confined heavy water within the microgel (h2 with its relaxation time of $\square_{h2}$), was evaluated in the high frequency relaxation spectrum (Figure 1). At any temperature, irrespective of VPTT, $\square_{h2}$ is only 1.4-1.8 larger than $\square_{h1}$, which implies that the dynamics of heavy water is not significantly constrained inside the microgel particle even in the collapsed state of the PNIPAM microgel. Also there is no apparent change in the dielectric parameters observed before and after VPTT. Temperature dependence of relaxation time follows a single Arrhenius behaviour with an activation energy of 17.52 kJ/mol and 13.26 kJ/mol for h1 and h2 process respectively. The obtained results are compared with the dynamics of water in PNIPAM microgels[1] in order to understand the effect of isotopic substitution on the dynamics.

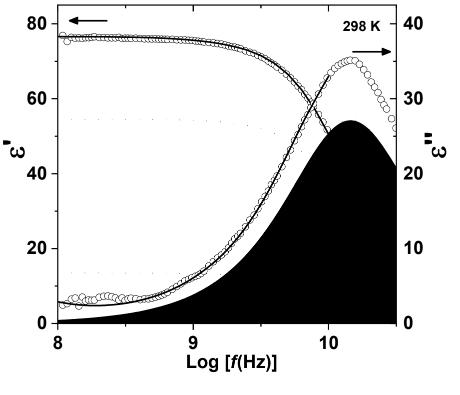

Figure 1: Complex dielectric permittivity spectra and the h1 and h2 relaxation process of 10wt.% PNIPAM microgel dispersed in heavy water at 298 K.

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The nature of the low temperature crossover of water in hard confinement

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Interactions of water molecules with organic and inorganic materials hydration centres and how interfaces affect water's dynamics, structure, and properties, especially in confinement, is still one of the most intriguing questions of Soft Condensed Matter Physics[1-4]. The low temperature crossover, observed in the relaxation map of hydration water in confinement, attracts special attention because of its unique position in the vicinity of 180K for a very broad class of materials. This unclear phenomenon gives the motivation of current research to study the dynamics and structure of water in the most primitive well-defined hard confinement.

Broadband dielectric spectroscopy (BDS) in combination with nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC) are powerful techniques to investigate the properties of confined water and to assess the molecular dynamics on various time and length scales. Porous borosilicate inorganic glasses (hard-rigid confinement) with silica gel globules inside the pores (hard-soft confinement) were studied in the current research to clarify the mechanism of the water dynamic crossover.

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Quantitative Structure–Property Relationship approach to estimate the α-relaxation dynamics of molecular glass-formers

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The Glass Transition Temperature (T_g) is one of the key properties of interest when developing brand-new materials. It is associated with a sudden change of the dynamic properties of a compound, concerning in particular its relaxation time. Broadband Dielectric Spectroscopy (BDS) is the most extended technique to measure the relaxation time of a compound, by perturbating the system on a wide range of frequencies. Although this characterization is only possible after synthesizing the new materials, recent advances in the computational calculus, in particular Quantitative Structure–Property Relationship models (QSPRs), are becoming valid tools in the estimation of the physical properties of new materials. In this work, we propose a QSPR approach with the aim of estimating the α-relaxation dynamics of molecular glass-formers only based on their chemical structure. Firstly, we predict the T_g of the compound using a Fully Connected Network trained with a Simplified Molecular Input Line Entry System representation of the molecules. Then, we use the predicted value of the T_g as the input value for the Elastic Collective Non-linear Langevin Equation, which outputs the estimated α-relaxation dynamics of the compound. Finally, we validate our method by comparing the predicted results with experimental BDS measurements. We believe that this approach is a powerful tool in the design of new materials, as it allows not only to predict a physical property, but also to estimate a meaningful sector of the relaxation map even before the synthesis of a new material, saving financial and time resources.

Effect of star architecture on the dynamics of 1,4-*cis*-polyisoprene under nanometer confinement

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The dynamics of a series of *cis*-1,4-polyisoprene stars located inside nanoporous alumina was investigated as a function of functionality, f, ($2 \leq f \leq 64$), arm molar mass, M ($2.6 \leq M \leq 13.5$ kg·mol^{-1}) and degree of confinement ($0.01 \leq 2R_g/d \leq 0.6$; R_g, is the radius of gyration and, d, is the pore diameter) by dielectric spectroscopy.[1] In the bulk, dielectric spectroscopy revealed broadening of the chain modes with increasing functionality. In addition, a slower dielectric process was found in the vicinity of the soft-colloidal process identified earlier by rheology. The latter associates with the cooperative reorganization of the stars and involves rotational and translational motions. The effect of confinement on the dynamics of stars was stronger than for linear chains.[2,3] First, the dielectric strength of the normal modes was reduced in the stars and, second, the chain dynamics were slower. The reduced dielectric strength was employed as a measure of the thickness of the interfacial layer. Based on the dielectric strength, we can account for possible arm star configurations in the vicinity of the pore walls. The slower chain dynamics reflect the increased entanglement density due to extra topological constraints imposed by the adsorbed arms near the pore walls.[4] Functionalization of the pore walls restored partially the dielectric strength of the chain modes. Overall, star-shaped polymers are more prone to adsorption effects when confined in nanopores as compared to linear chains.

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Subtle Influence of Hydrogen-Bonded Structures in Phenylalcohols

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Several alcohols show a distinct behaviour in the low frequency range of their dielectric (BDS) and mechanical responses believed to be due to supramolecular, hydrogen-bonded structures. We present the results of a systematic study of the dielectric and shear rheological response of 1-, 2- and 3-phenyl-1-propanol and compare to other monoalcohols, including 1-propanol. The phenylpropanols show a simpler behaviour in the mechanical response, and only slight changes between the three compounds, in contrast to a greater difference between phenylpropanols in BDS spectra [1].

These findings indicate that any supermolecular structures forming in the phenylalcohols are short lived as opposed to systems like 2-ethyl-1-hexanol [2], which show polymer-like spectral contributions. We interpret this as a sign that transient structures only have a minor effect on the shear mechanical response, even if they are dominant in the dielectric spectroscopy.

The remarkable similarity of the spectral shape across the different alcohols is reminiscent of results from light scattering (PCS) experiments, where a general shape of the α relaxation is seen [3]. This supports the idea that the α relaxation is mainly driven by the same underlying physics in PCS and shear rheology, namely a molecular self-correlation function, in contrast with the dielectric signals that are dominated by h-bonded networks and molecular cross-correlation functions.

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Towards experimental detection of crystallization in individualized polymer chains

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Although crystallization of polymers has been investigated since decades, it is not yet fully understood. One way to gain more insight is to study the difference between bulk polymer and confined polymer chains with focus on how crystallization characteristics change depending on the size and type of confinement. Until now, most studies have used confinement in thin films or nanopores but the approach to study crystallization and aggregation in individual chains was accessible only to computer simulations.

Since detection of phase transitions in individual polymer chains poses a severe challenge to most experimental methods, the measurement of ensembles of individual chains is desirable. However, maintaining the individual character requires a sophisticated method to separate them. Here, we use block copolymer micelle lithography (BCML) to deposit a regular pattern of well-separated gold nanodots on a silicon substrate to chemically graft end-functionalized polymer chains on these nanodots to individualize them. Instead of common thermodynamic methods (which require considerably more sample material), we employ dielectric spectroscopy using a nanostructured electrode arrangement since it is much more sensitive. Albeit being typically considered a dynamics method, it also allows to examine density changes and thus phase transitions of polymers.

Dielectric relaxation processes in semicrystalline polymeric thin films

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In this work we present the results of a study of the relaxation phenomena associated to the melting and crystallization of semicrystalline polymers. In our work, we investigated the dielectric relaxation between 1Hz and 1 MHz of ultrathin films poly(ethylene oxide) (PEO) between room temperature and 75° C, that is about 15 K above the nominal melting point. The dielectric characterization carried out on samples of different thickness provides a way to discriminate between genuine molecular processes and other polarization contributions, which may mask other intrinsic relaxation dynamics. Thin films of thickness ranging between ~15 and ~100 nm were characterized both in temperature scan and isothermal conditions. The melting and crystallization temperatures were evaluated considering the temperature dependence of the dielectric constant measured at high frequencies.

The results show the occurrence of a Slow Arrhenius Process (SAP) in the liquid state[1], which in our work seems affected by the contribution of adsorbed layers [2]. In addition to that, we were also able to identify another contribution to the dielectric losses arising from polarization effects taking place between the crystalline lamellae in solid state (MWS relaxation). This phenomenon persisted in liquid state as a polarization between the adsorbed layers at the electrodes' interface follows the same dynamics as the SAP. The concerned molecular dynamics and polarization processes were discussed considering their dependence on film thickness, temperature, and annealing time.

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Broadband dielectric spectroscopy on lithium-salt-based and choline-chloride-based deep eutectic solvents

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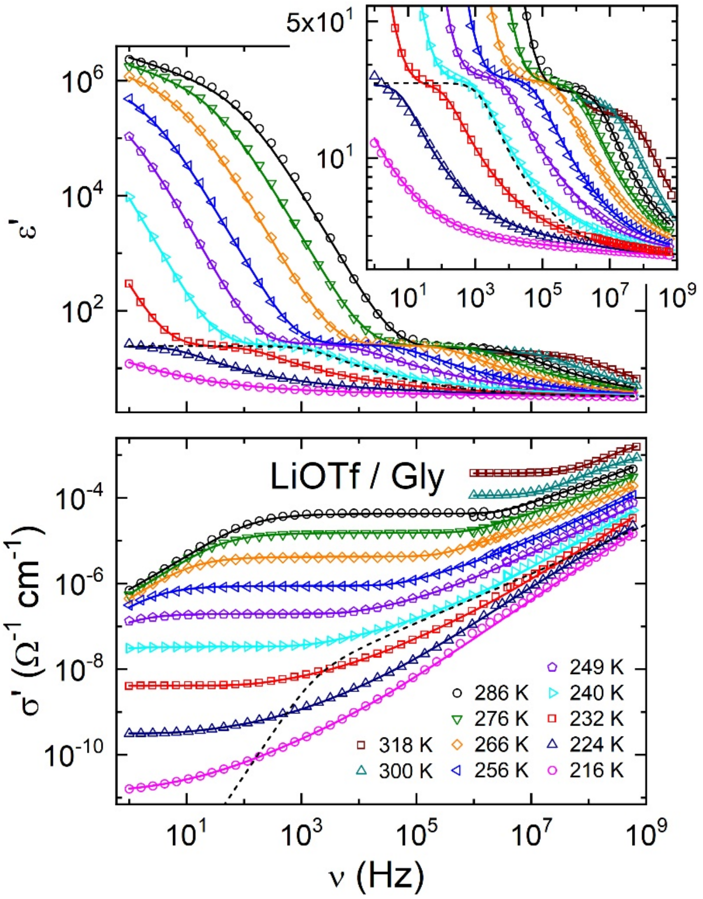
Experimental Physics V

We have performed broadband, dielectric spectroscopy on three lithium-salt-based deep eutectic solvents (DESs), where the only cations are Li+, covering a broad frequency and temperature range, the latter extending from the low-viscosity liquid around room temperature down to the glassy state. We observe a relaxational process that can be ascribed to dipolar reorientational dynamics and exhibits the clear signatures of glassy freezing. The presented spectra on the right are obtained for a eutectic mixture of LiOTf and glycerol. In addition to non-intrinsic electrode effects, they display a clear relaxational contribution, as is highlighted for the 240 K curve by a black, dotted line. Furthermore, we find that the temperature dependence of the ionic dc conductivity and its room-temperature value are also governed by the glassy dynamics of these systems, depending, e.g., on the glass-transition temperature and fragility. Compared to similar, previously investigated DESs,[1] both, the reorientational and ionic dynamics, are significantly reduced, due to variations of the glass-transition temperature and the higher ionic potential of the lithium ions.



