BDS2018

10th Conference on BROADBAND DIELECTRIC SPECTROSCOPY AND ITS APPLICATIONS

under the patronage of the
International Dielectric Society

26 – 31 August 2018
Brussels, Belgium

Program
& Book of Abstracts

Edited by *@tgandtau*

We warmly thank Żaneta Wojnarowska and Marian Paluch (University of Silesia, Poland) for having kindly provided us the original template of this document.

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we thank *visit.brussels* for providing the opportunity for participants to use the Brussels public transportation free of charge.

The organization of BDS2018 would have not been possible without the patroonship of the *International Dielectric Society* and the scientific contribution of all the participants to this meeting.

PREFACE

August 2018

Welcome to the 10th Conference on Broadband Dielectric Spectroscopy and its Applications (BDS2018), the 2018 meeting of a series organized under the patronage of the International Dielectric Society (IDS). Over the recent decades, dielectric spectroscopy has matured into a versatile and powerful technique that provides insight into the dynamics and structure of a wide range of materials: from bulk liquids and glasses to thin polymer films, biological and aqueous systems, soft matter, and conductive materials. Dielectric techniques have also contributed to the understanding of interfacial and confinement situations, as well as to advancing the nonlinear regime, where high electric fields modify the structure and dynamics of the sample. This meeting combines contributions to a variety of aspects of the BDS field: fundamental developments, theoretical advances, novel techniques, and connections to industrial applications.

The *Laboratory of Polymer and Soft Matter Dynamics* of the Université libre de Bruxelles (ULB) is proud to host the 10th edition of the BDS conferences. ULB has a long tradition of successful studies on molecular dynamics, nonequilibrium phenomena and on the investigation of materials properties, fitting with the scope of this series of meetings of IDS. In addition to the names of Ilya Prigogine and Raymond Defay, probably familiar to all the participant of this conference, we remind also André Bellemans, a former student of the Nobel laureate for Chemistry in 1977, who started an innovative line of research on the microscopic origin of the dielectric relaxation, via 'computer experiments'.

The BDS2018 meeting in Brussels will provide a platform for the exchange of knowledge and results across various boundaries, enabling the discussion of everything related to dielectric: from historical backgrounds to most recent advances in experiment, theory, and simulation. The meeting is preceded by a tutorial that introduces a selection of fields to young researchers.

We hope that your stay at ULB and in Brussels will be extremely productive and that you will enjoy the program of BDS2018

Simone Napolitano | Ranko Richert

Chair of BDS2018 | *President of IDS*

Program

SUNDAY

Registration 13:00 – 19.00

Tutorial Lectures 14:00 – 18.00

CHAIRPERSON: *Catalin Gainaru*

14:00 **Introduction to dielectric relaxation**
Case study: ***performing 'bulk' experiments in nanoconfined systems***
Aurora Nogales

15:00 **Dynamics of water**
Case study: ***molecular relaxation in aqueous solutions of synthetic and biological materials***
Silvina Cerveny

16:00 **High pressure dielectric spectroscopy**
Case study: ***charge transfer in ionic glass-formers***
Zaneta Wojanarowska

17:00 **Maxwell-Wagner polarization**
Case study: ***analysis of crystallization kinetics***
Kristine Niss

Welcome Drink 18:00 – 19.00

MONDAY

8:30 **Welcome**

SESSION S1: BDS in relation to other techniques 1

08:50 – 10.30

CHAIRPERSON: *Alexei Sokolov*

08:50 **Dielectric spectroscopy with optical detection – a realistic perspective?**
O-1 Friedrich Kremer

09:20 **Broadband dielectric and thermally-stimulated electrochemical impedance spectroscopies for the analysis of organic coatings**
O-2 Aurélien Roggero

09:40 **Depolarized Dynamic Light Scattering of Ionic Liquids combined with Dielectric Spectroscopy**
O-3 Florian Pabst

10:00 **Simultaneous dielectric and scattering techniques in the temperature-pressure plane**
O-4

Alejandro Sanz

COFFEE BREAK

10:30 – 11:00

SESSION S2: BDS in relation to other techniques 2

11:00 – 12.00

CHAIRPERSON: *Friedrich Kremer*

11:00 **Kinetics of irreversible adsorption: thermodynamics vs molecular mobility**
O-5 David Nieto Simavilla

11:20 **What shear mechanics see that dielectrics doesn't: slow modes in glycerol and glycerol-water mixtures**
O-6 Tina Hecksher

11:40 **Infrared and dielectric spectroscopy to unravel the nature of the structural- and the secondary-relaxation in glycerol, threitol, xylitol and sorbitol**
O-7 Wilhelm Kossack

SESSION S3: Terahertz Spectroscopy 1 12:00 – 13.00
CHAIRPERSON: *Mohsen Sajadi*

12:00 **Nano-confined water: from incipient ferroelectricity to ferroelectric relaxor behavior**
O-8 Boris Gorshunov

12:30 **Terahertz Spectroscopy – Great Expectations**
O-9 Paul Ben Ishai

LUNCH 13:00 – 14:30

SESSION S4: Terahertz Spectroscopy 2 14:30 – 15:10
CHAIRPERSON: *Boris Gorshunov*

14:30 **Non-linear THz spectroscopy of liquids**
O-10 Mohsen Sajadi

14:50 **Broadband Dielectric Spectroscopy on Proteins and Lipid Bilayers from sub-GHz to THz region**
O-11 Keisuke Tominaga

SESSION S5: Industrial applications 1 15:10 – 16:00
CHAIRPERSON: *Madalena Dionisio*

15:10 **Physical stability of amorphous drugs: the role of molecular mobility**
O-12 Marian Paluch

15:40 **Insights from dielectric spectroscopy on the physical states of an Active Pharmaceutical Ingredient reached by milling**
O-13 Emeline Dudognon

COFFEE BREAK & POSTER SESSION 16:00 – 17:00

P1-P25

SESSION S5: Industrial applications 2 17:00 – 18:10

CHAIRPERSON: *William Hunter Woodward*

17:00 **Stabilizing high internal energetic states of pharmaceutical drugs by nanoconfinement**
O-14 Madalena Dionisio

17:30 **Influence of chirality on ibuprofen molecular dynamics and hydrogen bonding organizations**
O-15 Natalia Correia

17:50 **Impact of crosslinking and degassing on conductivity and morphology of polyethylene**
O-16 Roger Walker

EVENT FOR INVITED SPEAKERS 19:45 -

TUESDAY

SESSION S6: Young Researchers’ Session 08:30 – 10:30
CHAIRPERSON: *Simone Napolitano*

08:30 O-17	**Combined dielectric spectroscopy and neutron scattering study of a Polymer Blend as a Simplified Industrial System** Thomas Gambino
08:42 O-18	**Predicting the localization and interconnectivity of carbon nanotubes in compatibilized bi-phasic polymer blends** An-Sofie Huysecom
08:54 O-19	**Molecular dynamics of chiral amorphous compounds: Original case study of Nac-MBA** Bienvenu Atawa
09:06 O-20	**Correlating the ionic conductivity and Morphology of Pendant and Backbone Polymerized Ionic Liquids** Preeya Kuray
09:18 O-21	**Polythiophene-based polyelectrolytes from polymerized ionic liquids. Self-assembly and dc conduction** Achillefs Pipertzis
09:30 O-22	**Coexistence of two structural relaxation processes in mixtures involving monohydroxy alcohols** Sebastian Peter Bierwirth
09:42 O-23	**Molecular mobility and ionic conductivity of Ionic Liquid Crystals Forming a Hexagonal Columnar Mesophase** Arda Yildirim
09:54 O-24	**The analysis of molecular relaxation in thermo-responsive polymer hydrogels** Anna Czaderna-Lekka
10:06 O-25	**Dynamics of ice in ice nucleating protein (INP) solutions** Jorge Melillo

10:18 **Surface imprinting surface characterization for cell detection by dielectric relaxation spectroscopy**
O-26 Alessia Gennaro

COFFEE BREAK 10:30 – 11:00

SESSION S7: Nanoconfinement 1 11:00 – 13:00

CHAIRPERSON: *Daniele Cangialosi*

11:00 **Asymmetric interfacial dynamics and glass transition in stacked thin polymer films**
O-27 Koji Fukao

11:30 **Growth kinetics and molecular mobility of irreversibly adsorbed layers in thin polymer films**
O-28 Andreas Schönhals

12:00 **Mapping the Dynamic Heterogeneities in Thin Films of Miscible PVME/PS Blend by Nano-sized Relaxation and X-ray Spectroscopies**
O-29 Sherif Madkour

12:20 **How does the vitrification of the interfacial layer affects the Molecular Dynamics of Glass-Formers at the Nanoscale? The Impact of Interactions**
O-30 Magdalena Tarnacka

12:40 **The Impact of Interactions On the glass transition suppression of Polystyrene in SBS Rubber**
O-31 William Hunter Woodward

LUNCH 13:00 – 14:30

SESSION S8: Nanoconfinement 2 14:30 – 16:00

CHAIRPERSON: *Andreas Schönhals*

14:30 **Size effects on the segmental dynamics of sub 10-nm segregated polydimethysiloxane**
O-32 Angel Alegría

15:00 O-33 **Confinement induced changes in the Relaxation Dynamics and Crystallization Behavior of Glass-Forming Liquids**
Karolina Adrjanowicz

15:30 O-34 **Glass transition and molecular mobility by calorimetry in confined glasses**
Daniele Cangialosi

COFFEE BREAK 16:00 – 16:30

SESSION S8: Pressure & Volume 16:30 – 18:40

CHAIRPERSON: *Marian Paluch*

16:30 O-35 **The Cooperative Free Volume Rate Model for pressure dependent dynamics**
Ronald White

16:50 O-36 **Relaxation in bulk and thin films: Insights using the Cooperative Free Volume Model**
Jane Lipson

17:20 O-37 **Mapping isobaric aging onto the equilibrium phase diagram**
Kristine Niss

17:50 O-38 **Isochronal superposition, density scaling and the nature of the β relaxation**
Daniel Fragiadakis

18:20 O-39 **Isochronal superposition from picosecond to second investigated with simultaneous dielectric and neutron spectroscopy**
Henriette Wase Hansen

WEDNESDAY

SESSION S9: Scaling of the α– and β– processes 1

08:30 – 10:30

CHAIRPERSON: *Simone Capaccioli*

08:30 **Microscopic nature of β process of sugar alcohols**
O-40 Ryusuke Nozaki

09:00 **The JG β–relaxation / primitive relaxation never fail to show up in binary mixtures and polymer blends**
O-41 Kia Ngai

09:30 **Nuclear resonant scattering as microscopic probe for the Johari-Goldstein relaxation process in supercooled liquids**
O-42 Federico Caporaletti

09:50 **New link between structural and Johari-Goldstein Relaxation Parameters in Glass Formers**
O-43 Shimon Lerner

10:10 **Linear and non-linear orientational correlation factors from the rotational Dean-Kawasaki equation**
O-44 Pierre-Michel Dejardin

COFFEE BREAK

10:30 – 11:00

SESSION S10: Scaling of the α– and β– processes 2

11:00 – 12:00

CHAIRPERSON: *Tina Hecksher*

11:00 **Microscopic modelling of dielectric α and β relaxation in glasses and orientationally disorder crystals based on Generalized Langevin Equations**
O-45 Alessio Zaccone

11:30 **Qualitative change in temperature dependence of Structural Relaxation: Diverge or not Diverge**
O-46 Alexei Sokolov

SESSION S11: Soft Matter 1 12:00 – 13:00

CHAIRPERSON: *Tiberio Ezquerra*

12:00 **Control of Crystallization Outcomes in Molecular Glass-Formers by Electric Fields**
O-47 Ranko Richert

12:30 **Competing order phenomena and peculiar crystallization kinetics of polyamide 12 as revealed by dielectric spectroscopy**
O-48 Michael Wübbenhorst

LUNCH 13:00 – 14:30

SESSION S12: Soft Matter 2 14:30 – 16:00

CHAIRPERSON: *Joshua Sangoro*

14:30 **Relaxations and Relaxor-Ferroelectric-like Response of Poly(vinylidene fluoride) confined in cylindrical nanocavities**
O-49 Aurora Nogales

15:00 **Soliton excitations in multiferroic $LiCuVO_4$**
O-50 Christoph Grams

15:20 **Further insights into vapour deposited ultrastable glasses from dielectric spectroscopy**
O-51 Cristian Rodriguez-Tinoco

15:40 **Asymmetry liquid-liquid criticality in the refractive index and the dielectric constant coexistence curves**
O-52 Patricia Losada-Pérez

COFFEE BREAK & POSTER SESSION 16:00 – 17:00

P25-P51

SESSION S13: Soft Matter 3 17:00 – 18:10

CHAIRPERSON: *Ivan Popov*

17:00 O-53 **The interplay between crystallization and glass transition in nematic liquid crystal 2,7-bis(4-pentylphenyl)-9,9-diethyl-9H-fluorene (5P-EtFLEt-P5)**
Małgorzata Jasiurkowska-Delaporte

17:20 O-54 **Dynamics in weakly disordered solids**
Josep Tamarit

17:50 O-55 **Dynamics in mesoscopic Structured Liquids**
Joshua Sangoro

SESSION S14: Nonlinear Dielectric Response 18:10 – 19:30

CHAIRPERSON: *Ranko Richert*

18:10 O-56 **Nonlinear dielectric response beyond structural relaxation in glass-forming materials**
Catalin Gainaru

18:40 O-57 **Third and fifth harmonic responses in liquids**
François Ladieu

19:00 O-58 **Nonlinear electrical and rheological responses of glass formers**
Roland Böhmer

IDS BOARD MEETING 20:00 –

THURSDAY

SESSION S15: Polymer Dynamics 1 08:30 – 10:30

CHAIRPERSON: *Shiwang Cheng*

08:30 **Effect of chain topology on segmental dynamics**
O-59 George Floudas

09:00 **Network formation and molecular dynamics in hydrogen-bonding telechelic polymers: a competition between association lifetime and structural relaxation**
O-60 Martin Tress

09:20 **Understanding the evolution of entanglements upon the dielectric relaxations in dis-UHMWPE in the presence of Al_2O_3 catalytic ashes**
O-61 Stavros Drakopoulos

09:40 **Molecular dynamics of novel poly(pentamethylene 2,5-furanoate): Exploring a complete landscape of molecular dynamics and finding unexpected results**
O-62 Daniel Martínez-Tong

10:00 **Dynamics of raw and vulcanized rubber. What can we learn from dielectric spectroscopy studies?**
O-63 Silvina Cerveny

COFFEE BREAK 10:30 – 11:00

SESSION S16: Polymer Dynamics 2 11:00 – 12:40

CHAIRPERSON: *George Floudas*

11:00 **Straightening effect of the polymer chains around nanoparticles**
O-64 Ivan Popov

11:30 **Dramatic effect on the slower component topology on the matrix dynamics in polymer mixtures**
O-65 Beatriz Robles-Hernández

11:50 **Rigid amorphous phase in Nanocomposites as Revealed by Relaxation Spectroscopy**
O-66 Paulina Szymoniak

12:10 **Analyzing the interfacial layer properties in nanocomposites by broadband dielectric spectroscopy**
O-67 Shiwang Cheng

LUNCH 12:40 – 14:10

SESSION S17: Dynamics of water, water solutions, H-bonding liquids and Biomaterials 1
14:10 – 15:40

CHAIRPERSON: *Apostolos Kyritsis*

14:10 **Water and its dielectric signature. New markers for biosensing**
O-68 Yuri Feldman

14:40 **Depolarized Dynamic Light Scattering and Dielectric Spectroscopy: Two Perspectives on the Debye-Relaxation in Monohydroxy Alcohols**
O-69 Thomas Blochowicz

15:00 **Advantages of examining alcohols containing a phenyl group by the means of Broadband Dielectric Spectroscopy**
O-70 Sławomir Kołodziej

15:20 **How various strength of the H-bonds is reflected by relaxation dynamics of associated liquids**
O-71 Sebastian Pawlus

CONCERT 18:15 – 19:30

10th Anniversary PARTY 20:00 – 23:00

2018 Debye Prize Awarding Ceremony

FRIDAY

SESSION S18: Dynamics of water, water solutions, H-bonding liquids and Biomaterials 2

08:50 – 10:30

CHAIRPERSON: *Yuri Feldman*

08:50 O-72 **Dynamics of hydration water in gelatin – hyaluronic acid hydrogels 2**
Apostolos Kyritsis

09:20 O-73 **Dynamics of freeze-dried solvated proteins revealed by broadband dielectric spectroscopy**
Simone Capaccioli

09:50 O-74 **Application of BDS to follow cis to trans isomerism in photoswitchable molecule Aberchrome 670**
Kamil Kaminski

10:10 O-75 **BDS and TSDC measurements on $Ca_{10}(PO_4)_6(OH)_2$, β–$Ca_3(PO_4)_2$ and biphasic bioceramics**
Pedros Santos Prezas

COFFEE BREAK

10:30 – 11:00

SESSION S19: Charge transport 1

11:00 – 13:00

CHAIRPERSON: *Michael Wubbenhorst*

11:00 O-76 **Scaling behavior of electric conductivity and structural relaxation in supercooled ionic liquids**
Zaneta Wojnarowska

11:30 O-77 **On protonic and electronic charge transport in eumelanin**
Bernard Mostert

11:50 **Charge transport and glassy dynamics in polymeric Ionic Liquids as reflected by its Inter- and Intramolecular Interactions**
O-78 Arthur Markus Anton

12:10 **Impact of mesoscale organization on charge Transport and Dynamics in Ionic Liquids**
O-79 Tyler Cosby

12:30 **Coupled electrical/mechanical investigation on elastomeric composite materials**
O-80 Anatoli Serghei

LUNCH 13:00 – 14:30

SESSION S19: Charge transport 2 14:30 – 15:10

CHAIRPERSON: *Anatoli Serghei*

14:30 **Dielectric properties of jute fibers reinforced Poly(lactic acid) / Poly(butylene succinate) blend**
O-81 Asma Triki

14:50 **BDS as a novel tool to probe phase separation in compatibilized polymer blends**
O-82 Avanish Bharati

CLOSING REMARKS 15:10 –

BOOK OF ABSTRACTS

ORAL

contributions

Dielectric spectroscopy with optical detection – a realistic perspective?

F. Kremer, A.M. Anton, W. Kossack, F. Frenzel

University of Leipzig, Germany

In dielectric spectroscopy relaxation processes are conventionally studied by measuring the frequency and temperature dependence of the complex impedance of a sample capacitor. This restricts the dielectric response to the orientational polarization of only the polar groups in the material under study. However, one could imagine to measure in the InfraRed (IR) “fingerprint” spectral range the dynamic dichroic response of specific absorption bands reflecting characteristic molecular moieties. By that a wealth of novel information would be obtained with detailed insights how the different, also non-polar parts of a molecule respond to an external electric field. First steps in this direction were carried out more than 20 years ago using 2D-Fourier-Transform InfraRed (2D-FTIR) spectroscopy on ferroelectric liquid crystals [1,2]. But with the availability of tunable lasers in the IR spectral range the experimental situation has fundamentally improved offering perhaps the exiting perspective for the development of dielectric spectroscopy with optical detection (DSOD).

[1] Shilov, S.V.; H. Skupin, F. Kremer, T. Wittig and R. Zentel *Phys Rev Lett* **79**, 9, 1686-1689 (1997)

[2] Shilov, S.V.; M. Müller, D. Kruerke, G. Heppke, H. Skupin and F. Kremer *Phys Rev E* **65**, 021707 (2002)

Broadband dielectric and thermally-stimulated electrochemical impedance spectroscopies for the analysis of organic coatings

Aurélien Roggero[1], Nicolas Caussé[1], Eric Dantras[2], Laura Villareal[1,3], Audrey Santos[3], Nadine Pébère[1]

[1] Université de Toulouse, CIRIMAT-ENSIACET, Toulouse, France [2] Université de Toulouse, CIRIMAT-UPS, Toulouse, France [3]PEINTURES MAESTRIA, Pamiers, France

Organic coatings are frequently used to protect metal surfaces against corrosion because they act as an efficient barrier by slowing down the diffusion of aggressive species (particularly water) towards the metal/paint interface. The barrier properties are linked to various parameters such as the polymer matrix, the fillers, the pigments and additives, the solvent and the coating thickness. For the assessment of the corrosion protection performance, electrochemical impedance spectroscopy (EIS) is a very popular technique. In EIS studies of organic coatings, low impedance values are associated with low barrier properties and as a consequence to an easy water uptake which is monitored through the paint high-frequency relative permittivity. Despite the close proximity of EIS and broadband dielectric spectroscopy (BDS) apparatus, EIS studies do not focus on polymer molecular mobilities.

In the present work, an epoxy based commercial coating used for the corrosion protection of steel was investigated by BDS and EIS. The aim was to better understand the EIS response of the film and determine if molecular mobility could be emphasized in the spectra. A BDS study allowed the characterization of the epoxy matrix dielectric relaxation modes in the dry state. Then, EIS measurements were performed on coated steel plates immersed in NaCl solutions. A thermostated cell allowed isothermal EIS measurements to be obtained in the temperature range [20;75] °C, which encompassed the glass transition temperature (T_g) of the studied paint (measured by DSC at ~50 °C and ~35 °C when fully plasticized by water).

The combination of thermal stimulation and the choice of adequate dielectric formalisms allowed us to evidence the α-mode of the plasticized polymer matrix in EIS. Z* formalism traditionally used in EIS experiments is extrinsic therefore not as suitable as ε^* or σ^* for the study of molecular mobility and charge transport phenomena. This study also evidenced a Vogel-Tammann-Fulcher dependence of both the low-frequency conductivity and its cut-off frequency, the latter of which is the most apparent feature of the EIS spectrum. The correlation of BDS and EIS allowed better understanding of the influence of electrolyte absorption on the barrier properties of the coating.

Depolarized Dynamic Light Scattering of Ionic Liquids combined with Dielectric Spectroscopy

Florian Pabst[1], Jan Gabriel[1], Thomas Blochowicz[1]

[1]*TU Darmstadt, Institut für Festkörperphysik, Hochschulstr. 6, 64289 Darmstadt, Germany*

The treatment of dielectric spectra of ionic liquids (ILs) is usually complicated, as various processes contribute, like conductivity, electrode and interfacial polarization and dipolar reorientation, which overlay each other. Thus, there is no common interpretation of these spectra in the literature. We show that depolarized dynamic light scattering (DDLS), which is sensitive to reorientational motions of the ions only, can be used to unambiguously identify the part of the dielectric spectrum that is due to dipolar reorientation and thereby help to disentangle the different contributions.