Additionally, we analyzed a range of DESs composed of choline chloride and a carboxylic acid (e.g., maline, for which a relatively high room-temperature conductivity was reported[2]) using broadband dielectric spectroscopy. The nature of the observed dynamic processes, as well as the evidence for and strength of their coupling are compared to previously investigated choline-chloride-based DESs,[1] taking the effect of the presence of water in the solvents into account.

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Effects of Nanometer Confinement on the Self-assembly and Dynamics of Poly(*γ*-Benzyl-L-Glutamate) and its Copolymer with Poly(isobutylene)

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An achievement in recent years has been the synthesis of macromolecules with the ability to mimic the structure and dynamics of proteins. In this respect, synthetic polypeptides play a vital role in biomedical science because of their exceptional similarity to proteins. Poly(*γ*-benzyl-L-glutamate) (PBLG), a model rigid-rod polymer,[1-3] and its copolymer with poly(isobutylene) (PIB) are studied in the bulk and under nanometer confinement in pores with emphasis on the self-assembly and dynamics, respectively, with X-ray diffraction, ^{13}C-NMR and with dielectric spectroscopy, differential scanning calorimetry.[4] PBLG segments located within the α-helical and amorphous regions have distinct dielectric fingerprints. We have analyzed the dielectric signal from the segmental and from the helical segments to show that the α-helices are short, and furthermore, interrupted by amorphous segments. The effect of confinement is two-fold: First, to speed-up the segmental process, and second, to destabilize - in part - the secondary structure. The block copolymer architecture combined with confinement further destabilizes the α-helical secondary structure by introducing phase mixing. The results on the synthetic polypeptide demonstrate that both the chain configurations and the associated dynamic processes are affected when PBLG chains are confined within narrow pores. These results could pave the way for a better understanding of the behavior of more complex proteins in confined space.

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Pressure dependence of structural relaxation parameters in thermoplastic amorphous polymers

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In recent years, the use of the broadband dielectric spectroscopie (BDS) with a controlled atmosphere under pressure contributes additional constraint to the macromolecule mobility. This technique allows to contrast the different theorical approaches of the glass transition with physical values such as the activation volume of isochoric fragility, thanks to the contribution of pressure. Moreover, this technique gives access to the evolution of the cooperatively rearranging region (CRR) size as a function of the temperature under several isobaric conditions.

The present study compares the response of segmental relaxation times of three amorphous thermoplastic polymers widely used in the packaging industry: poly(lactide acid) PLA, poly(ethylene terephthalate glycol) PETg and poly(vinyl acetate) PVAc. These polymers are studied by BDS at pressures up to 600 MPa, and for temperatures scale from -30 up to 120°C.

The results clearly show the confrontation of the thermal and volumetric contributions on the relaxation time through the variation of the segmental relaxation peaks in the response of the imaginary permittivity. The impacts of the temperature and pressure on the relaxation times are approximated by a VFT and a VFT-like laws respectively. In this way, the contribution of pressure acts on the glass transition temperature. This last one varies of approximately 20°C for a variation of 100 MPa. In order to evaluate precisely these phenomena, fragility indicators obtained at constant pressure or volume enable to analyse the temperature dependence of structural relaxations. The material volume is calculated from the Tait equation [1] to determine the isochoric fragility. In addition, these results are correlated to another method [2] to obtain isochoric fragility without knowing the exact volume of the material, which is sometimes difficult to determine. Finally, by using the Donth's approach [3-5], the evolution of the CRR size can be followed as a function of pressure.

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Ion dynamics of trihexyltetradecylphosphonium-based ionic liquids with big anions at ambient and elevated pressure

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Although the first-order liquid-liquid phase transition (LLT) phenomenon has been reported to exist in various systems (i.e., phosphorus, silicon, water, triphenyl phosphite, etc.), it is still one of the most challenging problems in the field of liquid science. Recently, we found that the LLT phenomenon also exists in the family of trihexyl(tetradecyl)phosphonium ($P_{666,14}^{+}$) based ionic liquids with small sizes of anions (Wojnarowska, Z., Cheng, S., Yao, B. *et al. Nat Commun **13,** 1342, 2022*). To better understand the structure-property relationships governing LLT, we use dielectric spectroscopy at ambient and elevated pressures to monitor the ion dynamics of $P_{666,14}^{+}$ based ionic liquids with bigger sizes of anions over a wide temperature range. Our results suggest that their conductivity relaxation times (τ_σ) display the regular behavior of most ionic liquids, and their distribution obeys the time-temperature superposition (TTS) rule. However, the Stickel operator analysis for the tested system with relatively small anions exhibits similar anomalous behavior to ionic liquid with hidden LLT. The viscosity measurements also proved these results. Moreover, our high-pressure studies have shown that the sample with hidden LLT has relatively strong pressure sensitivity compared to the one without LLT. The $\tau_\sigma(P)$, dT_g/dP coefficient, and activation volume $V^{\#}$ were found to be the same. Finally, we discuss the pressure dependence of the fragility (m_P) for studied ionic liquids by using the Avramov model.

Broadband dielectric spectroscopy on pectin-based hydrogels

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Water is the basis of social and economic development; it is vital to every human being; it is essential for growing food, health, and safety. Moreover, water is related to the economic vitality of our society, and, at present, there is no substitute for water on the earth's crust. However, water on the planet is under pressure because of population growth (we need more and more water to produce food), the overexploitation of freshwater resources used in different industries, and climate change.

In addition, contamination is observed in almost all sources of available water bodies. A fundamental environmental challenge posed by water contamination is the presence of emerging contaminants (such as pharmaceutical products, industrial chemicals, heavy metals and metalloids, and pesticides), which reduce drinking water quality drastically.

Contaminated water can be remediated or cleaned to some extent for its reuse. In recent years, different methods for cleaning water have been explored, such as chemical precipitation, ion exchange, electrodeposition, filtration, or photocatalysis[1,2]. However, adsorption seems to be the cheapest, reusable, and easily scalable industry method for water remediation.

We have developed a new generation of pectin-based hydrogels to remove heavy metals and pharmaceuticals from contaminated water through adsorption. Adsorption occurs when a contaminant molecule in water binds to the surface of the hydrogel[3]. Studying the adsorbed water inside the hydrogel is one of the factors to consider that will help to increase the efficiency of the water remediation.

In this work, we apply Broadband Dielectric Spectroscopy (BDS) combined with X-Ray Diffraction (XDR) to characterize our pectin-based hydrogel with different humidity levels (0 - 32 wt%). By XRD, we determined that dry hydrogel loses part of its crystalline structure during hydration. On the other hand, dielectric results on hydrated hydrogels show two main processes, one corresponding to water absorption and the other to pectin β-relaxation. For high humidity levels, i.e., 32 wt%, the relaxation times of the water process are similar to that for water in MCM-41[4]. Our results suggest that the remaining crystalline part of our hydrated pectin-based hydrogel forms pores similar to rigid confinements.

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Liquid Dynamics in Confinements and Mixtures: Combined BDS, NMR and MD Simulation Approaches

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Broadband dielectric spectroscopy (BDS) is a powerful tool to characterize liquid dynamics over very broad frequency and temperature ranges. However, the interpretation of the dielectric spectra is often challenging in applications to confined and mixed liquids. For example, the assignment of the relaxations to the components may be challenging, conductivity contributions may interfere, and it is usually not straightforward to discriminate between processes from molecular dynamics and internal polarization in heterogeneous media. Therefore, it is highly desirable to complement BDS approaches to liquid dynamics in confinements and mixtures by other suitable experimental and computation studies.

It is well established that nuclear magnetic resonance (NMR) methods are capable of providing component-selective information, which is free of unwanted polarization and conductivity effects. In particular, NMR field-cycling relaxometry, possibly supplemented by isotope labeling strategies, is very useful because it directly yields dynamical susceptibilities of defined system components over broad dynamic ranges for comparison with the dielectric spectra [1]. Furthermore, MD simulations are meanwhile able to handle chemically realistic and sufficiently large models for reasonably long times and, hence, to yield unrivaled details of the motional behaviors [1]. For example, such computational approaches allow us to quantify the cross-term contributions to the dielectric spectra [2] or to determine the gradients of the molecular mobility across a confinement [3].

Here, we combine BDS studies with NMR experiments, including field-cycling relaxometry, and MD simulations to obtain comprehensive insights into the dynamics of confined and mixed liquids. Specifically, we apply such combined approach to hydrogen-bonded liquids [4,5], particularly water [6], in various types of confinements and in mixtures with proteins or peptides [7,8]. In this way, we determine the effects of severe confinements and/or partial crystallization on the glassy slowdown of pure [4,6] and mixed [5] hydrogen-boned liquids, in particular, on the noteworthy dynamical crossovers in the case of supercooled water [6]. Moreover, we analyze the dynamical couplings between these liquids and dissolved proteins [7] or peptides [8], which form the basis for biological functions.

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Influence of polymer chain length on non-equilibrium phenomena in cylindrical nanopores.

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Effects caused by nanoconfinement can be reduced or even eliminates with time. Thus, the glass transition dynamics of the nanopores-confined system are strongly non-equilibrium. Faster molecular mobility observed in confined geometry slows down with time, and it is possible to recover the relaxation times characteristic of the bulk sample. By reducing the pore diameter and lowering the annealing temperature below the glass transition temperature of the interfacial layer, the equilibration time increases.[1] In this lecture, we would like to draw attention to the influence of the polymer chain length on the equilibration phenomena in anodic aluminium oxide (AAO) nanoporous matrix. In this study, we have used poly (phenylmethyl siloxane) with high and low molecular weight. We have found that the molecular weight significantly influences the time necessary for rearrangement and approaching denser packing of the polymer chains in nanopores. The influence of polymer chain length on the relationship between the equilibration kinetics time constant and the characteristic time of the viscous flow in the cylindrical channels was also investigated.

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Dynamic Disorder in a Nano-Sized Channel-Shaped Pharmaceutical Cocrystal Architecture

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Cocrystals are molecular solids that are neutral crystalline single-phase materials composed of two or more different molecular compounds associated via weak supramolecular interactions such as van der Waals, hydrogen, halogen or π-π stacking. Cocrystals have shown a considerable increase of interest in recent years due to their possibility to improve many properties of pharmaceuticals (API) such as aqueous solubility, dissolution rate, hygroscopicity bioavailability, or mechanical properties.

In this work, we aim to demonstrate that cocrystals may offer a new type of interesting confinement environments including the possibilitty to investigate rotational and translational dynamics in a true nanometric size channel-like architecture. Some results will be presented based on complementary Broadband Dielectric Spectroscopy, Powder X-ray Diffraction and ^{1}H-^{13}C CP/MAS solid-state NMR experiments combined with Molecular Dynamics simulations.

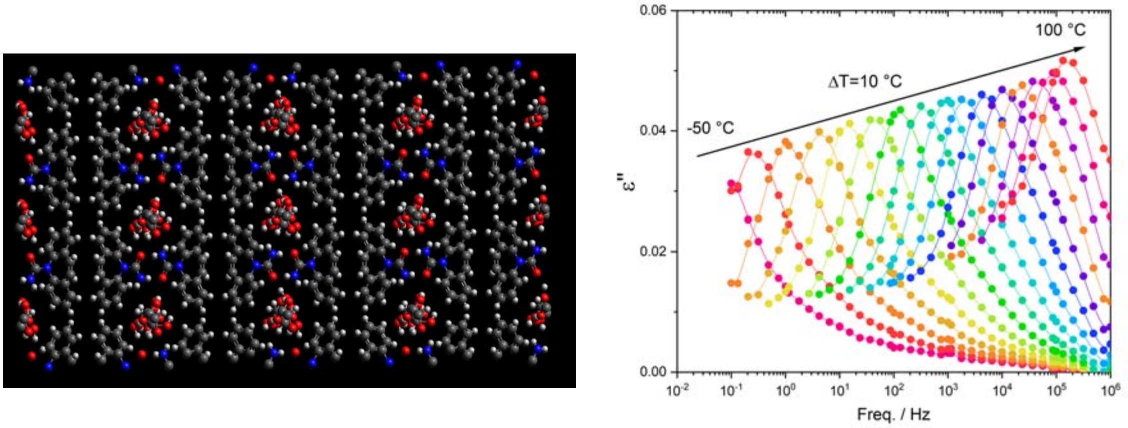

Figure 1. Left-hand: Snapshot of the cocrystal channel-like structure with coformer molecules inside the channels made by the API. Right-hand: Temperature dependence of the cocrystal dielectric loss.

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A New Approach to an Old Idea Understanding the Fröhlich *B(T)* Function

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In 1949 Herbert Froelich published the Theory of Dielectrics[1]. While it is a relatively slim volume, it is widely regarded as one of the fundamental theoretical texts in the science of dielectrics. One of the more thorny subjects he covered was the meaning of the dielectric strength and its relationship to dipole correlation within the material. His conclusion was a reworking of ideas first put forward by Onsager[2] and Kirkword[3]. It was condensed into a function, commonly called the *B(T)* function, that linked the macroscopic parameters of a dielectric relaxation to the microscopic state of the dipole-dipole interaction, responsible for that relaxation. While elegant, the final equation could be related to correlated, uncorrelated or anti-correlated dipoles only, in terms of an averaged angle, $<\theta>$, such that $<\boldsymbol{m}\cdot\boldsymbol{m}> \sim 1+ z<\cos\theta>$, where $<\boldsymbol{m}\cdot\boldsymbol{m}>$ is the ensemble averaged scalar multiplication of the dipole moments and z is the number of nearest neighbours. We present a new derivation of the *B(T)* function based on the concepts of a correlation length, rather than relative dipole-dipole directions. Using this idea, we show that *B(T)* function actually presents population distributions of dipole moments, each within its own correlation radius. These lengths can then be used to define one of the less tangible concepts in dielectric physics, namely the mesoscale. The paper will show some examples in complex systems of the approach and discuss the implication of the new approach compared to the traditional view.

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Studies of molecular dynamics in electrospun polimer/pharmaceutical drug fibers.

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In recent years, electrospun fibers as drug delivery systems have been the subject of great interest due to their high surface area, adjustable morphology, and diameter of fibers. The advantage of drug-loaded fibers is the ability to control drug release by the composition and structure of fibers. These studies deal with polycaprolactone (PCL) fibers containing different weight percentage values of ornidazole (ORN). ORN shows the glass transition at a much higher temperature (T_g=277 K) than PCL (T_g=209 K). PCL/ORN fibers behave like miscible blends, and only one glass transition depending on drug concentration in the system is revealed by Differential Scanning Calorimetry (DSC) measurements. Three relaxation processes are found for PCL/ORN fibers by broadband dielectric spectroscopy (BDS): i) the α-relaxation process due to fluctuation of PCL segments, ii) the secondary β-relaxation of PCL, iii) the slow relaxation process at high temperatures originating from constrained ORN molecules. The β-relaxation of the PCL component is not affected by the presence of ORN molecules, whereas the two other processes are sensitive to the composition. In this contribution, we will discuss the impact of ORN content on the glass transition temperature and molecular dynamics of PCL/ORN fibers. Finally, we will present the kinetics of drug release from fibers monitored by UV-vis measurements.

How can dielectric spectroscopy be used to investigate molecular mobility in amorphous and semi-crystalline biobased polyesters? From defective to improved applicative biopolymers…

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Polyesters are used in several domains of the industry for packaging applications mainly. Since decades for polyesters family, poly (ethylene terephthalate) (PET) represents a reference material for the packaging industry, especially when food contact and barrier properties are absolutely essential. Several attempts to replace PET with other biosourced polyesters that are compostable (poly(lactic acid) (PLA)) or even biodegradable in a natural environment (polyhydroxyalkanoates (PHA)) have not produced the expected results. One of the reasons for the drawbacks of these biopolymers is related to their relative brittleness compared to industrial polyesters. Several strategies have been employed to try the bring solutions for these biopolyesters at different levels from chemistry, formulation and processing.

PLA lack of ductility is predominant in amorphous material and during thermal crystallization is accompanied by faulty barrier properties related to large amounts of defective rigid amorphous fraction (RAF) at the interface between mobile amorphous fractions (MAF) and crystallites. To reduce this problem plasticization strategy has been employed to enhance molecular mobility and reduce brittleness using the addition of small plasticizing molecules [1] or using PLA oligomers [2].

PHA main issue is related to its progressive embrittlement during room temperature storage just after processing during cold crystallization. The understanding of the embrittlement process was a key point [3] that led in a second time to propose a chemistry and processing strategy, in order to investigate molecular mobility in modified PHAs with the goal to reduce crystallization ability.

The development of poly(ethylene 2,5-furandicarboxylate) (2,5-PEF) brought on the market one of the most credible biobased alternative to poly (ethylene terephthalate) (PET). Chemistry and copolymerisation strategies have been used to obtain a family of furan-based biopolymers with adjusted physical properties, glass transition temperatures and ability to crystallize [4].

On these very different biopolyesters, the study of molecular mobility and microstructures at different levels from very local fluctuations to segmental relaxation gave rise to the identification of the complexity and the heterogeneity of the biopolymers. The molecular mobility was investigated by cross-comparing the results obtained by advanced calorimetry techniques (FSC and MT-DSC), Dielectric Relaxation Spectroscopy (DRS) and Thermo-Stimulated Depolarization Currents (TSDC), with the aim of evaluating the local and segmental molecular mobilities. The time dependent evolutions of these biopolymers, due to crystallization, required the use of very strict thermal protocols in order identify the dramatic evolution from amorphous state to very complex semi-crystalline heterogenous materials. Molecular mobility analyzes in these semi-crystalline biopolymers appears to be a great challenge.

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Analyzing the α-relaxation of epoxy in immersion: crossover from VFT to Arrhenius dependence of the relaxation times

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In this work, we focus our attention on the influence of water absorption on the α-relaxation of an epoxy network. The fine analysis of this molecular mobility is made possible by an experimental setup (developed in the lab) able to perform dielectric measurements while the sample is kept in immersion at a controlled, fixed temperature [1].

The most striking feature in these results is the observation of a theoretically anticipated – yet rarely observed – crossover from a Vogel-Fulcher-Tammann to an Arrhenius dependence of the α-relaxation times as the epoxy is cooled below its glass transition temperature (Figure 1).

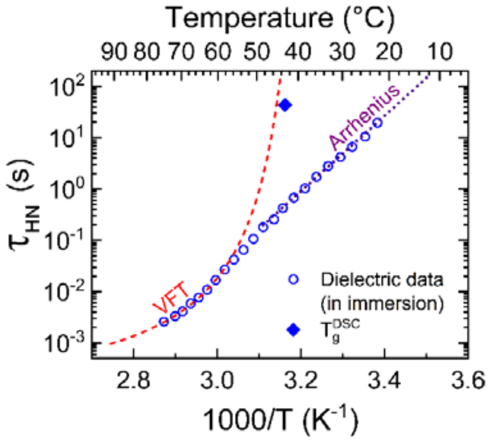

Figure 1 – VFT-Arrhenius crossover observed by means of isothermal dielectric measurements in constant immersion.

The idea that such a crossover is the direct manifestation of the slowing down of the segmental dynamics, although seducing, appears too simple. Indeed, complementary experimental analyses performed in various hydration states (namely, broadband dielectric spectroscopy, differential scanning calorimetry, thermally-stimulated currents) show that the VFT-Arrhenius crossover is accompanied by a decrease in the amplitude of the α-relaxation and a localization of the molecular mobility as a result of water absorption. Based on these experimental results and the literature reporting similar observations, we propose three hypotheses for the physical origin of this crossover [2], including a "confinement-like" effect due to water saturation [3]. We believe that studying deeply plasticized polymers with this setup casts a new light on the molecular dynamics involved in the glass transition.

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Is the sub-glass temperature relaxation of furan-based polymers related to their high gas barrier properties?

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Poly(alkylene 2,5-furanoate)s, (PAF)s, are fully biobased homopolyesters based on 2,5-furandicarboxylic acid that have recently emerged as promising alternative to petroleum based poly(alkylene terephthalate)s. In addition to a lower production carbon footprint poly(alkylene 2,5-furanoate)s have received significant attention due to their outstanding gas barrier properties in comparison to traditional poly aromatic esters [1]. The influence of chain dynamics on barrier properties has also devoted some attention. Dielectric spectroscopy experiments performed in poly(trimethylene 2,5-furanoate) revealed that the subambient relaxation, below its glass transition temperature, exhibited an inhibition of the mode corresponding to the ester oxygen linked to the aliphatic subunit which efficiently relaxes in the poly(trimethylene terephthalate) counterpart [2]. Fourier Transform Infrared (FT-IR) spectroscopy can provide precise information of intra-molecular motions at the molecular level [3]. By evaluating the vibrational frequencies and the corresponding oscillator, strength from the IR spectra information about the intra-molecular dynamics can be available. In this study, we present a combined IR spectroscopy and BDS study focused on the sub-glass temperature molecular dynamics of poly(trimethylene 2,5-furanoate) in comparison to that of poly(trimethylene terephthalate) in order to shed light on the influence the dynamics on the barrier properties of Poly(alkylene 2,5-furanoate)s.

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Dielectric spectroscopy as an effective tool to unveil the origin of the outstanding functional properties in biopolymers

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In order to cut down the explotation of the limited fossil sources and reduce the environmental impact of plastic materials, both the academic and industrial communities are heavily engaged in the development of biopolymers, i.e. materials produced from renewable resources and/or biodegradable.

2,5-furandicarboxylic acid (FDCA) displays a large potential as green monomer [1] for the synthesis of new polyesters with outstanding mechanical and gas barrier properties, thus able to replace the currently used petroleum-derived ones. 1,4-cyclohexanedicarboxylic acid (CHDA), is another monomer potentially derived from renewable resources [2], whose polyesters proved to be biodegradable [3]. From the chemical point of view, the furan moiety of FDCA is an aromatic ring fixed in its planar conformation, while in tha case of CHDA the presence of an aliphatic saturated ring permits conformational isomerism, not possible for the aromatic one [3]. Moreover, the presence of an oxygen atom in the furan ring enables the increase of polar inter-chain interactions. Both FDCA and CHDA can be combined with different linear glycols characterized by different number of methylene groups as well as with glycols containing side branches. In this view, several polyesters have been synthesized by two-step melt polycondensation and the structure-dynamics relationship has been investigated by means of broadband dielectric spectroscopy (BDS), focusing on the sub-glass relaxations. BDS analysis evidences chemical structure, specifically bond length and angle and polarity of the repeating unit, has a direct effect on the local and segmental dynamics. As concern the subglass temperature region at which the β process is located, the relaxation time position, as well as the intensity and the multiplicity of the relaxation process directly depend on the ring nature.

The results also confirm an *ad-hoc* chemical modification is a powerful tool to properly tune the crystallization capability and kinetics, allowing the detection of relaxation processes otherwise not detectable.

BDS reveals also to be a very useful technique, complementary to diffractometric ones, to shed light on the macromolecular arrangements established in the polymer matrix that are responsible for the macroscopic functional properties.

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VFT-type cooperative dynamics in “simple” supercooled liquids, liquid crystals and plastic crystals

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The Vogel-Fulcher-Tammann [1, 2] law is succesfully used for about 100 years to describe the temperature dependence of the structural relaxation time or viscosity of glass forming systems. Its popularity is based on various reasons: a) It is the simplest mathematical expression among various approaches, b) the VFT law can be linked to meaningfull physical quantities like free volume [3] or excess configurational entropy (Adam Gibbs approach [4]) and can be readily derived using simple assumptions, and c), the VFT law works for most supercooled liquid pretty well in the entire range between the glass transition (T_g) and melting temperature. The common idea behind these theories is the existence of cooperative dynamics on a temperature dependent length scale x(T) [5].