By combining photon correlation spectroscopy and Tandem-Fabry-Perot-Interferometry, a frequency range covering up to 16 orders of magnitude is obtained, which allows to follow the structural relaxation from the decomposition point of the ILs down to the glass transition temperature. In this way a similar frequency and temperature window like in state-of-the-art broadband dielectric spectroscopic techniques can be explored.

We demonstrate for an aprotic and a protic IL how the combination of DDLS and BDS not only allows to disentangle different contributions but also to obtain further information on the motional mechanism underlying the relaxation process, and it turns out that translational and reorientational motions are strongly coupled [1]. Furthermore, we show for a series of Alkyl-Imidazolium ILs ($[C_nC_1Im][NtF_2]$ with $n = 3,6,8$), that no dynamic signature of nanostructuration is found, which was reported previously in these ILs by X-Ray-scattering and was assigned to chain segregation [2]. Instead, we interpret our data in terms of an average ordering of the polar moieties, which are spaced by the alkyl-chains, without formation of long-lived aggregates.

[1] F. Pabst, J. Gabriel, P. Weigl, T. Blochowicz, *Chemical Physics*, **494**, 103-110 (2017)

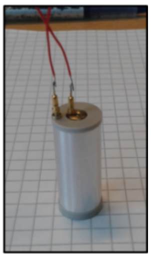
[2] O. Russina, A. Triolo, L. Gontrani, R. Caminiti, D. Xiao, L.G. Hines Jr, R.A. Bartsch, E.L. Quitevis, N. Plechkova, K.R. Seddon, *J. Phys.: Condens. Matter*, **21**, 424121 (2009)

Simultaneous dielectric spectroscopy and scattering techniques in the temperature-pressure plane

Alejandro Sanz[1], Henriette W. Hansen[1,2] and Kristine Niss[1]

[1] *Glass and Time, IMFUFA, Department of Science and Environment, Roskilde University, Denmark* [2]*Institut Laue-Langevin, CS 20156, 38042 Grenoble Cedex 9, France*

We present a novel setup for performing simultaneous incoherent quasi-inelastic neutron scattering and dielectric spectroscopy at high pressures. The cell was designed to be used for a maximum pressure of 500 MPa at temperatures between 5 and 315 K approximately. High tensile aluminium alloy was selected for constructing the pressure vessel due to its low neutron absorption and incoherent scattering cross section. In order to measure the scattered neutron intensity and the sample capacitance simultaneously, a cylindrical capacitor is positioned within the bore of the high-pressure container. The capacitor consists of two concentric electrodes separated by insulating spacers (see the figure below). The performance of this device has been verified by collecting simultaneous dielectric and neutron spectroscopy data on several liquids, using both neutron backscattering and neutron time-of-flight instruments [1]. This setup is a unique tool for studying a variety of systems with dynamics on a large window of time scales, such as viscous liquids, polymers and proteins. By doing dielectric and neutron spectroscopy experiments at the same time, we are able to monitor slow and fast dynamics under exactly the same environmental conditions, which is especially important when the sample is not stable, for instance, due to physical or chemical processes. We have successfully employed this setup to explore the phase diagram of simple van de Waals liquids in an unprecedented range of time scales. Our results agree with the predictions of the isomorph theory [2]. Previous setups to carry out simultaneous dielectric spectroscopy and neutron or synchrotron X-ray diffraction at atmospheric pressure will also be dicussed.



[1] Sanz A. et al., *Review of Scientific Instruments*, **88**, 023904 (2018).
[2] Hansen H.W. et al., *Nature Communications*, **9**, 518 (2018).

Kinetics of irreversible adsorption: thermodynamics *versus* molecular mobility

David Nieto,[1] Weide Huang,[1,2] Caroline Housmans,[1] Philippe Vandestrick,[1] Jean-Paul Ryckaerts,[1] Michele Sferrazza[2] and Simone Napolitano[1]

[1]Polymer and Soft Matter Dynamics, Faculté des Sciences, Université libre de Bruxelles (ULB), Brussels, Belgium [2]Department de Physique, Université libre de Bruxelles (ULB), Brussels, Belgium

Irreversibly adsorbed polymer layers represent an intriguing class of novel nanomaterials with unexpected properties, strongly deviating from what observed in unbounded polymer melts. These extremely thin layers (thickness < few tens of nanometers) are obtained via a small number of successive steps, easily reproducible in a laboratory environment: a polymer melt is placed in contact with an adsorbing substrate and nonadsorbed chains are washed away by soaking the sample in a good solvent. Importantly, tuning the thickness of the adsorbed layer, an operational parameter equivalent to the number of chains adsorbed on a unit surface, allows modifying the performance of polymer coatings without affecting the interfacial chemistry [1].

Here, we discuss on the physics behind the formation of irreversibly adsorbed layers onto solid substrate [2,3], highlighting the differences between measurements performed via dielectric spectroscopy and those via ellipsometry or atomic force microscopy. By analyzing the outcome of experiments and simulations, we show how changes in thermal energy and interaction potential affect the equilibrium and the nonequilibrium components of the kinetics. We identify a universal linear relation between the growth rates at short and long adsorption times, suggesting that the monomer pinning mechanism is independent of surface coverage, while the progressive limitation of free sites significantly limits the adsorption rate.

We show that the equilibrium adsorbed amount is given by thermodynamics and depends on the interface interaction only (i.e. it is temperature independent in experiments). Importantly, in neat disagreement with current ideas on surface science, the equilibrium adsorbed amount – and, hence, interfacial interaction potential – is affected by nanoconfinement [4].

[1] D. N. Simavilla, et al *Macrom Chem Phys* **219**, 201700303 (2017).
[2] C. Housmans, *et al* Macromolecules, **47**, 3390 (2014).
[3] D. N. Simavilla *et al.*, *ACS Macro Letters*, **8**, 975-979 (2017).
[4] D. N. Simavilla, W. Huang, C. Housmans, M. Sferrazza, S. Napolitano, *ACS Central Science*, **4** 755-759 (2018)

What shear mechanics see that dielectrics doesn't: slow modes in glycerol and glycerol-water mixtures.

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Broadband dielectric spectroscopy is a powerful and popular tool to investigate the dynamics of supercooled liquids, mainly because it involves a relatively simple experiment that routinely covers 9 orders of magnitude in frequency from mHz to MHz (and can cover as much as 18 orders of magnitude). Rheology is a useful complementary technique, both in obvious cases where BDS fails due to too little dielectric signal (e.g. liquids with no dipole moment) or too much (e.g., ionic liquids where the signal is dominated by DC conductivity) and in cases where the two techniques can act as a pair of pincers and give different insights into the dynamics. Mono-alcohols are known to display an intense, mono-disperse dielectric signal at frequencies lower than the alpha relaxation. The signal is ascribed to linear hydrogen-bonded structures effectively giving a large end-to-end dipole moment. In recent works [1-4], shear and bulk modulus measurements have shown that these structures also leave a clear, but much more subtle low-frequency signature in the mechanical response, comparable to what is observed for short-chain polymers. Here we show a similar spectral anomaly for a poly-alcohol, the prototypical glass-former glycerol [5]. This slow mode curiously weakens when water is added and vanishes for a molar concentration of glycerol between 0.5 and 0.6. Dielectric spectra of glycerol-water mixtures [6-7] in the same concentration range show a quite different behavior: neat glycerol displays a single narrow relaxation loss peak while primary peak broadens, when water is mixed in.

We propose that the observed slow rheological mode is caused by the hydrogen-bonded network. The dielectric invisibility of that mode may be due to cancellation of dipoles in the network structure. The qualitative difference in shear and dielectric spectra stresses that in combination they form a powerful tool for investigations into supercooled liquid dynamics.

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Infrared and dielectric spectroscopy to unravel the nature of the structural- and the secondary-relaxation in glycerol, threitol, xylitol and sorbitol

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Polyalcohols, in particular glycerol, threitol, xylitol and sorbitol, are among the best analyzed glassy systems. They are characterized by two dielectrically relaxations, an α-relaxation and a secondary β-relaxation. With decreasing molecular weight the calorimetric glass transition temperature shifts from T_g = 274 K for D-sorbitol to T_g = 185 K for glycerol. Simultaneously, the β-relaxation changes its nature from an isolated Arrhenius-like relaxation to an excess-wing-like process tightly coupled to the Vogel-Fulcher-Tamman temperature dependence of the structural α-relaxation. Aside of dielectric methods, we apply Infrared spectroscopy to unravel the underlying molecular processes. Our results prove that, independent of the chain length the hydrogen bonding network, ie the intermolecular arrangement, is identical. Density changes control the strength of this network, but leave the intermolecular arrangement qualitatively unaltered. Therefore, qualitative and quantitative differences in the dielectric response (and in T_g) must be driven by the chain connectivity, in particular the relative molecular weight of backbone and terminal groups. Consequently, we explain our observations by a comparison of the length scales involved in hydrogen bonding, structural-, and secondary-relaxation, as well as the chain length itself. A close analogy of this set of polyalcohols with oligomeric systems and polymers is outlined and supported by the convergence of IR-spectroscopic-, dielectric- and calorimetric-results.

Nano-confined water: from incipient ferroelectricity to ferroelectric relaxor behavior

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Earlier [1], using radio-frequency (RF) and terahertz (THz) spectroscopy, we discovered incipient ferroelectric behavior of water molecules localized within nano-cages formed by ions of crystal lattice of beryl. While cooling below 300 K, dielectric contribution and frequency of the THz ferroelectric soft mode show Curie-Weiss and Cochran behaviors, respectively. Below ≈10 K, both dependences saturate due to quantum tunneling within hexagonal potential [2]. Like in beryl, in cordierite water molecules are confined within nano-cages and experience effective 2-well potential with the depth of ≈10 meV when rotating around c-axis. Using dielectric spectroscopy, we show that the subsystem of H_2O molecules spread over matrix of nano-sized cages formed by atoms of cordierite crystal lattice reveals typical relaxor-like response: maximum in the temperature dependence of quasi-static permittivity with frequency-dependent low-temperature slope, broad soft RF relaxation with complicated lineshape, Curie-Weiss behavior of dielectric constant above 50 K with negative Curie temperature (≈-20 K), signs of Burns temperature (≈50 K) that signals emergence of H_2O molecular cluaters. At THz frequencies, sharply anisotropic soft-mode response is observed caused by dynamics of water molecular ensemble. We present temperature-dependent RF-THz-IR spectra of water-containing cordierite crystals and interpretations of the observed phenomena.

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Terahertz Spectroscopy – Great Expectations

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In 1989 THz Spectroscopy burst forth on the scene with the description of a table top Time Domain THz Spectrometer, based on a femtosecond laser [1], [2]. In the ensuing decade it gained prominence (20 papers in 1990, 1400 papers in 2010 [3]) and nowdays could be described as “mature”. Yet there are still many unanswered questions and applications of THz are still in their infancy. Bridging the gap between collective dynamics, dominant in dielectric spectroscopy, and the individual oscillations that characterize the Infrared, THz spectroscopy is applicable to many areas of research from solid state and polymer science to biological systems. But where is it going?

The paper sets out the current State of the Art for THz Spectroscopy and points out some of the expected near-future developments in the science, including non-linear THz spectroscopy and time resolved spectroscopy. The search for electronic, rather than photonic sources of broadband radiation are also examined. Finally, we address the question, “What is the added benefit to Broadband Dielectric Spectroscopy?”