While the rational behind the VFT law is straightforward for fully disordered, liquid systems, a VFT dependence is often also observed for ordered liquids or even plastic crystals. These systems are characterized by partial orientational and/or translational order and show reorientational dynamics, the temperature dependence of which either shows Arrhenius or “super-Arrhenius” (thus VFT) behaviour.

This presentation focuses on VFT-type relaxation processes in a variety of systems: nematic and smectic calamitic liquid crystals, columnar liquid crystals, plastic crystals and nanoprorous guest-host material. Extensive data from broadband dielectric spectroscopy over 11 decades in frequency will be discussed in terms of length scales and dimensionality of cooperative motions with the aim to derive a conclusive physical picture [6].

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A hidden relaxation process under DC conductivity in poly(2-vinylpyridine) and nanocomposites

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Polymeric systems show various types of dynamical processes. Although broadband dielectric spectroscopy (BDS) can reveal the nature for most of the processes, some processes are totally covered with the contributions from the DC conductivity, and as a result, the detailed properties of such hidden processes cannot be accessed by BDS. Recently we have found that introducing an air gap between the top electrode and the polymer sample reduces DC conductivity substantially, allowing the study of low frequency relaxations, whose signal would otherwise be hidden by the DC conductivity signal. In this presentation, we would like to show an interesting example, that is, poly(2-vinylpyridine) (P2VP) homopolymers, copolymers with styrene, and nanocomposites with octa(aminophenyl) silsesquioxane (OAPS). In this polymeric systems, an extra process slower than the α-relaxation process can clearly be observed in the imaginary part of the dielectric permittivity, consistent with some earlier reports. Figure 1 shows the frequency dependence of the imaginary electric capacitance for P2VP. With the increase in the thickness of the spacer, an extra process could clearly be observed at the lower frequency than that of the α-process. This "slower process" was studied in two heterogeneous systems to examine the interaction between the 2VP and other species to elucidate the mechanism behind the slower process signal. In a random copolymer of styrene and 2VP, the relaxation strength of the slower process relative to the α-process increases substantially at low 2VP mole fractions. Additionally, in a composite of P2VP and OAPS, the presence of OAPS increases both the strength and timescale of the slower process, leaving the α-relaxation process relatively unchanged. This suggests that the slower process could be caused by cooperative polymer relaxation coupled to the transport of heterogeneous components and impurities. Further studies are needed to probe the molecular-level mechanism of this slower process and its effect on interfacial properties.

In our presentation on BDS2022, we plan to show other examples also in addition to those of P2VP, if such data could be available.

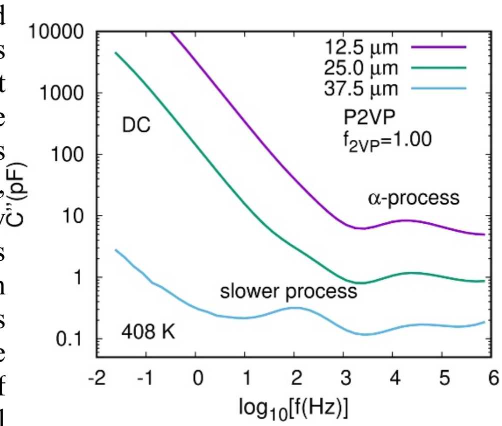

Fig.1: Imaginary part of electric capacitance for P2VP with various thickness of Kapton spacers.

NMR relaxometry: catching up with dielectric spectroscopy accessing the relaxation spectra in glassforming liquids

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Field-cycling (FC) NMR relaxometry, measuring the frequency dependence of the spin-lattice relaxation and thus the dynamic susceptibility, gained momentum as commercial and home-built FC relaxometers have become available which allow to routinely study the dynamics of molecular liquids undergoing the glass transition. Like dielectric spectroscopy (DS), NMR relaxometry probes predominantely rotational dynamics, but in the case of ^{1}H NMR also translational dynamics. An advantage of NMR is its selectivity, which enables one to probe site-specific dynamics. This can be achieved by labelling of different molecular sites by a single NMR nucleus or using several nuclear probes.[1]

By accessing broad-band relaxation spectra, FC NMR not only catches up with DS but also allows to contribute to the currently discussed question whether a “generic relaxation” pertains to liquids close to T_g and whether cross-correlation effects contribute to the DS relaxation. ^{2}H relaxometry directly addresses the latter point as it probes single-particle reorientation only. Also, the issue is tackled whether conformational changes expected for non-rigid molecules are reflected in different relaxation stretchings for different molecular sites. In the case of m-tricresyl phosphate (m-TCP; Fig. 1) and of glycerol, the FC 1H, FC 31P, and PCS spectra virtually agree. Thus, the molecules (actually flexible ones) reorient iso- tropically as a rigid entity with a stretching parameter being close to β_K=0.6. Yet, the DS spectra are narrower for reasons to be discussed. In contrast, for (non-polar) o-terphenyl the spectra of all techniques coincide. An excess wing in addition to an α-peak is recognized. Such site-independent relaxation is not always observed. However, upon cooling of flexible-molecule liquids, indications are found that the different site-specific dynamics merge, suggesting that the molecules generally reorient as a rigid entity near T_g. This could present a resolution for the lower stretching parameters reported at high temperature that contrast with the ones that were reported to be universal in a PCS study.[2]

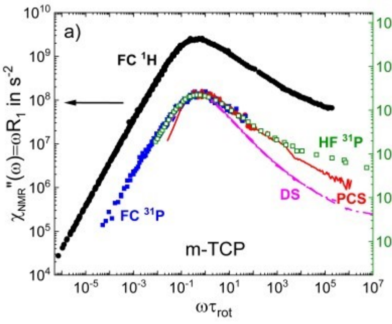

Fig. 1. *NMR susceptibilities of m-TCP as probed by FC ^{1}H and FC ^{31}P relaxometry compared to data from high- field (HF) ^{31}P NMR, DS, and PCS.*

We discuss two further issues: (i) the consequences of the applicability of frequency-temperature superposition including the excess wing, and (ii) the possibility to simultaneously monitor translational and rotational dynamics by FC ^{1}H NMR. The latter allows to identify the failure of “Stokes-Einstein-Debye” in a series of liquids with an increasing hydrogen bond network.

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Dielectric spectroscopy reveals the structural relaxation of tributyl phosphate

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The combination of experimental techniques probing different degrees of freedom yields a powerful tool for the material sciences which helps to understand the interplay of various microscopic processes. Applying dielectric spectroscopy and light scattering, in recent investigations self- and cross-correlation dynamics of supercooled liquids were reported to display generic and system-dependent spectral signatures, respectively [1]. In that work it was suggested that the generic self-correlation dynamics accessed via the photon correlation technique, and in general not the dielectric dynamics, probe the genuine structural relaxation of viscous liquids [1] an assertion that is subject to various debates, see, e.g., [2,3]. In this talk, we assess the assumption advanced in [1] by focusing on the relaxation behavior of tributyl phosphate, a moderately polar, non-associating liquid [4] for which self- and cross-correlated dynamics were clearly distinguished [1]. Employing physical aging and oscillatory shear rheology we demonstrate that the structural rearrangements in this viscous liquid are largely governed by its molecular, dielectrically detectable cross-correlations [5]. Our results thus provide evidence that the cross-correlated and not the self-correlated part governs the structural relaxation, thus underscoring the important role broadband dielectric spectroscopy plays for the exploration of the glass transition.

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The material time of physical aging: dynamic light scattering vs. dielectric spectroscopy

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As early as 1971, the concept of a material time has been proposed by Narayanaswamy [1] to explain the characteristics of physical aging in glasses. Until now his hypothesis has only been verified indirectly [2,3]. To this end, we investigate aging molecular liquids in a multi-speckle dynamic light-scattering experiment using a CMOS-camera. By simultaneously probing a large number of independent speckles, we are able to determine the time-resolved orientational correlation function C(tau,t) of molecular dynamics. This approach enables us to directly validate the existence of a material time that dictates molecular dynamics during aging and furthermore, to straightforwardly determine this material time xi(t) as a function of the laboratory time. The validity of xi(t) can be verified by confirming that transformation of the time axis from laboratory time to material time eliminates all signatures of non-linearity during aging.

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The Generic Lineshape of Glassy Dynamics: Experimental Conditions for its Visibility

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Recently, we have shown that structural relaxation in a broad range of supercooled liquids, including simple van der Waals, hydrogen bonding and ionic liquids, follows, to good approximation, a generic line shape in depolarized dynamic light scattering with a high-frequency power law $\omega^{-1/2}$ [1]. In dielectric spectra, on the other hand, this behavior is oftentimes masked by contributions of dipolar crosscorrelations so that dielectric spectra usually show a wide variety of different line shapes [1]. However, crosscorrelations need not be the only reason for deviations from the generic lineshape in particular when intramolecuar degrees fo freedom play an important role for the dynamics.

In the talk we summarize the experimental findings that lead to the conclusion of the existence of a generic spectral shape and discuss why certain substances deviate from the generic behavior. Particularly instructive for that purpose is a series of polyalcohols, frequently used as model-systems in glass-science, because the width of their respective dielectric loss spectra varies strongly along the series. Our results reveal, that the microscopic origin of the observed relaxation behavior varies significantly between different polyalcohols: While short-chained polyaclohols like glycerol rotate as more or less rigid entities and their light scattering spectra follow the generic shape, long-chained polyalcohols like sorbitol display pronounced intramolecular dynamic contributions on the time scale of the structural relaxation, leading to systematic deviations from the generic shape.

Based on these findings we discuss conditions and limitations for experimentally observing the generic shape in a supercooled liquid: Crosscorrelations need to be well-separated or negligible and the dynamics that is probed needs to reflect reorientation of a molecule as a whole and must not be superimposed by effects of intramolecular dynamic heterogeneity.

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POSTER contributions

Low-Frequency Ionic Motion in Non-crystalline Part of Polymer Solid

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In our laboratory, motions of impurity ions have been investigated in relation with the variety of free spaces in non-crystalline parts in polymer crystalline solids by the method of Broadband Dielectric Spectroscopy (BDS). In those studies, we separated the polymers investigated into two groups. One is the polymers with inhomogeneous size distribution of free spaces, another is without the distribution. Specifically, plural kinds of motion of impurity ions is recognized from the electric modulus as a function of frequency [1] in low frequency region below 10 Hz for low-density polyethylene (LDPE) crystallized from a melt. Furthermore, plural processes of ionic motions were found around the temperature of the form transformation of crystallite by the similar electrical method for isotactic polypropylene (iPP). Similar result was also observed for the polyvinyl chloride-polybutadiene blends (PVC-PBD), though the cause is different inhomogeneity from the crystalline polymers. On the other hand, as the single relaxation process of ionic motion was observed in plasticized polyvinyl chloride with dioctyl phthalate (p-PVC), polyethylene terephthalate (PET), polychlorotrifluoroethylene (PCTFE) and polyvinylidene fluoride (PVDF), the structure of the non-crystalline parts of these polymers is considered to be homogeneous. [2]- [5]

In this study, the above knowledge about the inhomogeneity of the free spaces in the non-crystalline parts is examined experimentally from the point of view of static structure by the experiment of the X-ray diffraction (XRD).

The electrical measurement was made by the method of BDS by using Schlumberger SI1260 Impedance Analyzer with an amplifier of Keithley428. The experiment of XRD was made by Malvern Panalytical diffractometer (X'Pert PRO MPD model pw 3040/60) using Cu Ka (l = 0.154 nm) irradiation at a scan rate (2u) of 0.02 °/ s and a 2θ range of 5–80 °operated at 40 kV and 30 mA. The samples are melt-crystallized film of LDPE, p-PVC, PET and PCTFE. The thickness of each film is the order of 0.1mm.

The experimental results was analyzed and summarized by a two dimensional plots of the logarithm of conductivity relaxation time [1] against the crystallinity. This plots shows tendency of the linear relationship between the conductivity relaxation time and the crystallinity with a positive slope. Consequently, it is suggested that the inhomogeneity of the non-crystalline parts from the point of ionic motion corresponds with that of the experimental result of RDF.