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Nonlinear THz Spectroscopy of Liquids

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Low-frequency intermolecular dynamics of liquids below ~10 THz (1 THz ≈ 33 cm^{-1}) have strong influence on the outcome of (bio-)chemical processes [1]. In this frequency range the underlying molecular dynamics are complex and include reorientational, vibrational and translational motions of single molecules and/or molecular clusters. To access such dynamics in liquids, dielectric spectroscopy (DS) is commonly implemented. However, as the measured response in DS scales linearly with the applied external electric field, the microscopic molecular origin of the response and the nature of intermolecular inetractions remain still unrevealed.
To gain insights into the microscopic origin of the intermolecular motions in liquids, we implement nonlinear THz spectroscopy. In this approach, the resonant excitation of the low-frequency intermolecular motions by an intense THz electric field leads to an optical anisotropy in the liquid. Comparing this response with the one after an optical (Raman) excitation enables us to draw conclusion on the nature of the resonantly excited molecular motion and also gain information on the type and the strength of the intermolecular interactions. Here we discuss few examples of the protic and aprotic polar liquids including water, methanol and dimethyl sulfoxide [1,2].

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Broadband Dielectric Spectroscopy on Proteins and Lipid Bilayers from sub-GHz to THz region

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Broadband dielectric spectroscopy (BDS) has been applied to proteins to study temperature and hydration dependence on dynamics such as reorientational relaxation of the whole molecule, side-chain relaxation, and rotational relaxations of hydration water. Recently we reported a BDS study of lysozyme of a powder form in the dehydrated and hydrated states to show the effects of hydration and thermal excitation on the low-frequency dynamics of protein [1, 2]. In this work we have extended the BDS work to purple membrane and lipid bilayer, DMPC (1,2-Dimyristoyl-sn- glycero-3-phosphocholine) to study hydration and thermal effects on the low-frequency dynamics of these systems. In order to analyse the obtained dielectric spectra from sub-GHz to THz for the hydrated and dehydrated samples, it has been found that the following model function is needed,

$$\varepsilon^*(\nu)=\frac{\sigma_0}{i2\pi\nu\varepsilon_0}+\frac{\Delta\varepsilon}{1+\left(i2\pi\nu\tau\right)^{\beta}}+\sum_{k=1}^{2}\frac{A_k}{\nu_k^2-\nu^2+i\nu\gamma_k}+\varepsilon_{\mathrm{inf}} \tag{1}$$

We found that there exists a spectral component due to the relaxational mode in the GHz to THz region for the three systems at room temperature. Interestingly, the spectra of all the samples have a tail of the high-frequency side in the THz region at room temperature, though the parameters such as the relaxation time are different among the three. This fact may be important for the functional expression of proteins.

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Physical stability of amorphous drugs: the role of molecular mobility

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The vast majority of solid forms of drugs (tablets) contain Active Pharmaceutical Ingredients (APIs) being in crystalline state. The main reason of this is that the crystalline API are characterized by very high physical and chemical stability. As a consequence, their physicochemical properties remain the same even after long period of storage. However, as reported in literature, many crystalline API have a serious limitation because of weak water solubility. The magnitude of this problem is quite serious because it is estimated that nearly 40% of the marketed drugs and about 75% of future drug candidates are poorly soluble in water. It turns out that this problem can be tackled by converting crystalline API to disordered – amorphous state [1]. Unfortunately, this solution has one potential weakness. The amorphous drugs are, in general, physically unstable systems and they may simply re-crystalize during storage losing their original advantages.

How to improve the physical stability of API will be the main issue discussed during this presentation. A lot of attention will be paid to the analysis of structural dynamics which is commonly believed to be one of most relevant factor determining the physical stability of amorphous drugs. We will show that by controlling the molecular mobility we can significantly improve the physical stability of many amorphous drugs. Also, other strategies to stop recrystallization of amorphous API will be presented.

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Insights from Dielectric spectroscopy on the physical states of an Active Pharmaceutical Ingredient reached by milling

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Most of the pharmaceutical compounds are formulated in the solid state. During the industrial manufacturing of dosage forms, several unit operations take place and the first step is often a mechanical milling of powder to reduce the particule size in order to facilitate subsequent processing and product performances (improved flow properties, minimised segregation, increased surface area…). However, it has been shown that milling can modify the physical state of molecular compounds by inducing either polymorphic transformation or an amorphisation. If these transformations are not controlled, it is an obvious problem for the stability of the drugs but, on the contrary, if they are under control, milling become an interesting tool to reach physical states with enhanced properties (for example an increased solubility in the case of drugs having a poor solubility in water).

In the past, a lot of works has been devoted to the study of the effects of milling on molecular compounds that have shown the key role played by the milling temperature, amorphisations resulting from a milling performed below the glass transition (Tg) of the compound whereas polymorphic transformations occurring for milling performed above Tg [1]. However, the mechanisms that lead to these modifications of the physical state are still not fully understood [2].

The study by Dielectric spectroscopy presented here focuses on the dynamic of the physical states that are reached under different milling conditions of an Active Pharmaceutical Ingredient (API), poorly soluble in water. It will show that Dielectric spectroscopy by giving information on the molecular mobility of these states also gives us an insight on the way modifications of the physical states occur under milling.

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Stabilizing high internal energetic states of pharmaceutical drugs by nanoconfinement

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An overview will be provided on the work developed to answer to the pharmaceutical industry demand for more soluble drug formulations. Insolubility compromises bioavailability being costly in drug development, and coming with a negative prize to the patient owing to excessive dosage. A strategy is to obtain the drug in high internal energetic states, relative to the thermodynamically stable crystal, as amorphous and metastable polymorphs. This constitutes a major challenge since, for real-life applications, physicochemical stability must be ensured during the entire shelf-life and the high energetic and intrinsically mobile amorphous materials are unstable, showing a tendency towards crystallization. Therefore, the confinement of drugs in silica host systems with nanosized pores is a solution to this hurdle, allowing producing long-term stable amorphous drugs with stabilization periods extended over years. [1] The tunability of host pore size and surface chemistry, key factors that determine the internal guest mobility, have been exploited for the design of drug delivery systems. It will be shown how the inter-play between the detected different motional regimes, probed by dielectric relaxation spectroscopy, determine the drug release kinetics from the matrix. [2]

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Influence of chirality on ibuprofen molecular dynamics and hydrogen bonding organizations

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The study of chiral molecules has been the subject of considerable work due to numerous potential industrial applications. The separation of the enantiomers is, for example, fundamental in pharmacological development. In contrast to the two pure R and S enantiomers, a mixture of R and S may remarkably possess some different physical properties either of the pure enantiomers. Different ability of molecules to crystallize, crystalline structure, melting points or solubility has been commonly reported. Oppositely, molecular dynamics in the liquid, undercooled liquid or glassy states obtained from dielectric relaxation spectroscopy (DRS) are usually found very similar for different enantiomeric mixtures.

In the present study, different ibuprofen enantiomeric mixtures have been investigated in the liquid, undercooled liquid and glassy states using combined broadband dielectric spectroscopy experiments and molecular dynamics simulations. At first glance, dipolar dynamical properties for all mixtures show identical features characterized by: i) the existence of two main dynamical processes above the glass transition temperature T_g, one corresponding to the α relaxation and the other to a Debye-like process and ii) two secondary relaxations below T_g: one corresponding to a genuine J-G process and one associated to local mobility. DRS experiments indicate that all relaxation times, as well respective temperature dependencies, do not seem to be affected at all by the enantiomeric content. These results are well in line with recent DRS works performed on diprophylline [1] and ketoprofen [2] glass-forming liquids. Interestingly, a thorough analysis of the peculiar Debye relaxation only found so far in ibuprofen reveals that its relative strength is always slightly more intense for the racemic mixture. This small but remarkable change is confirmed from MD simulations and analyzed in term of the dipolar difference between the anti- and syn-conformation of the —COOH carboxyl group in the ibuprofen molecule suggested to be at the origin of the Debye relaxation.

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Impacts of crosslinking and degassing on the conductivity and morphology of polyethylene

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Crosslinked polyethylene (XLPE) is the main material used for high voltage alternating current power cable insulation due to its mechanical stability, low dielectric loss, and low conductivity. It is made by taking low-density polyethylene (LDPE) and connecting chains together using dicumyl peroxide (DCP). The crosslinks are a source of stability and reduced conductivity [1]. However, the crosslinking process leaves behind DCP byproducts that are sources of excess conductivity and shallow trap states. Their presence has been correlated with degradation and early failure of XLPE insulation, particularly under direct current conditions [2,3]. As such, they are typically removed via degassing [4]. During the degassing procedure, polyethylene is exposed to temperatures within its melting range (50-110°C) that may enhance crystallization [5]. This combination of byproduct removal and crystallization would be implicated in the improvement of insulating properties, but the impact of crystallinity on XLPE electrical properties is understudied. In this work, XLPE fabrication parameters such as the amount of DCP and crosslinking temperature were used to determine how variations in byproduct concentration and morphology impact the electrical properties. As thin films are expected to degas faster than cables, it was determined that the concentration of DCP byproducts in our XLPE films was too small to have a significant impact on the loss and conductivity when the amount of DCP added is comparable to the amounts used in industry (e.g. 2 wt%). Using higher amounts of DCP (e.g. 8 wt%) can lead to increases in the dielectric loss. Meanwhile, the crosslinking temperature, which impacts XLPE morphology, was always effective in controlling the loss. Preliminary analysis reveals that the degassing process is effective both in reducing loss and tuning the thermal expansion, which may be more due to impacts on XLPE morphology than the byproduct concentration. Degassing will thus be useful in delivering the desired XLPE properties regardless of crosslinking method.

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Combined Dielectric Spectroscopy and Neutron Scattering study of a Polymer Blend as a Simplified Industrial System.

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In this work we apply the methodology and concepts developed over the last years for the study of segmental dynamics on athermal miscible polymer blends [1] to the investigation of a blend made of styrene-butadiene rubber (SBR) and an oligomer of polystyrene (PS), as an example of simplified industrial system. In this way we obtain detailed information about the segmental dynamics of both components within the blend. To this end, a judicious combination of broad-band dielectric spectroscopy (BDS) and quasi-elastic neutron scattering (QENS) results on partially deuterated blends was required. Difficulties on the comparison between isotopically different samples arose due to the uncontrolled changes in polymer microstructure associated with the obtention of deuterated polymers. Nevertheless, the strategy for data analysis developed in this work made it possible to readily resolve the component's segmental dynamics of the investigated mixtures. It was found that gaussian distributions of the component's effective glass-transition temperatures provide a very good description of all the experimental data collected in the SBR/PS (50/50 wt%) mixtures over the whole accessible temperature range, not only by BDS and QENS but also those obtained by differential scanning calorimetry (DSC) and by neutron elastic-fixed-window-scans (EFWS) experiments [2].

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Predicting the localization and interconnectivity of carbon nanotubes in compatibilized bi-phasic polymer blends

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Broadband dielectric spectroscopy (BDS) is often used to probe the electrical percolation threshold (EPT) of multiwalled carbon nanotubes (MWNTs) in polymeric systems [1]. In this regard, phase separation of polymer blends with selectively localized MWNTs [2] and stabilization of the cocontinuous morphology by block and random copolymers [3, 4] are valuable tools to reduce the EPT. We now present novel routes to simultaneously tune the phase-separated morphology and MWNT network in 60/40 PMMA/PαMSAN blends and thereby reduce the EPT. We developed a method based on BDS to successfully predict the localization and interconnectivity of MWNTs in the resulting conductive blends and validated our predictions by (S)TEM images. An improved dispersion and hence overall connectivity of MWNTs in solution mixed blends compared to melt mixed blends was discerned by comparing the electrical properties in the blends to that in equivalent PMMA and PαMSAN monophasic nanocomposites, thereby decreasing the EPT from 2 wt% in melt mixed blends to 0.5 wt% in solution mixed blends. Morphology stabilization and refinement were achieved by employing novel types of compatibilizers in solution mixed blends, including short PS-Br polymers and long PMMA-SH polymers, which further reduced the EPT from 0.5 wt% MWNTs to 0.15 wt% MWNTs in presence of 2 wt% of compatibilizer. The kinetic competition between the migration of the compatibilizers to the blend interface and the migration of the MWNTs to their energetically preferred PαMSAN phase during phase separation, gave rise to different MWNT localization, either in the PMMA phase, in the PαMSAN phase or at the interface, depending on the polymer compatibilizer. This in turn resulted in disparate interfacial polarization peak characteristics. The amount of entrapped polymer between adjacent MWNTs in the microcapacitor assembly was estimated by the dielectric interlayer model. The gap spacing of the microcapacitors, on the other hand, was deduced from the relaxation time of charge migration by fluctuation-induced tunnelling [5]. Both these parameters allow to model the interfacial capacitance of the various MWNT microcapacitor networks in the compatibilized bi-phasic blends.

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Molecular mobility of chiral amorphous compounds: Original case study of Nac-MBA

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Chiral molecules are coumpounds non-superimposable to their mirror images. For example, couples of enantiomers (or antipodes) are couples of 3D objects that differ from their image through inversion symmetry [1]. The stereochemical, structural and thermodynamic implications of such molecular property play an important role in many biological and physico-chemical processes [2]. In particular, more than half of the commercialized Active Pharmaceutical Ingredients (API) are chiral. However, the impact of chirality on the amorphous state of organic molecules remains a scientific field still poorly understood. The few cases reported in the literature illustrate different crystallization kinetics from the amorphous state dependent on the enantiomeric excess (ee) [1, 3-4].

The present work deals with the investigation of the molecular mobility of a chiral molecule (namely N-acetyl-α-methylbenzylamine) below and above Tg at different ee. For this purpose, the amorphous state of the model compound has been studied by broadband dielectric spectroscopy coupled to molecular dynamic simulations.

The first results highlight an unexpected Debye process (already observed in the case of monohydroxy-alcohols, secondary amides and other small organic molecules [5]) taking place concomitantly with the structural relaxation process α. So far, the impact of the ee seems to be mainly expressed in this Debye relaxation, by contrast to α and secondary relaxation processes. The Debye relaxation may be related to supramolecular hydrogen bond aggregates, which can remain even in the amorphous state. The latter bond chains are traduced by the giant value of the dielectric strength in the supercooled liquid region and is function of the ee.

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Correlating the Ionic Conductivity and Morphology of Pendant and Backbone Polymerized Ionic Liquids

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Polymerized ionic liquids (PILs) are single ion conductors, in which one of the ionic species is incorporated in the polymer chain while the other is nominally free to be transported.[1] Due to their solid-like nature and conductive properties, PILs are attractive as electrolytes in battery applications and other areas where liquid electrolytes are undesirable.[2,3] In PILs, the ionic species can either be directly incorporated into the polymeric backbone (backbone PILs) or placed as pendant groups to the chain (pendant PILs).[4] Here, we examined the conductivity and morphology of imidazolium-based pendant and backbone PILs with TFSI, CPFSI, and NfO counter-anions. We employed temperature-dependent X-ray scattering to measure the correlation distances of the PILs and dielectric relaxation spectroscopy to measure their conductivity as a function of temperature. We found that pendant PILs yielded higher ionic conductivity when scaled to Tg, but backbone PILs exhibited higher ionic conductivity on an absolute temperature scale. We also found a thermally reversible ionic aggregation peak using small-angle X-ray scattering for backbone PIL with the NfO counter anion. This study gleans insight on relating conductivity of equivalent backbone and pendant PIL structures to morphology, leading to a deeper understanding on the fundamental relationship between conductivity and morphology in PILs.

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Polythiophene-based polyelectrolytes from polymerized ionic liquids. Self-assembly and dc conduction

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Recently, there has been considerable interest in developing materials that combine electronic with ionic conduction[1]. Furthermore, earlier studies[2-3] concentrated on the decoupling of ion motion from segmental relaxation in Polymerized Ionic Liquids (PILs). Herein, we designed PILs consisting of a polythiophene backbone, a side group with a cation covalently bonded and a mobile anion. We report on the ionic conductivity as a function of backbone molecular weight, side group length (from n-butyl to n-decyl), and anion size (Br^-, BF_4^-, ClO_4^-, PF_6^-, Picrate, $[B(Ph)_4]^-$). Increasing side group length increases the room temperature conductivity by four orders of magnitude (internal plasticization). The anion size (anionic radii from 0.19 nm to 0.44 nm) affects both the structure (lamellar-smectic to amorphous by increasing anion radius as evidenced by WAXS) and the measured conductivity. The dc-conductivity increases by six orders of magnitude by increasing anion size at ambient temperature. As a result, conductivities as high as 2×10^{-3} S/cm could be measured at high temperatures. Differences in dc - conductivity are discussed in terms of changes in glass temperature that is increasing with increasing anion size. In a T_g-scaled representation there is an additional dependence of conductivity on anion size and the value of dielectric permittivity.

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Coexistence of two structural relaxation processes in mixtures involving monohydroxy alcohols

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Evidence for the coexistence of two glass transitions is found in binary mixtures involving monohydroxy alcohols by means of dielectric spectroscopy and, remarkably, also of shear rheology [1]. One important aspect of our findings is that the observation of bimodal motional heterogeneity is possible despite the fact that the glass transition temperatures of the mixing partners differ by only 40 K. To explain this interesting behavior, we propose that the formation of supramolecular structures, driven by hydrogen bonds in one of the mixture components, facilitates the emergence of a dynamical heterogeneity which for other binary liquids was so far only observed in the presence of a large mobility contrast of the two molecular species [2, 3, 4, 5, 6, 7]. Our results open new perspectives for the clarification of the fascinating structural complexity revealed in an already very large number of binary glass-forming materials.

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Molecular Mobility and Ionic Conductivity of Ionic Liquid Crystals Forming a Hexagonal Columnar Mesophase

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For the first time, the molecular mobility of two linear-shaped tetramethylated guanidinium triflates ionic liquid crystals (ILCs) having different length of alkyl chains was investigated by a combination of broadband dielectric spectroscopy (BDS) and specific heat spectroscopy (SHS). By self-assembly, these ILCs can form a hexagonal ordered mesophase besides plastic crystalline phases and the isotropic state. SHS was carried out by differential AC-chip calorimetry at higher frequencies and temperature-modulated DSC at lower frequencies.

Two relaxation processes were found by BDS for both samples. At low temperatures, a γ-processes is observed which is assigned to specific localized fluctuations. At higher temperatures, α_1-processes take place. α_2-processes were also detected by SHS but with a completely different temperature dependence of the relaxation times. Different molecular assignments of α_1- and α_2-processes are suggested. At even higher temperatures, conductivity was detected by BDS. An increase in the DC conductivity by four orders of magnitude at the phase transition from the plastic crystalline to the hexagonal columnar mesophase is found. This result is traced to a change in the charge transport mechanism from a delocalized electron hopping in the stacked aromatic systems (in the plastic phase) to one dominated by an ionic conduction in the quasi-1D ion channels formed along the supermolecular columns in the ILC hexagonal mesophases. [1]

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The analysis of molecular relaxations in thermo-responsive polymer hydrogels

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Stimuli-responsive polymer hydrogels made from biocompatible poly(oligo(ethylene glycol)methyl ether methacrylates) POEGMAs are regarded as potential ‘smart’ carriers in drug delivery systems. Bioactive substances may be rapidly released from the hydrogel as a result of so-called volume phase transition (VPT) accompanying by an abrupt shrinkage of the polymer network [1]. From a practical point of view very slow response to stimuli is one of the most important problem that remains to be solved [2].

It is known, that the dynamics of VPT, aside from the polymer network architecture, solvent diffusivity and polymer-solvent interactions, depends on dynamics of polymer chain [3-4]. Therefore, the aim of this study assumed to compare relaxation process in: (i) linear POEGMAs differing on chain length (ii) POEGMAs network with various crosslinking density and side (oligoether) chain length.

Irregular POEGMAs networks are produced by radiation-induced free radical polymerization, while the regular networks (with controlled chain length between crosslinks) and linear polymers are synthetized by atom transfer radical polymerization. To obtain networks with different density of crosslinks, various radiation doses or different amount of crosslinker are applied (for details see [5-6]).

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Dynamics of ice in ice nucleating protein (INP) solutions

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The freezing of water is one of the most common everyday processes that happen on Earth and it is of high relevance to an enormous number of technological and environmental phenomena. There are two well-known mechanisms of ice nucleation: homogeneous (235 K) and heterogeneous (at higher temperatures) [1]. In particular, heterogeneous ice nucleation is more commonly observed and it occurs due to the presence of foreign ice-nucleating agents which can be organics or inorganics. Among others mineral dust particles or the so-called ice nucleating proteins (INPs) can catalyze the ice nucleation. INPs have the ability to freeze water between 263 and 269 K [2].

Here we studied well-diluted solutions of an INP to analyze the dynamics of ice at supercooled temperatures by broadband dielectric spectroscopy (BDS). Two different cooling protocols (fast and slow) were used in the BDS experiments. In addition, differential scanning calorimetry (DSC) was used to determine the crystallization temperature.

The dielectric results show two different processes due to crystallized water, one of them strongly affected by the protein. We also analyzed samples with and without salts in order to analyze the conductivity effects and how the presence of salt affects the relaxation processes. In addition, comparison with other experimental data of ice in normal proteins will be discussed.

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Surface imprinting polymers characterization for cell detection by dielectric relaxation spectroscopy

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Many disease diagnosis depends on the identification of cells and pathogens contained in body fluids. Due to natural receptors' high cost and inadequate stability amongst other limitations [1], studies on cell detection are focusing on better alternatives for biosensor applications such as biomimetic recognition elements. An example of such recognition layer is the so-called surface imprinted polymers (SIPs) which is produced by cell imprinting on polymer layers. These receptors have been shown to be suitable for specific and selective cellular recognition. However, their working mechanisms are not fully understood.

Therefore, in this study, various factors that control the cell recognition were explored using dielectric relaxation spectroscopy (DRS). Specifically, the molecular dynamics of surface-imprinted and non-imprinted polyurethane (NIP) layers was studied with focus on the dielectric relaxation signatures of cell membrane entities.

The results revealed a relaxation process that was not observed for NIP, which suggests that imprinting transfers lipid molecules from the cell membrane to the polymer layer. Such a process is attributed to the intrinsic lipid dynamics. Therefore, we have shown that DRS is a reliable technique for exploring the dynamic and temperature-dependent dielectric relaxation signatures of lipids left during the imprinting on the SIP [2].

In addition, controlling and monitoring the adhesion of cell both under static and dynamic conditions is crucial to different bioengineering and medical applications, such as tissue engineering and biosensors [3]. Currently, most techniques for controlling cell adhesion while monitoring in real-time are limited. In this study, we employ DRS for probing cell-substrate interactions on different surfaces and monitoring their response reversibly as a function of time and physico-chemical properties.