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P1

Polymorphism of crystalline alcohols under nanoscale confinement

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Normal alcohols exhibit a series of solid-solid phase transitions prior to melting and high heat of fusion making them candidates for thermal energy storage.[1] At low temperatures, depending on the number of carbon atoms (n), longer alcohols ($n \geq 11$) exhibit two monoclinic crystal phases, β (odd n) or γ (even n). These phases differ in the tilt of the long molecular axis with respect to the normal layer of the lamellar structure. On heating, the low-temperature phase undergoes a transition into the α-phase (also known as the rotator phase[2]). The unit cell of the α-phase is reported to be monoclinic [1,3] or hexagonal. [4] Within the α-phase the molecules perform hindered rotation or flips about their long axis between three equal orientations. In this study, [5] we investigate the polymorphism of crystalline alcohols with a number of carbon atoms, n, ranging from 6 to 12. The phase transformations and melting temperatures of the bulk alcohols are studied by both Dielectric Spectroscopy and Differential Scanning Calorimetry measurements. The α-phase is present in all alcohols. At lower temperatures this phase transforms into the β- or γ-phase for odd or even n, respectively. The contributions per methylene group and of the chain end groups in the heat of fusion and in the change of entropy during melting are extracted by using certain restrictions. The much higher melting temperatures of n-alcohols than in the respective n-alkanes are justified by the molecular order of alcohols in the liquid phase due to hydrogen bonds. Next, we construct the effective phase diagrams under confinement, and investigate the stability of crystal phases. In pore sizes below 200 nm the supercooling effect is strong. The melting temperatures of confined alcohols can be described by two Gibbs-Thomson equations for larger and smaller pores. In addition, we calculate the interfacial energy between solid and liquid, σ_{sl}, corresponding to the melting under weak and strong confinement. We find that confinement strongly affects the interfacial energy. In the smaller pores σ_{sl} is significantly reduced compared to the larger pores (weak confinement). Moreover, the study of the dynamics in shorter alcohols reveales that the dynamics is distinct within the different phases. In general, the more ordered the phase the higher the activation energy. Finally, the effect of alumina pores surface treatment by silanization is studied. The activation energies of the dynamic processes increase compared to the native AAO suggesting a better arrangement of the molecules within the crystal phases.

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P2

Dynamics of Hydrogen bonds and related structures in glass forming liquids

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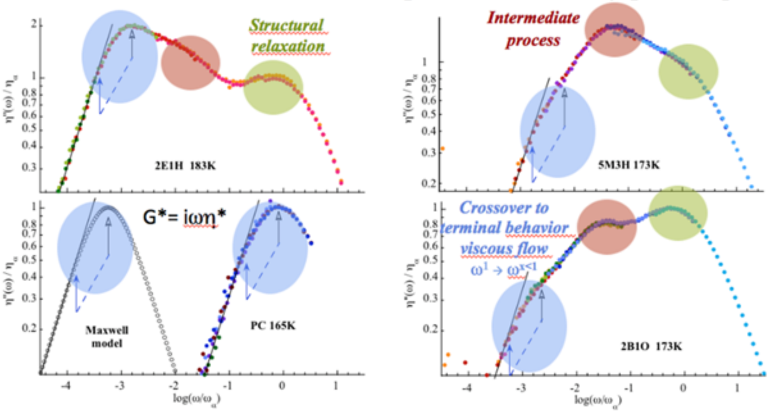
The presence of hydrogen bonds (HB) introduces further complexity on the dynamics of glass forming liquids. A paradigmatic example is that of monoalcohols MA: as a result of HB interaction molecules order in a particular way and create patterns producing mesoscopic features in the static structure factor and rich phenomenology and dynamics that still is far from being completely understood. In recent years there has been a substantial progress on the understanding of fundamental aspects of the so-called 'Debye' relaxation in MA and its relation with supramolecular structures created by HB [1]. The observation of this process by techniques other than dielectric spectroscopy remained elusive for a long time but the detection of slower processes than the structural relaxation by other techniques is opening new perspectives [2-4]. In this line, our group has recently resolved a third rheological contribution not reported before for MAs with characteristic times between the a-relaxation and the Debye process [5]. In our view, the intermediate contribution would reflect HB exchange dynamics at the chain-like aggregates proposed in the Transient Chain Model for the Debye relaxation [6]. This intermediate rheological process seems not to have a counterpart in the dielectric response. However, we have found indications that HB exchange could explain the observed dielectric non-exponential Debye-processes with distributions of times reported for some mono-alcohols [7]. Clarifying the posible contribution of HB switch dynamics to the dielectric response of glass forming systems would also help to shed light on the recent debate opened around the contribution of cross-correlations (intermolecular interactions!) on the dielectric response of relatively polar liquids.



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P3

Origin of Apparent Slow Solvent Dynamics in Binary Mixtures

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Due to their size disparity, the dynamics of solvent molecules in a soft confinement of polymer chains can be faster by several orders of magnitude compared to the polymer matrix. Despite these observations, past research suggests that a fraction of the solvent contributes to the slow dynamics on the timescale of the polymers. By combining depolarized dynamic light scattering and molecular dynamics simulations, we show that long-lived solvent−solvent cross-correlations cause these slow solvent contributions. They originate from the energy landscape that the solute imprints onto the neighboring solvent, leading to enhanced correlations between the positions and orientations of different solvent molecules until the solute relaxes. This mechanism explains the discrepancies found between the results of techniques probing collective and single-particle dynamics, such as dielectric and nuclear magnetic resonance spectroscopy. Our findings shed new light on how solvents behave in the vicinity of macromolecules or soft confinement and are of relevance for materials ranging from polymer-plasticizer systems to hydrated proteins.

P4

Structure of confined supercooled water: size does matter.

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Confinement in mesoporous materials is a well-established technique to supercool water into No-man's land. Crystalline materials such as MCM-41 (1) or MOFs (2) allow a very precise control of confinement, but usually confinement down to 2 nm is required to prevent crystallization. Whether water maintains its bulk properties in such strong confinement is still debated (2). Here we investigate the influence of pore size on the structural properties of supercooled water confined in mesoporous silica-gel pores with sizes ranging from 9.0 nm to 2.2 nm. The amorphous structure of silica gel inhibits crystallization even in the 6 nm pores, thus allowing us to probe supercooled water under weaker confinement. We find that in the 2.2 nm pores HDL-like water is the dominant component at all temperatures, while a structural transition from HDL to LDL-like water takes place in the 6 nm pores at $T \simeq 230$ K. These results suggest that the properties of confined water strongly depend on the size of the confining environment, with a cross-over as the confinement size becomes comparable to the characteristic length of the structural fluctuations of water.

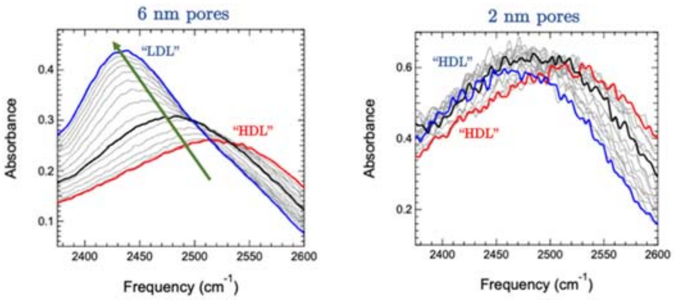

Figure 1: Temperature-dependent FTIR spectra of the OD-stretch band of water confined in 6.0 nm and 2.2 nm pores. The 290 K spectra are shown in red, the 228 K spectra in black (approximate midpoint of transition) and the 105 K spectra in blue. Picture taken from [3].

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P5

Ionic Liquids during Imbibition in Nanopores

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Ionic liquids (ILs) represent an extended family of salts composed solely of organic cations and inorganic/organic anions, with melting points below 100 °C. Their high ionic conductivity, high thermal and electrochemical stability, nonflammability, nonvolatility, and a wide temperature range of the liquid state, make ILs ideal substitutes for conventional organic electrolytes in electrochemical systems, especially in lithium batteries and supercapacitors.

In order to improve the energy density of electrochemical devices, the use of porous materials as electrodes is a hotspot of current research. To this end, it is crucial to understand the behavior of ILs in confined space. In our research, we employ the imidazolium-based cation with different anions (Cl^-, Br^-, I^-, BF_4^-, PF_6^-, $TFSI^-$) in the investigation of the effect of anion on the conductivity under nanometer confinement within self-ordered nanoporous alumina (AAO). In particular we address the following open questions: What are the relevant length scales involved (Bjerrum, Debye, Gouy-Chapman, pore radius, glass temperature)? What is the structure of the confined ILs relative to the bulk? What is their effective viscosity during flow in nanopores? How the ionic conductivity is influenced during and after imbibition?

Based on the present results, the conductivity of ionic liquids during and after flow in nanopores is reduced relative to the bulk and furthermore it decreases with increasing degree of confinement. The anion size plays also a role in the conductivity reduction. This situation for ILs is distinctly different from polymer electrolytes investigated earlier by us.[1] There, the tendency of polymers chains for adsorption drives ions to the pore walls thus reducing the ionic conductivity.

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P6

Effects of the clay loading on conductivity behavior of sulfonated polyetheretherketone (s-PEEK) and crosslinked polyvinyl alcohol (XL PVA) composite films

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In this work we study composites of 50-65% sulfonated polyether ether ketone (s-PEEK) and 20% crosslinked polyvinyl alcohol (XL PVA); reinforced by a commercial montmorillonite at various Wt%. We aim to use our composites as electrolyte membranes for fuel cells. Obtained films were characterized by X-ray diffraction, differential scanning calorimetry, direct current conductivity at various relative humidity rates and dielectric measurements between 10^{-1} Hz and 1 MHz in the temperature range from 10 to 220°C. XRD Results show the presence of characteristic peaks of the MMT, with gradual reduction of the grain size of ordered regions in the polymer matrix after the sulfonation, the crosslinking and/or the clay addition. For both polymers, the cited three operations increase the glass transition, indicating the lowering of the polymer chain mobility. This affects also the proton conductivity σ_{dc} which decreases due to these modifications. In all cases we find acceptable fit of $\sigma_{dc}(T)$ by an Arrhenius law with activation energy compatible with ionic transport and depends on the clay Wt%. The Ac conductivity is well fitted by the Jonscher law with a dominant effect of the electrode/sample polarization at low frequencies; this effect appears at higher temperatures. From the high frequency power law we deduce the dominance of the correlated barrier hopping mechanism (CBH). By the dielectric modulus we show the presence of two non-Debye relaxation modes attributed to interface polarization and charge hopping processes.

P7

Proton conductivity and dielectric relaxation of sPEEK and Basolite® F300 composites

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Sulfonated Poly(Ether Ether Ketone) (sPEEK) is a acidic polymer, which is used as proton exchange membranes in Proton Exchange Membrene Fuel Cell (PEMFC).The high proton conductivity and its chemical stability are important for the application in Fuel Cell. The additions of Metal-Organic Frameeworks (MOF) in the polymeric structure are important for increasing the proton conductivity and chemical stabitity, improving the performance of the fuel cell membrane. MOF are crystalline materials based on the combination of transition metal ion coordinated to multidentate organic ligads to form three-dimensional crystalline strutures. Basolite® F300 is an example of MOF and chemically is iron 1, 3, 5-benzenetricarboxylate.

In this work, we have prepared one serie of membranes based on sPEEK and Basolite® F300 composites. These membrenes have been characterized by Broadband Dielectric Spectroscopy in wet conditions where high proton conductivity was observed. These membranes in dry conditions have a different dielectric behavior. Proton conductivy contribution in dielectric spectrum is negligible at high frequency and dipolar contribution is predominante. These dry membranes have been characterized one dielectric relaxation, which is affected by the presence of Basolite® F300 in the composite.