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Asymmetric interfacial dynamics and glass transition in stacked thin polymer films

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As a physical origin of deviation of the glass transition temperature of thin polymer films from the bulk, the effects of surface/interfaces and adsorbed layer near substrate on the glass transition have been investigated by many researchers recently. In this presentation, the relationship between interfacial dynamics at the interface of the two layered thin films and glass transition dynamics in thin polymer films has been clarified using dielectric relaxation spectroscopy and neutron reflectivity measurements. For this purpose, multi-layered thin films of deuterated PMMA and hydrogenated PMMA have been prepared. For two layered thin films, two different sets of layered thin films were used as follows: 1) Tg of h-PMMA layer is fixed and Tg of d-PMMA layer is controlled by blending of two different molecular weight samples, and 2) Tgs of h-PMMA layer and the bulk d-PMMA are fixed, and only the thickness of d-PMMA layer was changed between 50nm and 15nm. Dielectric relaxation spectroscopy and neutron reflectivity measurements during the annealing process of the layered thin films above Tg have given us the following results. 1) The roughness at the interface between two thin layers increases with the annealing time, whereas the relaxation rate and strength of the alpha-process decrease with increasing annealing time, i.e., a strong correlation between the time evolution of the interfacial structure and the dynamics of the alpha-process during annealing, 2) the changing rate of thickness of d-PMMA layer with respect to annealing time is *positive*, while that of h-PMMA layer is *negative*, if the bulk Tg of d-PMMA is by 3K larger than that of h-PMMA. As the Tg of d-PMMA decreases by blending with low Tg component and the Tg of h-PMMA layer is fixed, the annealing time dependence of the thickness of d- and h-PMMA layers changes and finally the changing rate of d-PMMA layer becomes *negative* and that of h-PMMA layer becomes *positive*. 3) As thickness of d-PMMA layer decreases keeping the thickness of h-PMMA layer constant, it could be observed that the changing rating rates of the thicknesses of d- and h-PMMA layers change in accordance with those observed in 2). This result strongly suggests the decrease in Tg of d-PMMA layer with decreasing film thickness of the d-PMMA layer. The detailed discussions will be given in my talk in Brussels.

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Growth kinetics and molecular mobility of irreversibly adsorbed layers in thin polymer films

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In well-annealed thin polymer films, with non-repulsive polymer/substrate interactions, an irreversibly adsorbed layer is expected to from. These adsorbed layers have shown greate potential for technological applications. However, their growth kinetics and molecular dynamics are still not fully understood. This is partly due to the hard accessibility of these layers in thin films. Here, the irreversibly adsorbed layers of homopolymer thin films are revealed by solvent-leaching experiments. First, the growth kinetics of these layers is investigated as a function of annealing time, annealing temperature, leaching time and the original film thickness. The film thickness, topography and the quality of the adsorbed layer is controlled by Atomic Force Microscopy (AFM). Secondly, the molecular mobility of the adsorbed layer is investigated by Broadband Dielectric Spectroscopy (BDS). A recently developed nanostructured capacitor arrangement is employed to measure the layer with a free surface. The results are quantitatively compared and discussed with respect to recently published work. [1]

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Mapping the Dynamic Heterogeneities in Thin Films of Miscible PVME/PS Blend by Nano-sized Relaxation and X-ray Spectroscopies

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Nowadays, the structure-property relationship of nanoconfined polymers is one of the most active research topics, due to their potential in impacting various thin-film applications. The glass transition phenomenon and the related segmental dynamics have been one of the main properties investigated. However, most investigations were done on homopolymers [1]. Understanding the nano-confinement effects on miscible polymer blends present extra challenges, due to the interplay of different parameters, e.g. surface enrichment, asymmetry of both components, compositional hetero-geneities, etc.

In this work [2-4], a combination of nanosized relaxation spectroscopies; Broadband Dielectric Spectroscopy (BDS) and Specific Heat Spectroscopy (SHS), was utilized to probe the glassy dynamics of thin films of PVME/PS 25/75 wt% blend (4 nm – 200 nm). BDS measurements of supported and capped films, employing novel nano-structured and cross- electrode capacitors, respectively, revealed a complex dynamic behavior. Moreover, SHS, employing an AC-chip calorimeter, further confirmed the claims.

This complex behavior revealed multiple confinement effects on the segments at the polymer/substrate interface as well as the PVME segments within the bulk-like layer. In addition, it unveiled a fine interplay between the effect of the free-surface and the adsorbed layers, along with the strong influence of thickness dependent compositional heterogeneities. Furthermore, X-ray Photoelectron Spectroscopy (XPS), and energy resolved XPS measurements were carried out in a complementary manner to map out these compositional heterogeneities at the interfaces. In this talk, the nanoconfinement effects on the segmental dynamics will be discussed in detail, in the light of the XPS results.

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How the Vitrification of Interfacial Layer Affects the Molecular Dynamics of Glass-Formers at the Nanoscale? The Impact of Interactions.

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The effect of 2D confinement on the molecular dynamics of a series of chemically modified poly(propylene glycols) has been studied with the use of Broadband Dielectric Spectroscopy (BDS) and Differential Scanning Calorimetry (DSC). It is shown that crossover from VFT to the Arrhenius-like behavior of molecular dynamics is strictly related to vitrification of the adsorbed polymers and freezing of the system's density. Moreover. the annealing of the samples below the crossover temperature, T_c, leads to a systematic shift of the examined modes towards lower frequencies, due to the equilibration of systems' density. After annealing, a system with higher density characterized by more homogeneous dynamics can be obtained. It is therefore possible to modify and control properties of the confined material by using different thermal treatment protocols [1]. Furthermore, we studied impact of the interfacial energy γ_{SL} between host and guest materials on the glass transition temperature of the core and adsorbed polymers. Although generally reduction in T_g of core material correlates well with the trend reported previously for polymers incorporated into nanoporous materials [2], it was found that also specific interaction contributes to this phenomenon. We have shown that scale of reduction of T_g varies in the following order PPGOH → $PPG\text{-}NH_2$ → $PPG\text{-}OCH_3$. That simply means that strength of the specific interaction (H bonds) between host and guest material seems to be very impotant parameter that also should be taken into account. Finally, it was clearly demonstrated that treduction of the Tg of the core macromolecules is strictly related to the vitrification of the adsorbed polymers which chages accordingly to the strength of the H bonds. *K.K. is thankful for a financial support from the Polish National Science Centre (Dec. no 2015/17/B/ST3/01195).*

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On the Glass Transition Suppression of Polystyrene in SBS Rubber

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It is known that the measured glass transition temperature (T_g) of some polymers can be dependent on both the thickness of the sample and adjacent materials.[1] It is also known that block copolymers with incompatible blocks can undergo microphase separation.[2] One common example combining these two effects is the block copolymer poly(styrene-butadiene-styrene) (SBS), in which microphase separation of the two polymer types can create nanometer-scale polystyrene phases which exhibit T_gs up to 50 K lower than bulk polystyrene.[3] A large amount of research has been performed on both this polymer and on thin-film polystyrene in order to understand why this T_g suppression exists. To what extent is the adjacent supercooled polybutadiene affecting the polystyrene dynamics? What if the polybutadiene were to be replaced with an amorphous glass? Existing research has utilized multi-layer films and copolymers with varying blocks to examine the relationship between the neighboring polymers. Here, we have selectively halogenated the polybutadiene block in SBS rubber in order to elevate its T_g above that of polystyrene. Broadband dielectric spectroscopy and calorimetry measurements of the glass transitions of this block copolymer suggest that the suppression of the T_g of the polystyrene phase persists even though the polybutadiene phase is an amorphous solid. This work also offers a unique way of tailoring the glass transition of a specific block of a copolymer for future studies.

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Size-effects on the segmental dynamics of sub 10-nm segregated polydimethysiloxane.

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Confining glass-forming polymer melts has been a way to look for the size effects on the segmental scale dynamics, which would be expected to occur on cooling down the liquid towards the glass transition, in connection with the corresponding growing size of the cooperatively rearranging regions. As far the growing size becomes comparable to the confinement distances, a change in the temperature dependence of the segmental mobility time has been anticipated. Despite of this expectation, reported experimental results obtianed so far are rather contradictory. A reason for the discrepancies is the important role of interfaces, which in many cases largely affects the segmental dynamics. Unraveling the genuine size effects from those attributable to the presence of interfaces can be extermelly difficult.
In this work we show how the segmental dynamics of poly(dimethylsiloxane), PDMS, is modified in systems pressenting PDMS segregated phases of varying geometry and sizes. Most of the considered systems present obvious changes in the dynamics that can be mainly attributed to the presence of interfaces. However, there is a single case where effects directly connected with the growing size of the cooperatively rearranging regions are found. In this particular case, a segregated PDMS phase with sub-10 nm size in the three dimensions is present.[1] Contrarly, segregated sub-10 nm lamellar PDMS phases do not manifest such a behavior, the single effect in the later case being the general slowing-down of the segmental dynamics induced by the presence of rigid interfaces.

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Confienement-Induced Changes in the Relaxation Dynamics and Crystallization Behavior of Glass-Forming Liquids

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In the presence of geometrical restrictions at the nanoscale level, the glass-transition dynamics and crystallization tendency of the molecular systems can be much different from their bulk behavior. For that reason, the macro and nanoscopic behavior of molecular liquids and polymers are often regarded as two non-connected realms, governed by their own rules. The motivation behind our work is to look for a universal link that can tie up the most important features of the glass-forming liquids reported in macro- and nano-scales to get a consistent picture of their glassy behavior. To achieve that, we have made use of the knowledge that comes from high-pressure studies of glass-forming systems and transfers it to nanoscale research. This includes in particular (1) the density scaling concept which is considered as one of the most important and general findings reported for (bulk) glass-forming materials, (2) isochronal superposition, and (3) 'sensitivity' of the glass-transition dynamics to pressure/density fluctuation effects. The most important outcome from our study is that the glassy dynamics in 2d-hard confinement might obey the density scaling relation, ρ^γ/T [1], just like the bulk fluids but not essentially the isochronal superposition [2]. Finding that for 'simple', non-hydrogen bonded liquids the same value of the scaling exponent γ superposes the α-relaxation time measured at different state points in nanoscale confinement and upon increased pressure implies that, in many cases, we can predict the dynamic features of the nanoconfined system close to its glass-transition temperature from the high-pressure studies of the bulk liquid and vice versa. In this contribution, we will also demonstrate and compare changes in the crystallization progress as a function of lowering pore diameter and increasing pressure, i.e. two different strategies allowing to affect the molecular packing in the molecular glass-formers [2,3].

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Glass transition and molecular mobility by calorimetry in confined glasses

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Measuring glassy dynamics by broadband dielectric spectroscopy (BDS) entails, in the vast majority of cases, the application of a linear perturbation of the polarization. The great advantage of this technique is that it allows covering a broad range of frequency and, as a consequence, exploring the behavior of molecular motions over a wide temperature interval [1]. Given these premises, BDS presents several limitations. Among them *i*) the inability of measuring all aspects of glassy dynamics, in particular the kinetics of irreversible vitrification, so-called thermal glass transition; and *ii*) the ubiquitous presence of phenomena related to ionic conductivity, which, in some cases, prevents the detection of relaxational processes. The latter limitation is especially relevant in heterogeneous systems such as nanocomposites or, in general, systems with large amount of interface.