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P8

High proton conductivity of the homo- and heterometallic oxalate-based compounds of different dimensionality

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Recently, proton conductivity of the metal-organic frameworks (MOFs) has been considered as a new functionality, mainly due to their crystallinity, high porosity, designability and tunability in structure and properties, and potential application in solid-state electrolytes. The simplest method to introduce proton carriers is to include a counterion such as hydronium (H_3O^+), ammonium [NH_4^+, $(CH_3)_2NH_2^+$,...] or an anion (SO_4^{2-}), resulting in charged compounds. The counterions form the hydrogen-bonding arrays with the guest water or other constituents of compound, creating proton-conducting pathways.[1,2]

A very important role in the design and synthesis of multifunctional materials belongs to the oxalate moiety, $C_2O_4^{2-}$, due to its various possibilities of coordination to metal centers and its ability to mediate electronic effects between paramagnetic metal ions. The proton conductive materials must have good water and chemical durability under the influence of humidity and temperature, and in general, oxalate-based systems have regular structures and stable frameworks. In addition, the oxygen atoms of the oxalate group can construct complex hydrogen-bonded networks, which are more than suitable for proton conduction. Although high proton conductivity is often found in two-dimensional (2D) and three-dimensional (3D) oxalate-based compounds, the low-dimensional structures can have excellent proton conductivity properties *via* the hydrogen-bonding chain because a low void space can be advantageous for proton hopping.[2,3]

We explored the proton conduction behaviour of three oxalate-based compounds of different nuclearity and dimensionality, prepared and characterized in our group: homometallic discrete mononuclear $(NH_4)_2[Fe(H_2O)Cl_3(C_2O_4)]\cdot H_2O$ (**1**) and one-dimensional (1D) $\{[NH(CH_3)(C_2H_5)_2][FeCl_2(C_2O_4)]\cdot H_2O\}_n$ (**2**), and 2D heterometallic $\{[NH(CH_3)_2(C_2H_5)]_8[Mn_4Cl_4Cr_4(C_2O_4)_{12}]\}_n$ (**3**). The proton conductivity of **1**, **2** and **3** at 298 K increases with increasing relative humidity (RH), achieving values of 2.17×10^{-3} $(\Omega\ cm)^{-1}$ at 74% RH, 2.70×10^{-4} $(\Omega\ cm)^{-1}$ at 93% RH and 1.6×10^{-3} $(\Omega\ cm)^{-1}$ at 90% RH, respectively. From the obtained values, it can be confirmed and concluded that the amount of protonated proton carriers acting as proton donors, the number of non-protonated sites acting as proton acceptors, and the efficient proton transport pathway made of H-bonding network are extremely important for obtaining materials with high conductivity, rather than their dimensional arrangement.

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P9

Non-equilibrium effects of polymer dynamics under nanometer confinement: Effects of molar mass and architecture

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A series of linear and star-shaped *cis*-1,4-polysiorpenes with different molar masses (M_n) were studied by dielectric spectroscopy within nanoporous alumina templates with a diameter, *d*. We have employed two cooling protocols: (i) abrupt cooling followed by prolonged annealing and (ii) cooling at various effective rates (β) to the same final temperatures, to show that the polymers regain the bulk dynamics with time, while the dielectric strength ($\Delta\varepsilon$) increase.[2] The kinetic pathways to equilibrium are compared. Surprisingly, the studies revealed that the polymers, irrespective of the thermal protocol, are out of equilibrium even at temperatures of $T_g^{bulk} + 20$ K, and this despite the weak confinement. The change of the relaxation times and of the dielectric strength are discussed in terms of changes in density, adsoprion and of dipole-dipole interactions. The latter, play a dominant role during annealing.[3] Lastly, the characteristic recovering (equilibrium) time of the bulk dynamics (t_{eq}), during annealing, is studied as a function of topology (*f*; number of arms), degree of confinement ($2R_g/d$; R_g is the radius of gyration) and arm molar mass[4] ($t_{eq} \sim M_n^{2.13}$ at $T - T_g^{bulk} \sim 10$ K). We report that both the T_c and t_{eq} increase with the increasing functionality.

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P10

Combined dielectric and infrared spectroscopy on thin films of polyethylene terephthalate.

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Dielectric and infrared spectroscopy are combined to study the molecular dynamics of a 0.5 μm thick foil of polyethylene terephthalate. In the dielectric measurements, (frequency range 10^{-1} Hz – 10^{6} Hz, temperature 210 K – 390 K) two broad relaxation processes are observed. IR-measurements in the same temperature range allow tracing in detail the evolution of the bands representing the carboxylic acid, the (C-O), the O-H moieties and the terephthalate ($OOCC_6H_4$- COO) unit as a whole. By that, the interplay between inter- and intra-molecular interactions is unraveled in detail.

P11

Confinement induced relaxations and phase behavior of a nanoconfined ionic liquid crystal

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Liquid crystalline mesophases in nanoconfinement exhibit intriguing phase transition behaviors and relaxation dynamics. Here in, we investigate the molecular dynamics and electrical conductivity of a linear shaped guanidinium based ILC confined in self-ordered nano porous alumina oxide membranes of pore size ranging from 180nm down to 25nm by employing broadband dielectric spectroscopy (BDS) and calorimetry. Calorimetric investigation reveals a complete suppression of the columnar – isotropic transition, while the plastic crystalline – columnar transition temperature decreases with inverse pore size and deviates from the Gibbs – Thomson equation.

For the bulk case, BDS detects two relaxation modes in the crystalline phase, the γ relaxation and the α_1 relaxation, and two relaxation modes in the columnar phase, the α_2 and α_3 relaxation. For the confined case, all relaxation modes slow down compared to the bulk. However, for the least pore size (25 nm), the α_2 relaxation is absent. We discuss the possible molecular origins of the different relaxation modes observed. For the bulk ILC, a clear jump of 4 orders of magnitude in the absolute values of DC conductivity occurs at the transition from the plastic crystalline to hexagonal columnar phase, for the confined ILC, this transition is smooth. DC conductivity is reduced for the confined case, except for the 25nm, where the values is similar to the bulk.

P12

Water dynamics at biological surfaces studied by ^{2}H NMR and BDS

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The dynamics of water near biological surfaces and the interactions of water and biomolecules are fundamental for understanding chemical processes and biological functionality. To reduce the complexity found in hydrated proteins, we investigate a much simpler model system containing dipeptides in aqueous solution.

Explicitly, we study water (D_2O) dynamics near the hydrophilic N-acetyl-glycine-methylamide (NAGMA), serving as a model protein backbone. The NAGMA concentration is varied from hydrated powders to highly concentrated solutions. Furthermore we varied the structure of the dipeptide, by using different amino acid residues, namely N-acetyl-leucine-methylamide (NALMA) and N-acetyl-lysine-methylamide (NAKMA).

We use ^{2}H nuclear magnetic resonance (NMR) to characterize the microscopic rotational dynamics and gain access to correlation times in a large time window.

Depending on the NAGMA concentration, we observe partial freezing of water, but there always remains a liquid hydration layer near the dipeptide surfaces.

Using ^{2}H line-shape analysis and spin-lattice relaxation, we disentangle the signal contributions of the two water fractions from each other and from those of the dipeptide, providing us with correlation times for liquid hydration water between 10^{-12}s and 10^{-6}s. Moreover, we extend the accessible timescale to slower dynamics (10^{-6}s to 10s) with broadband dielectric spectroscopy (BDS) and ^{2}H NMR stimulated-echo experiments.

Our studies show that the dynamics of water differs at the surface of different dipeptides. At high temperatures the temperature dependence is similar to other mixtures of water and smal biomolecules and at low temperatures we find an Arrhenius like temperature dependence of the correlation times with activation energies of ~0.4eV.

P13

Charge and heat transport in halogen-free flame retarded polypropylene compounds

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Polypropylene (PP) is rising as an alternative polymer for the manufacture of cable protection conduits, replacing traditional PVC pipes. However, PP needs to be flame retarded in order to comply with the current stringent EU safety regulations regarding halogen content, smoke density and corrosiveness of released gases (EN50642, EN61034-2, EN60754-2). Herein, three flame retarded (FR) PP formulations (FR1-FR3) were developed by the incorporation of commercial FR additives into PP, by means of melt-compounding. A high impact strength heterophasic co-polymer (Repsol ISPLEN PB131N5E) was selected as reference PP. The additives used comprised: ammonium polyphosphate, a polymeric triazine derivative (PPM triazine HF) and a N-alkoxy hindered amine resulting in halogen-free formulations FR1 and FR2. The loading level for FR1 and FR2 additives in PP was 25 and 20 wt% respectively. For the low-halogen formulation FR3 (Br<1500 ppm) a mixture of aluminum hypophosphite (AHP) and a phosphorous-bromine salt was used with a low loading level of FR3 (only 2 wt%). All compounds were found to comply with the aforementioned European standards [1].

The focus of this work lies on the investigation of the effects of the additives on the molecular mobility of the compounds and in the corresponding dielectric and thermal conduction properties by employing Broadband Dielectric Spectroscopy, Thermally Stimulated Depolarization Currents and Thermal Conductivity measurements. Our results show that the compounds with relatively high content of additives (FR1 and FR2) exhibit enhanced molecular mobility, which is related to the glass transition of PP, and remarkable charge transport properties due to the high conductivity of the additives. Interestingly, the enhanced charge transport properties are not accompanied by an increased heat transfer capability in the compounds: all compounds are characterized by smaller values of thermal conductivity than neat PP. These findings are discussed in terms of heat transfer mechanisms in the polymeric matrix and alterations in the semi-crystalline morphology of the compounds.

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P14

Heat capacity and the dynamical crossover of supercooled water in confinement

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Bulk water unavoidably crystallizes in the temperature range from 150 to 235 K ("no man's land")[1]. However, water in solutions (soft confinement) or water confined in porous materials (hard confinement) can remain amorphous, i.e. not crystallized, as long as there are no water clusters larger than 2 nm[2]. The water dynamics in confinement has been extensively studied in the literature. In hard confinements, the temperature dependence of the water relaxation time shows a crossover between two different behaviors at a certain temperature[3]. However, there are different interpretations related to the nature of that crossover. In contrast to soft confinements, in which a glass transition is detectable by a standard differential scanning calorimeter (DSC) associated with Tg of the solute, in hard confinements, standard DSC measurements only show a flat signal during the heating scanning, when crystallization is avoided. Despite this, the heat capacity is one of the most essential thermodynamic quantities for looking into the hydrogen-bonding properties of low-temperature water[4].

In this work, by using temperature-modulated DSC, we analyze the heat capacity (c_p) of water on two types of rigid confinements of different nature: porous borosilicate glass (with a rigid surface) and the same glass but filled with silica gel, which has a softer surface. Both confinements were studied at different humidity levels ($h = 0 – 47$ wt%).

Above h = 6.4 wt% for both types of confinements, water crystalized during the cooling scan and showed a melting peak (230 – 260 K) during the heating scan. In the case of water confined in porous borosilicate glass and for all water contents, the heat capacity exhibited a flat signal. In contrast, water confined in porous borosilicate glass filled with silica gel shows a cp deviation around ~ 180 K. This temperature overlaps with the temperature where the dynamical crossover is produced as obtained by broadband dielectric spectroscopy.

Here, we will discuss the interpretation of the c_p deviation as a possible glass transition of the interfacial water that remains amorphous under confinement and its relation with the dynamical crossover observed by BDS.

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P15

Dynamics of adsorbed water on hydrogels for water remediation

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The water contamination problem demands sustainable, scalable, and easy-to-implement solutions. In recent years, different methods for cleaning water have been explored; however, adsorption is one of the most convenient wastewater purification techniques for removing pollutants from contaminated aqueous media because of its relatively straightforward design, cost-effectiveness, operation, and energy efficiency[1]. We have developed a new generation of pectin-based hydrogels to remove heavy metals from contaminated water through adsorption. Adsorption occurs when a contaminant molecule in water binds to the surface of the hydrogel[2]. Therefore, studying the adsorbed water inside the hydrogel is one of the factors to consider that will help to increase the efficiency of the water remediation.