In the present contribution, I show how new generation fast scanning calorimetry (FSC) [2], allowing cooling/heating rates as large as several thousands K/s, can deliver simulataneous information on the molecular mobility and the vitrification kinetics. Regarding the former, FSC allows accessing frequencies from the sub-Hz region to more than 100 Hz. Within this context, I will show how these aspects can be applied to study the glassy dynamics of geometrically confined polymers, that is, polymer nanospheres [3] and other systems [4]. Measurements of the molecular mobility indicate that the molecular mobility of these systems is essentially bulk-like. In contrast, the study of vitrification kinetics in these systems shows depressed glass transition temperature in comparison to the bulk. Such depression is larger for systems with shorter confinement length scale. Hence, these results provide compelling arguments on the decoupling between molecular mobility and vitrification kinetics. The main consequence is that the paradigmatic view on the connection between these two aspects of glassy dynamics must be revisited.

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The Cooperative Free Volume Rate Model for Pressure Dependent Dynamics

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Our recent work has demonstrated that inverse free volume ($1/V_{\text{free}}$) is the natural variable for describing the form of the volume contribution to pressure dependent dynamics.[1] We use thermodynamic analysis to quantify $V_{\text{free}} = V - V_{\text{hc}}$, where V_{hc} is a system's characteristic hard core volume at close packing. Unlike historical free volume models, our approach combines independent contributions from both, free volume and temperature. Our analysis of dielectric spectroscopy data on polymer melts and small molecule liquids shows that on isotherms, the log of the segmental relaxation time ($\ln\tau$) is a linear function of $1/V_{\text{free}}$, and that the slope of each isotherm increases with decreasing T. An important implication is that the form of the volume dependence is the same for all systems, and thus can be treated via simple thermodynamic analysis. We find that all systems show a general behavior where $\ln(\tau/\tau_{\text{ref}}) = (1/V_{\text{free}}) \times f(T)$. In this talk, we describe a rate model to formulate and explain this behavior. The "cooperative free volume model" is based on an activation free energy that increases with the number (n^*) of cooperating segments, wherein, it is the system's thermodynamic V_{free} value that determines n^*.[2] The model is tested against bead-spring polymer simulation results, where we focus first on the high temperature regime, and then discuss the implementation for predictive modeling at low T. For systems at high T, we can derive a simple form for the T-dependent contribution ($f(T)$) that is based on very clear physical assumptions. The resulting model $\tau(T,V_{\text{free}})$ expression describes the Arrhenius to non-Arrhenius crossover regime, as verified by comparison with extensive pressure dependent simulation data over a wide range of T,P. The model explains a key source of non-Arrhenius behavior on isobars, wherein, the cooperativity required for segmental rearrangement must increase as V_{free} decreases with T, and this drives up the activation energy. This effect explains the volume contribution to segmental dynamics at all temperatures, and is thus the source of the difference between a system's isobaric and isochoric fragility.

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Relaxation in Bulk and Thin Films: Insights Using the Cooperative Free Volume Model

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Molecular dynamic relaxation data in glass forming liquids can lead to significant insight regarding material properties and thus be important for designing applications. In recent work [1,2] we have mapped a clear path between thermodynamic characterization and local relaxation, via theoretical predictions for the free volume of a fluid. However, unlike earlier attempts to create such a link, we also find temperature (T) to be a crucial, second, independent variable. Our studies on experimental glass forming liquids begin with thermodynamic characterization of the pure fluid using the Locally Correlated Lattice (LCL) theory to predict the temperature- and pressure-dependant free volume. We find the inverse free volume to be a natural variable for analyzing relaxation data in all cases we have studied: isothermal plots of the logarithm of relaxation time against inverse free volume yield linear fan-shaped plots, whose slopes depend on temperature. To understand the role of free volume we have developed the Cooperative Free Volume (CVF) rate model, wherein the local relaxation process is characterized by an activation free energy that increases concurrently with the number of participating particles as T is lowered, reflecting changes in the system's free volume. This increasing need for cooperativity is a key source of non-Arrhenius behavior as the temperature is lowered along isobars. In addition, we have studied the role of temperature dependence in both simulated fluids, where the range of interest is broad, and experimental systems, where the focus is closer to the glass transition. Our most recent research focuses on supported thin films. We consider the whole film to comprise an interior region that behaves as bulk, bounded by an interfacial region that incorporates the 'film' character. Using experimental relaxation data [3] for a series of film thicknesses collected at a single temperature (at atmospheric pressure), we are able to make predictions about how film relaxation times change with temperature and pressure, as well as with film thickness. This initial study suggests that the effect of shifting from bulk to film is analogous to the effect of reducing pressure. The talk will cover both film and bulk results, with a focus throughout being on connections with experimental data.

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Mapping Isobaric Aging onto the Equilibrium Phase Diagram

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Close to the glass transition, where the relaxation time is in the order of hours, it is possible to perform aging experiments in which the liquid's properties are monitored as it approaches a new equilibrium after a change in temperature. The out-of-equilibrium liquid accesses parts of phase space that are not accessed by the equilibrium liquid. It is, for example, possible to change the volume without a concomitant change of the microscopic structure. Aging experiments can therefore give new information to the puzzle of what governs the relaxation time and could play a role analogous to that played by high-pressure measurements, the study of ultrastable glasses or glasses under confinement, which have led to important experimental advances in glass science during the last couple of decades. With dielectrics we can obtain very precise information during aging and it is therefore our preferred technique in aging studies [1-4]. The classical interpretation of aging data is based on the TNM formalism, which assumes the existence of a single structural parameter that connects the non-equilibrium aging to the equilibrium dynamics. In Roskilde we have over the years developed ways to test this fundamental idea without assuming specific models for the equilibrium dynamics [1-4]. Recent work connects the structural parameter directly to the density-temperature phase diagram [1], and it was subsequently shown that this interpretation of the structural parameter can be formalized in terms of isomorph theory [2]. Isomorph theory is only expected to describe the class of R-simple liquids which include van der Waals but not hydrogen-bonded liquids. Nevertheless, we find no difference in how well the TNM-formalism works for van der Waals vs. hydrogen-bonded liquids [4].

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Isochronal superposition, density scaling and the nature of the β relaxation

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The Johari-Goldstein (JG) β relaxation, involving all atoms of the molecule or the polymer repear unit is ubiquituous, and perhaps universal, in glass forming materials. From numerous studies the idea has emerged of a close connection between the faster JG and slower α relaxation, established based on several correlations between properties of the two.

Another way to assess the relationship between the JG and α relaxations is to test to what extent the JG relaxation is invariant under conditions where the α relaxation time and stretching exponent is unchanged (so-called isochronal superposition). By temperature and pressure-dependent dielectric measurements this invariance has been established for several molecular liquids. We find that this behavior is not universal; for 1,4-polybutadiene and polymethylmethacrylate the JG relaxation moves systematically to higher frequency with increasing pressure and temperature at constant α relaxation time.

We show using molecular dynamics simulations that the behavior of 1,4-polybutadiene, and perhaps of polymers generally, is a consequence of the torsional inflexibility of the polymer backbone. This accentuates the effect of constraints from local intermolecular barriers, with consequent deviation in the response of the JG and α relaxations due to their different dynamic length scales. Thus, although the Johari-Goldstein relaxation is related to and may even evolve into the structural relaxation associated with the glass transition, its response is not universal, but rather depends on the chemical structure.

Isochronal superposition from picosecond to second investigated with simultaneous dielectric and neutron spectroscopy

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By combining dielectric spectroscopy (DS) and neutron scattering (NS) in our newly developed high-pressure DS-NS cell [1], we show that both the fast and slow dynamics in simple glass-forming liquids along isochrones, i.e. constant relaxation time $\tau_\alpha(T,P)$, is invariant as predicted by isomorph theory. Experiments were carried out at Institut Laue-Langevin using DS and neutron backscattering from IN16B accessing nanosecond dynamics and neutron time-of-flight from IN5 accessing picosecond dynamics [2,3].

Dynamics in real glass-forming liquids is rich and includes a large range of dynamical processes taking place on different timescales. While the main dynamical feature is the α-relaxation, there is no common understanding yet of what governs the timescale and the spectral shape of the relaxation. It has several times been suggested that there is a close connection between the fast and slow dynamics, even though they differ in timescales by ten or more orders of magnitude.

A recent theoretical development in the physics of liquids, the isomorph theory, rationalises this [4]. The fundamental prediction of the isomorph theory is the existence of isomorphs, i.e. curves in the phase diagram along which all dynamical phenomena and structure are invariant. We can identify possible isomorphs by the isochrones.

We investigate the dynamics with NS on pico- and nanosecond timescales in combination with DS for three liquids along the glass transition isochrone, i.e. τ_α =100 s [2], and along faster isochrones with the alpha relaxation on nanosecond timescale [3]. We show isomorphs for simple van der Waals liquids, and how scaling breaks down for a complex H-bonded liquid.

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Microscopic nature of β process of sugar alcohols

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Sugar alcohols such as sorbitol and xylitol show two dielectric loss peaks in the temperature range above T_g corresponding to the structural α relaxation process and the local β relaxation process. The α relaxation time strongly depends on kinds of sugar alcohols, while the beta relaxation time does not depend on very much. We have demonstrated that mixtures of different sugar alcohols also show two dielectric loss peaks. One of them can be assigned to the α process and dielectric properties such as relaxation time show the intermediate feature of the two mixing materials. On the other hand, we couldn't examine the mixing effect on the β process because the β relaxation time at a temperature is almost the same for different sugar alcohols. Fructose shows γ process which is also a local relaxation process. Since both of fructose and sorbitol are hydrogen-bonding systems, mixing of these materials may provide useful information to understand microscopic nature of the β process. In this study, broadband dielectrics relaxation measurements have been performed on sorbitol, fructose and their mixtures in the frequency range between 10μHz and 100MHz at temperatures covering their supercooled liquids and glasses. Mixture of sorbitol and fructose shows two loss peaks. One of them seems to be the α process of the mixture. The peak frequency of the higher frequency process is located at the intermediate range between relaxation frequencies of the β process of sorbitol and the γ process of fructose. Discussion will be made on locality of the β process.

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The JG β-relaxation/primitive relaxation never fail to show up in binary mixtures and polymer blends

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In a series of papers on binary glass-forming mixtures of tripropyl phosphate (TPP) with polystyrene (PS), Kahlau et al. [J. Chem. Phys. **140**, 044509 (2014)], and Bock et al. [J. Chem. Phys. **139**, 064508 (2013), J. Chem. Phys. **140**, 094505 (2014), J. Non-Cryst. Solids **407**, 88 (2015). Pötzschner et al. J. Chem. Phys. **143**, 154506 (2015).] presented the data on the dynamics of the two components studied over the entire composition range by several experimental methods. These sets of data, obtained by multiple experimental techniques on mixtures with a large difference $\Delta T_g \approx 200$ K between the glass transition temperatures of two starting glass-formers. From the data, they obtained two α-relaxations, α1 and α2. The temperature dependence of the slower α1 is Vogel-Fulcher like, but the faster α2 is Arrhenius. We [1] have re-examined their data and show that their α2-relaxation is the Johari-Goldstein (JG) β-relaxation with Arrhenius T-dependence admixed with a true α2-relaxation with stronger temperature dependence. In support of our interpretation of their data, we made dielectric measurements at elevated pressures P to show the ratio of the α1 and α2 relaxation times, $\tau_{\alpha 1}(T,P)/\tau_{\alpha 2}(T,P)$, is invariant to variations of T and P while $\tau_{\alpha 1}(T,P)$ is kept constant. This property proves unequivocally that the α2-relaxation is the Johari-Goldstein (JG) β-relaxation, the precursor of the α1-relaxation. There is also approximate agreement between the JG β-relaxation time τ_{JG} and the primitive relaxation time τ_0 of the Coupling Model, which further supports the identification. Subsequently, the true but unresolved α2-relaxation is recovered, and it relaxation times with much stronger temperature dependence are deduced, as expected for the α-relaxation of the TPP component. The results are fully compatible with that found in another binary mixture of methyltetrahydrofuran with tristyrene and PS with $\Delta T_g \approx 283$ K, even larger than $\Delta T_g \approx 200$ K of the mixture of TPP with PS, and in several polymer blends [2]. The contrast between the two very different interpretations brought out in this paper [1] is deemed beneficial for further progress in this research area.