In this work, we show a general description of the hydrogel preparation and the protocol for water adsorption. The variation of the hydrogel structure as a function of hydration was studied using differential scanning calorimeter (DSC) and X-ray diffraction (XDR). On the other hand, the dynamics of the adsorbed water were analyzed by broadband dielectric spectroscopy (BDS). We determined that dry hydrogel loses part of its crystalline structure with hydration. However, the remaining crystalline part of our hydrogel is where the adsorbed water is located in the form of confined water. For humidity levels above 25 wt%, the relaxation times of the water process were similar to that for water in MCM-41[3]. Therefore, we conclude that our hydrated pectin-based hydrogel forms pore similar to hard confinements where the adsorbed water is located.

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P16

Relaxation dynamics and charge transport in a proton-conducting deep eutectic solvent

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Deep eutectic solvents (DESs) are an emerging class of green solvents characterized by significant reductions in melting points compared to those of respective precursors and they are promising for applications as inexpensive "designer" solvents showing a host of tunable physicochemical properties.[1], [2] In our previous research, the solvation effect of 1H-1,2,4-triazole ([TR]) towards imidazolium methanesulfonate ([Im][MS]) was studied by blending them with different molar ratios and the deep eutectic component ([Im][MS] vs. [TR] = 1 : 3) was obtained with a reduced melting point of around 78 °C.[3] In addition, we also pointed out that [TR] was effective to dissolve and dissociate [Im][MS] without protonation of [TR]. [3] Nevertheless, the studies were limited to the liquid state (above the melting points), and thus the charge transport in the solid state was neglected.

In this work, the deep eutectic component is revisited in terms of relaxation dynamics, charge transport and phase transitions by means of broadband dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC). Both BDS and DSC reveal that this blend undergoes a glass transition, followed by cold crystallization and finally melting upon heating from −150 °C to 100 °C. The temperature dependent conductivity relaxation time shows a well-defined crossover from Vogel–Fulcher–Tammann (VFT) type to Arrhenius behavior in the vicinity of the glass transition temperature. Moreover, the "conduction – free" dielectric loss reveals two distinct relaxation processes, denoted as slow relaxation and fast relaxation, which can be well modelled by two Cole–Cole functions. The relaxation times of them is separated by about three decades over the whole temperature range. The fast relaxation is coupled to the charge transport and is assigned to the ring reorientation of imidazolium cations based on the comparable activation energies reported by Goward et al. using solid state NMR spectroscopy.[4] Interestingly, the slow process also follows the temperature dependence of the conductivity closely, i.e. the Debye-Stokes-Einstein (DSE) equation is fulfilled, implying that the slow relaxation is related to charge transport at a larger length scale and time scale.

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P17

Study of the glass transition and the bond exchange reaction in Poly(thiourethane) covalent adaptable network through broadband dielectric spectroscopy

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Polythiourethanes (PTUs) are a covalent adaptable networks (CAN) polymers, which include reversible chemical bonds in the 3D structure. This type of chemistry allows these polymers displaying good, flexibility, optical transparency, or a more homogeneous structure. The origin of the networks' vitrimeric-like behavior in PTUs is attributed to the trans-thiocarbamoylation process. In this work, this covalent adaptable network with a fast exchange mechanism is sought in synthesizing containing dibutyltin dilaurate DBTDL in different percentages (1% and 4%), that were labelled HDI-S3-DBTDL 1% and HDI-S3-DBTDL 4%, respectively.[1,2,3] The dielectric spectra of the poly(thiourethane) network, HDI-S3 is complex, and at higher temperatures three relaxations were observed: the α_{Tg} relaxation relates to the glass transition, which is overlapped, by the α^* relaxation associated to the bond exchange reaction. Finally, the ρ process is produced by mobility of the charge carriers. Varying the catalyst concentration does not affect the low-temperature relaxation, nor the glass transition. However, as expected, the bond exchange reaction is facilitated in the HDI-S3-DBTDL 4% sample, as shown in **Figure 1.**

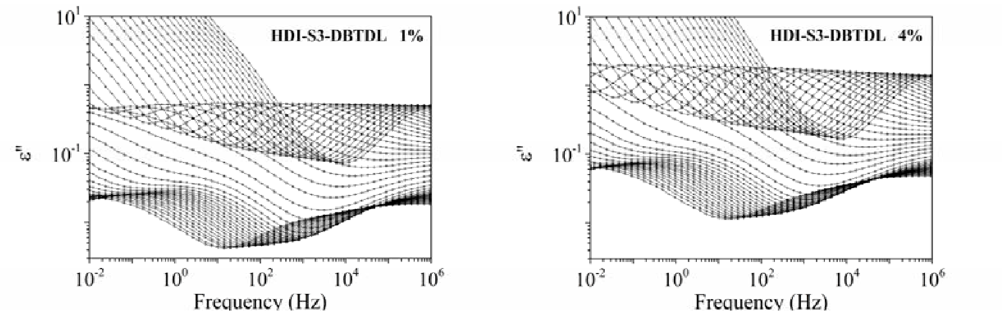

Figure 1. Isothermal curves for the HDI-S3-DBTDL 1% and HDI-S3-DBTDL 4% samples between 255.65K and 373K.

In this work, the characterization of the associative or dissociative of a covalent adaptable network nature of a polymer is also addressed. In many works, the decrease in viscosity is assessed through dynamic mechanical analysis (DMA). However, in broadband dielectric analysis the DC conductivity (σ_{DC}) is its counterpart. Consequently, the Jonscher's model is used to determine the DC conductivity (σ_{DC}). The relationship between the temperature and the DC conductivity (σ_{DC}) determines the dissociative nature of this covalent adaptable network.

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P18

P(VDF-TrFE) Copolymer Dynamics as a Function of Temperature and Pressure in the Vicinity of the Curie Transition

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We report on the phase behavior and the respective dynamics in random P(VDF-TrFE) copolymers using standard and temperature-modulated differential scanning calorimetry, X-ray diffraction, and a combination of temperature- and pressure-dependent dielectric spectroscopy measurements.[1] Depending on the copolymer composition, the coexistence of three/four weakly ordered phases was identified in the vicinity of the Curie temperature (T_c). With respect to the dynamics, we demonstrate that the segmental dynamics - reflecting the relaxation of constrained amorphous VDF segments at the crystal/amorphous "phase" - can be used as a marker of the Curie transition. The corresponding segmental relaxation freezes at about 50 K above the lower liquid-to-glass temperature associated with the freezing of amorphous segments away from the interface. Pressure-dependent dielectric measurements provided quantitative insight into (i) the molecular origin of the segmental processes (by employing the pressure sensitivity of relaxation times and the pressure coefficient of the respective T_g's), (ii) the nature of the phase transition at T_c, as well as (iii) information about the stability of phases under the variation of temperature and pressure (through the T-P phase diagram). We show that T_c increases linearly with pressure and is accompanied by small volume changes, implying a *weakly first-order* thermodynamic transition. Furthermore, pressure stabilizes the ferroelectric phase over a broader temperature range. This could extend the operating temperature range of ferroelectric devices based on P(VDF-TrFE) copolymers.

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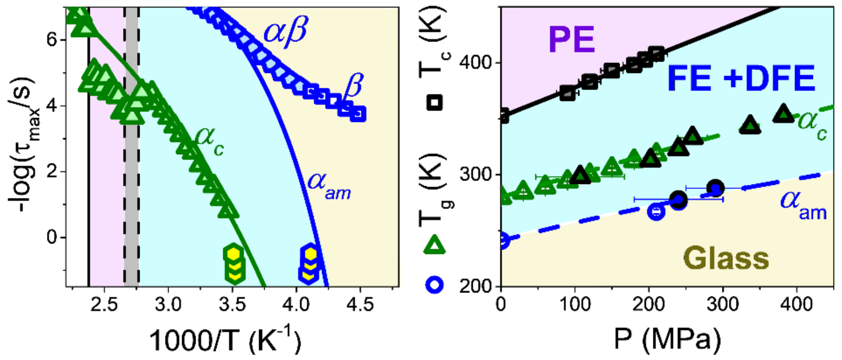

P19

^{2}H-NMR studies on the dynamics of supercooled water in porous boro-silicate glasses

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Water is one of the most intriguing liquids. Despite the paramount importance, the properties of water are not fully understood to this day. Especially the dynamics of water in different types of confinement is an extensive research topic. Previous studies on supercooled interfacial water in various confinements, hard and soft, found a common change in the temperature-dependent behaviour of correlation times [1,2]. However, the details of the dynamic crossover depend on the rigidity of the matrix. It is the subject of controversial discussions whether or not this phenomenon is indicative of a liquid-liquid phase transition of water [3]. To learn more about this phenomenon, we combine broadband dielectric spectroscopy (BDS) with ^{2}H nuclear magnetic resonance (NMR) to study water dynamics in a new combination of hard and soft confinements, explicitly porous boro-silicate glasses filled with silica-gel. This allows a comparison of the effects of rigid and soft surfaces within the same material.

BDS shows that the dynamic crossover occurs for samples with silica-gel in the glass matrix whereas an Arrhenius law is observed in the pure glass matrix for all temperatures. Performing ^{2}H NMR measurements for different water contents, we follow the evolution of not only the time constants but also the motional mechanism across the dynamic crossover. We find that the NMR and BDS correlation times agree. Moreover, the 1D and 2D NMR line shapes indicate that water reorientation is virtually isotropic both above and below the dynamic crossover.

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P20

Biomass-derived polymers: dynamic fragility and gas-barrier properties

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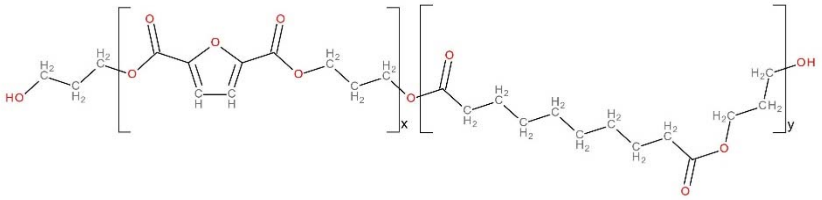
In this work, we present our study on the relaxation dynamics of a series of randomcopolymers based on bio-friendly comonomers with interesting gas barrier properties[i]. We analyze the relaxation response in the glassy and ultraviscous regime of poly(trimethylene furanoate/sebacate) random copolymers via broadband dielectric spectroscopy. Our results reveal lower values of dynamic fragility in comparison to popular polyesters widely used in industry, such as poly(ethylene terephthalate). Since these copolymers show a lower transmission rate for oxygen and carbon dioxide in comparison to poly(ethylene terephthalate), it is plausible to claim that they adopt a better and more compact chain packing as compared to PET. The present contribution underscores the relevance of a tentative correlation between dynamic fragility and the gas transport properties of polymeric matrices that deserves to be tested more carefully soon. We also discuss on different equations (phenomenological and theory-based approaches) for fitting the temperature-evolution of the alpha relaxation time.
The figure below presents the repeat unit of poly(trimethylene 2,5-furandicarboxylate-co-trimethylene sebacate) random compolymer and the specific compositions studied in this work.



PTF-co-PTSeb

PTF composition (mol %)
100
95
85
75

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P21

Dynamics of supercooled water in a metal-organic framework

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Understanding the properties of water in confinement is an important task due to its many applications in life science and technology. The complex behaviour of water, however, leaves many questions still unanswered, some owing to the inaccessibility of the ‘no man’s land’ for the bulk liquid. In this region between 150 and 235 K water immediately crystallizes, making experiments on bulk water very challenging.

Nano-confinement reduces the crystallization temperature of water to lower values and supercooling to temperatures even below the homogeneous nucleation temperature is possible. Different experimental methods show a dynamic crossover in the supercooled regime, the origin of which is controversially discussed [1]. Our previous studies using ^{2}H NMR and mesoporous silica as hard confinement revealed two dynamically distinguishable fractions of water coexisting within the pores at sufficiently low temperatures. These fractions corresponded to a liquid interfacial water layer and a distorted solid phase in the pore centre and suggested the crossover not being caused by a liquid−liquid phase transition but rather a change from bulk-like to interface-dominated dynamics [2], [3], [4].

The existence of the second solid phase, while posing many interesting questions, hampers the more detailed analysis of liquid water inside confinement. To take a closer look we choose a metal-organic framework, namely MFU-4l (**M**etal-organic **F**ramework **U**lm-4-l(arge)), which offer several advantages compared to silica nanopores. MFU-4l forms a 3D network of spheric pores with well-defined diameters (1.2 and 1.9 nm) and less hydrophilic surfaces than silica nanopores [5]. BDS experiments by Fischer et al. [6] show a similar behaviour to our previous studies employing MCM-41 with a crossover around 180 K.

Using ^{2}H NMR we are able to probe local and long-range water dynamics over a broad temperature and dynamic range. We find only one liquid water species and no freezing inside the pores. Despite the absence of freezing we observe a change in the temperature dependence of correlation times from VFT to Arrhenius behaviour and explore the shape of the spectral density with different NMR methods.

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P22

Impact of Intra- and Intermolecular Cross-Linking Density in Dielectric Properties of Methyl Methacrylate-based Copolymer

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Broadband dielectric spectroscopy (BDS) was used to study the effects of Intra- and Intermolecular cross-linking of polymer chains in the segmental dynamics. Copolymer composed of Methyl Methacrylate (MMA) and Acetoacetoxyethyl methacrylate (AEMA) at different cross link densities were studied. The intermolecular cross-linking was prepared from adding cross-linker to the dilute solutions of copolymer promoting the formation of the so-called the single chain nanoparticles (SCNPS). Intermolecular cross-link was promoted by using high copolymer concentration in solutions when adding the crosslinker. The dielectric spectra show electrical in all cases a conductivity contribution and three relaxation processes: a slow relaxation (α) and two fast relaxations (β and γ). Cross-linking density affects clearly the slow process, but the fast processes are less affected. The glass transition temperarture increases with increase of cross-linking density, and consquently the α-relaxation times also increase. There was also an increase of the dynamic heterogeneity and the relaxation intensity when increasing the cross-linking density in part attributed to the additional contributions from the crosslinking moiety. Clear differences in the dynamic heterogeneities where observed when comparing intra- and intermolecular cross-linking, which are associated to the sparse internal structure of the collapsed single chains obtained by intramolecular cross-linking.

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Calcium ferrite, ecofriendly synthesized, for energy storage applications

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This work proposes the synthesis of calcium ferrite ($CaFe_2O_4$) particles for application in electrical energy storage. The ferrites were prepared using calcium and iron nitrates as raw materials, by a protein sol-gel method, using coconut water, an ”eco-friendly” and sustainable route. The powders obtained were pressed in disks and heat-treated at temperatures between 400 to 1000 ºC. The samples were subjected of structural, morphological and electrical characterization. $CaFe_2O_4$ is present in the samples treated above 700 ºC. However, at 800 and 1000 ºC heat-treated present $CaFe_2O_4$ as a crystalline single phase without secundary phases. From the morphological analysis, $CaFe_2O_4$ grains with an average size of 0.3 µm (sample 800 ºC) and 1.2 µm (sample 1000 ºC) were obtained.

Regarding the electrical measurements, the most promising sample is the one treated at 1000 ºC since it presents high dielectric constant (ε’=87132) and dielectric losses of 1.79, at 300 K and 100 Hz.

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Dynamics of Poly(cyclohexene carbonate) as a Function of Molar Mass

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Carbon dioxide, the main greenhouse gas, offers exciting possibilities for polymer synthesis due to its low cost and natural abundance.[1-2] Stereoregular poly(cyclohexene carbonate) (PCHC) homopolymers were prepared via copolymerization of cyclohexene oxide and carbon dioxide (CO_2) using (*R,R*)-(salcy)-CoCl and bis(triphenylphosphine)iminium chloride as a catalyst.[3] The homopolymers had molar masses in the range of 4800 $g\cdot mol^{-1}$ to 33000 $g\cdot mol^{-1}$. PCHC is viewed as rigid and biodegradable, an alternative bio-based polymer to polystyrene. We employed differential scanning calorimetry and dielectric spectroscopy, the latter as a function of temperature and pressure, for the thermal properties and the molecular dynamics, respectively. The segmental dynamics in the vicinity of the liquid-to-glass temperature was very complex. The dual segmental processes were inseparable by decreasing temperature or by increasing pressure. Based on DFT calculations of the dipole moment, they were ascribed to different stereo sequences of the PCHC backbone. The limiting glass temperature, T_g, for very high molar masses was ~ 125 °C. The high T_g value obtained herein well justifies its application as a CO_2-based alternative for polystyrene in a variety of materials based on block copolymers. Moreover, fragility increased with increasing molar mass with values intermediate to poly(styrene) and poly(cyclohexyl methacrylate). The flexible cyclohexyl group in PCHC undergoing intra-molecular chair-to-chair conversion increases the packing ability and consequently decreases the fragility. PCHC is a brittle material, because it lacks entanglements even for the higher molar masses investigated herein, which is relevant for application as a polystyrene substitute. Within the investigated range of molar masses the dependence of the terminal relaxation times, τ_{NM}, and of the zero-shear viscosity, η_o, on molar mass, M, have respective dependencies as $\tau_{NM}/\tau_{SM} \sim M^{3.2}$ and $\eta_o \sim M^{1.4}$ revealing an intermediate behavior between Rouse and entangled chains.

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^{2}H NMR and BDS studies on water dynamics in amino-acid functionalized silica nanopores

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We investigate water dynamics inside various amino-acid functionalized silica pores with diameters of ~6 nm which serve as model biological confinements. Using these porous systems we are able to compare the influence of individual amino acids on water dynamics under confinement conditions. Specifically, we link basic lysine, neutral alanine, and acidic glutamic acid to the inner surfaces. We use a combination of ^{2}H nuclear magnetic resonance (NMR) and broadband dielectric spectroscopy (BDS) to disentangle the rotational motions of the surface groups and the crystalline and liquid water fractions coexisting below partial freezing. Unlike the crystalline phase, the liquid phase shows reorientation dynamics strongly depending on the modifications of the inner surfaces. In the temperature range of ~200-250 K we gain access to the rotational correlation times of the liquid water phase via spin-lattice relaxation. We observe that the time scale of water reorientation varies by about two orders of magnitude at the different surfaces [E. Steinrücken et al., J. Chem. Phys. 154, 114702, 2021]. Furthermore, we extend the accessible temperature range to lower temperatures with BDS measurements, gaining access to correlation times of both the liquid water phase and the internal ice phase. The studies consistently show that water reorientation is slowest for the lysine functionalization, followed by alanine and glutamic acid and, finally, the native silica pores.

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Surface Functionalized Mesoporous Silica Nanoparticles to Encapsulate Amorphous Fenofibrate

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Spherical mesoporous silica nanoparticles (MSNs) with a narrow distribution of external size around 49 nm and ordered cylindrical pores were synthetized and structurally characterized by SEM and TEM. The surface was posteriorly modified with (3-Aminopropyl) triethoxysilane (APTES) and trimethoxy(phenyl)silane (TMPS) and the density of grafted functional groups was quantified by ^{1}H-NMR. Fenofibrate (FNB) drug, was loaded in unmodified and modifies MSNs, respectively FNB@MSN, FNB@APTES and FNB@TMPS. A posterior washing of the nanocomposites with ethanol revealed that the capacity of FNB retention is clearly improved by the presence of any of the grafted functional groups, which may result useful to attain a long-term release profile.

To investigate the impact of surface functionalization over the drug physical state and molecular mobility, all the prepared composites were thermally (differential scanning calorimetry, DSC) and dynamically (dielectric relaxation spectroscopy, DRS) characterized, and the respective behavior compared with the neat drug.

The tendency of neat amorphous FNB to recrystallize was supressed when it was loaded in ~3 nm pore sizes, indicating that the critical nuclei diameter for FNB crystallization is above that value. Moreover, the onset of the glass transition (T_g) was slightly shifted to lower temperatures when the drug was loaded in unmodified MSN, and modified with APTES composite, while it increased in the case of incorporation in TMPS modified matrix. The former result is justified by a confinement effect due to the interference of incorporating dimensions with the cooperativity length scale of FNB dynamic glass transition; by other side, when FNB is loaded in nanoparticles modified with TMPS, the surface interaction lead to a T_g increase of FNB. Dielectric relaxation spectroscopy confirms these effects and allowed to disclose the calorimetric broad glass transition step in multiple relaxations associated to different FNB populations, from highly mobile in the pore core to anchored at the pore wall.

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Microstructural features of distinct ZnO particles studied *via* high-pressure induced powder X-ray diffraction

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Structural and microstructural features of ZnO particles prepared by different routes were determined by pressure-induced synchrotron powder X-ray diffraction measurements and complemented by the results of optical micrographs showing the morphological diversity of different ZnO polycrystals. In particular, the pressure-induced change in crystallite size and the contributions of internal strain to the mechanical properties of nanocrystalline ZnO were systematically scaled.

A transition from wurtzite to rocksalt phase in ZnO with spherical nanoparticles grown hydrothermally from ethanolic solution resulted in a strong ~21% collapse in unit cell volume at ~17.68 GPa, whereas compression of spindle-shaped ZnO particles prepared in NaOH with calcination treatment led to the formation of an exclusively cubic phase at 13.77 GPa, reflecting a ~20% unit cell volume collapse. Interestingly, the fingerprints of the cubic diffraction patterns in spherical ZnO did not reappear upon decompression from ~29 GPa - the hexagonal structures were preserved beyond the upward transition pressure, whereas in contrast, a very different trend was observed in spindle-shaped ZnO after depressurization, showing a reversible pressure-induced structural transition to single-phase hexagonal symmetry by slowly depressurizing from 15.46 GPa to ambient pressure. These different features point to a rather contradictory revresibility phenomenon that needs to be investigated: why do the phase-pure ZnO samples of the cubic assemblies show different transformation activities at the same pressure ranges? This tricky behavior results from the differences in surface energy between the crystalline phases and the volume collapse ratio. In addition, the particle size significantly affects the pressure range of phase stability and the final ratios of rocksalt and wurtzite phases at ambient conditions in different ZnO samples.

The microstrain response of ZnO particles to applied hydrostatic pressure was investigated up to 30 GPa and revealed that the diversity of ZnO particle size and shape determines the reversibility of wurtzite to rock salt transformation by dictating the microstructure-dependent deformation behavior and ultimately leading to different microstrain responses to hydrostatic pressure.

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Effects of Confinement on the Slow Arrhenius Process in Thin Polymer Films

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An open question in nonequilibrium physics is the search for the mechanism behind fast equilibration in the glassy state, i.e., equilibration processes taking place on relatively short timescales (hours, days, months), as opposed to what would be expected if they were controlled solely by segmental or molecular reorientation (years, centuries, millennia, …). Recent BDS measurements on thin polymer films show the presence of a simple thermally activated molecular process with the same activation energy as that of fast equilibration mechanisms, indicating a common origin mechanism [1]. This so-called Slow Arrhenius Process (SAP) can be detected as a Debye-like peak both in the glassy and in the liquid state, i.e., a crossover with the super-Arrhenius-like segmental α-process is observed.

Investigating the molecular mechanisms associated with the SAP (and thus, fast equilibration), we systematically characterise the impact of 1D-confinement on this process in poly(4-bromostyrene) (P4BS), a model system. Here we present dielectric spectra of spincoated P4BS films of variable thickness and their analysis based on the deconvolution of the contribution of the segmental and SAP relaxations.

We find a clear relation of film thickness and relaxation strength of the SAP, with thicker films featuring a more intense process, while no systematic impact of confinement on other parameters, including the activation energy, is observed. Analysis of isochronal data confirms that the activation energy remains constant over the whole temperature range, meaning both above and below the glass transition temperature. Our results hint that SAPs involve structures extending over length scales larger than those associated with segmental dynamics.

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