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Nuclear resonant scattering as microscopic probe for the Johari-Goldstein relaxation process in supercooled liquids

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Glass-forming liquids are characterized by two universal relaxation processes known as α and β [1]. The β-relaxation process is strictly related to and acts as a precursor of the α-relaxation; unveiling its microscopic origin remains therefore a crucial step toward the complete understanding of the glass transition [2]. This has not been accomplished yet since probing the dynamics of this process when its timescale is well separated from that of the α-one (>1 ns) and at the atomic length scale is extremely challenging both using simulations [3-4] and experimentally. Among the few techniques that can access this length- and time-range, nuclear γ-resonance time domain interferometry (TDI) is a very promising one [5-6]. TDI is indeed able to probe dynamics with characteristic times in the range 10ns-10μs at the Ångstrom length-scale.Exploiting the unique dynamical range of this technique we studied two glass-formers: 1-propanol and 5-methyl-2-hexanol [7], identifying at the microscopic length scale both the α and the β processes and comparing them with those probed by means of dielectric spectroscopy (DS).

Here, the main results of this investigation will be presented. A particular attention will be given to the superquadratic wave-number dependence of the β relaxation time at q's larger than the first peak of the static structure factor, similar to what reported in ortho-therphenyl [5]. Starting from these observations we will discuss our current view of the microscopic origin of the Johari-Goldstein relaxation.

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New Link between Structural and Johari-Goldstein Relaxation Parameters in Glass Formers

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Entropy-Enthalpy compensation effects in dielectric relaxation processes have been observed in a wide array of of glass forming liquids. These effects have been demonstrated in both the structural alpha process, as well as the secondary Johari-Goldstein (J-G) beta process. Despite the fact that these effects have been noted, little use has been made of the parameters extracted from the various types of analysis.

We have demonstrated that this type of Meyer-Neldel behavior can be accounted for using a Space-Time percolation model applied in relation with the cooperative rearranging regions. This provides the first step towards a more comprehensive model capable of providing physical meaning for some of the compensation parameters.

In addition to previous findings, results from high pressure studies are incorporated as well. These results allow for additional degrees of freedom in manipulating the energy landscape, providing vital insights into both the strengths and weaknesses of the model.

Based on these parameters and on the proposed model we further present a new connection linking the structural relaxation with the secondary J-G relaxation process across a wide range of glass forming systems. The proposed link between the compensation effects in these two distinct types of processes, sheds new light on the connection between them and provides further insights into their microscopic origins.

Linear and nonlinear orientational correlation factors from the rotational Dean-Kawasaki equation

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A method of calculation of the Kirkwood and Piekara-Kielich [1] correlation factors occurring in the Kirkwood-Fröhlich formula for the static linear dielectric constant and that derived by Piekara and Kielich for the static cubic dielectric increment is proposed. The method relies on solving the averaged rotational Dean-Kawasaki equation [2] in the stationary state in conjunction with the Ornstein-Zernike equation for the orientational pair correlation function, and allows the obtaining of *analytical* formulas for these correlation factors provided the pair interaction potential is specified. The results obtained compare favorably with the experimental temperature dependence of the linear dielectric constant of some simple polar liquids at normal pressures. From this comparison, it is deduced that the contribution of the distortional polarization contribution cannot be completely separated in the Kirkwood-Fröhlich formula, i.e., the Kirkwood-Fröhlich and Piekara-Kielich correlation factors contain this distortional polarization effects in a non-trivial way [3].

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Microscopic modelling of dielectric α and β relaxation in glasses and orientationally disorder crystals based on Generalized Langevin Equations

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A strong limitation to our understanding of relaxation processes in glasses comes from the absence of microscopic models. Almost a hundred years since Debye, modelling of dielectric relaxation in glasses is still performed in an empirical way, i.e. by taking Fourier transforms of simple exponentials and Kohlrausch stretched-exponentials. Sophisticated theories have been proposed such as Mode-Coupling theory, but their validity is limited to the liquid phase above Tg. We have recently developed a new approach which can be derived from first principles by schematizing the motion of a molecular dipole as a particle couple to a thermal bath represented by all other molecular (and intramolecular) degrees of freedom.

This leads to a Generalized Langevin equation for the dynamics which yields semi-analytical expressions for the real and imaginary parts of dielectric modulus which depend on the vibrational density of states (VDOS) of the system, thus providing a fundamental link between dielectric response and VDOS. I will show how this model can be used to rationalize puzzling aspects of glassy relaxation, such as the role of boson peak on the α-wing asymmetry of dielectric loss [1-2], and to clarify the microscopic origin of β relaxation and its interplay with alpha relaxation [3].

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Qualitative Change in Temperature Dependence of Structural Relaxation: Diverge or not Diverge

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High accuracy of the dielectric spectroscopy measurements provide an opportunity for detailed analysis of temperature variations of structural relaxation $\tau_\alpha(T)$ in glass forming liquids. We present a detailed analysis of $\tau_\alpha(T)$ in several supercooled liquids that revealed a qualitatively distinct feature - a sharp, cusp-like maximum in the second derivative of log $\tau_\alpha(T)$ at some T_{max} [1]. It suggests that the super-Arrhenius temperature dependence of $\tau_\alpha(T)$ in glass-forming liquids eventually crosses over to an Arrhenius behavior at $T<T_{max}$, and there is no divergence of $\tau_\alpha(T)$ at non-zero T. Our analysis demonstrates that T_{max} can be above or below T_g, depending on sensitivity of $\tau_\alpha(T)$ to change in density ρ quantified by the exponent γ in the thermodynamic scaling $\tau_\alpha(T) \sim \exp(A/T\rho^{-\gamma})$. We emphasize that these results turn the discussion of the glass transition to the new avenue – the origin of the limiting activation energy for structural relaxation at low T. Real activation energy for structural relaxation cannot grow indefinitely.

To understand better the steepness of the temperature dependence of $\tau_\alpha(T)$, (fragility) we performed detailed analysis of the static structure factor $S(Q)$ in several glass forming liquids. This analysis reveals that the temperature variations of the width of the main diffraction peak $\Delta Q(T)$ correlates with fragility of these liquids [2]. This observation suggests a direct connection between rather subtle changes in static structure and sharp slowing down of structural relaxation in glass forming liquids. We show that this observation can be rationalized using the Adam-Gibbs approach, through a connection between temperature variations of structural correlation length, $l_c \sim 2\pi/\Delta Q$, and the size of cooperatively rearranging regions. At the end we discuss specific case of polymers where chain connectivity leads to deviations from regularities observed for small molecules [3].

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Control of Crystallization Outcomes in Molecular Glass-Formers by Electric Fields

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High electric fields of magnitude E applied to polar molecular materials lead to situations which are practically always characterized by dipole energies (μE) that remain small compared with the thermal energy, i.e., $\mu E \ll k_B T$. As a result, most nonlinear dielectric effects are very small and electric fields are expected to have little impact on the net molecular orientation and on thermodynamic potentials. Nevertheless, static electric fields in the range from 40 to 200 kV/cm were observed to impact the crystallization outcome of a polar molecular glass-former: vinyl ethylene carbonate (VEC), a derivative of propylene carbonate [1].

Various field protocols have been employed to map out the effect of a static electric field on the crystallization behavior of VEC, while the volume fraction of the liquid state was measured by the dielectric permittivity. The rate of crystallization could be accelerated by more than a factor of 10, either by applying a field near T_g and then taking the sample to a higher temperature T_c without field, or by taking the sample directly from $T > T_m$ to T_c and then applying a field. Remarkably, crystallization promoted by electric fields led to a new polymorph that could not be obtained in the absence of an electric field, whose signature is a melting temperature that was observed to be 20 K below that of the ordinary crystal of VEC.

All field-induced changes in the crystallization behavior were found to be fully reversible and do not affect the dynamics of the VEC liquid. Because VEC is a simple polar molecule, these field induced features are expected to occur in many other materials having permanent dipole moments. Our results highlight the important role of an external electric field as additional control variable to influence the crystallization tendency of molecular glass-formers, and provide new opportunities in pharmaceutical science or organic electronics.

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Competing order phenomena and peculiar crystallization kinetics of polyamide 12 as revealed by dielectric spectroscopy

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In recent years, polyamide 12 (PA 12) has gained specific interest because of its excellent materials and processing properties for selective laser sintering, a 3D printing technique. In particular its moderate melting temperature (180° C), a high crystallization rate along with low shrinkage upon crystallization makes PA 12 a very suitable polymer for this purpose.

This study is devoted to the crystallization behavior of PA 12 in relation to molecular and cooperative dynamics. Like most semi-crystalline polymers, PA 12 forms a morphology consisting of stacked lamellas, however, recent XRD experiments have revealed a rigid amorphous fraction (RAF) that roughly equals the crystalline volume fraction, a fact that has lead to a specific morphological model for semi-crystalline PA 12.

To support the idea of coexisting crystalline and RAF fraction and its evolution during isothermal crystallization we have performed broadband dielectric spectroscopy experiments (BDS) in the frequency range from 10^{-2} and 10^{9} Hz. The main findings can be summarizes as follows:

- The known molecular relaxation processes (γ, β and α) have been investigated as function of the crystallinity and are discussed in detail.
- Upon crystallization, the α-process shows virtually no peak shift, however, significant broadening on the low frequency side can best be modelled by an emerging isolated slow mode, probably related to the RAF.
- The crystallization rate shows a nonmonotonic behavior as function of the crystallization temperature; this effect can be successfully be described by a discretization effect in the lamellar thickness governed by the large unit cell length of PA 12.
- Finally, we discuss the kinetics of interfacial relaxation as a manifestation of dielectric heterogeneities in comparison to the initial increase and subsequent decrease of the relaxation strength $\Delta\varepsilon_{\alpha}$.

Relaxations and Relaxor-Ferroelectric-like Response of Poly(vinylidene fluoride) confined in cylindrical nanocavities

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The impact of cylindrical confinement on the structure and relaxation behavior of poly(vinylidene difluoride) (PVDF) and how these affect the para-/ferroelectric behavior of this polymer is analyzed. We have performed dielectric spectroscopy measurements on PVDF nanotubes and nanorods. These cylindrical systems were prepared by solidification in anodic aluminum oxide (AAO) templates. The dielectric spectroscopy experiments evidence a bimodal relaxation process for PVDF nanotubes and nanocylinders with smallest diameters: besides the bulk-like α-relaxation, we detect a notably slower relaxation that is associated with the PVDF regions of restricted dynamics at the interface with the AAO pore. Strikingly, in PVDF nanotubes, both the bulk-like and the interfacial relaxation tend to become temperature independent as the temperature increases, a behavior that has been observed before in inorganic relaxor ferroelectrics. In line with this, we observe that the real part of the dielectric permittivity of the PVDF nanotubes exhibits a broad maximum when plotted against the temperature, which is, again, a typical feature of relaxor ferroelectrics. As such, we propose that, in nanotubular PVDF, ferroelectric-like nanodomains are formed in the amorphous phase regions adjacent to the AAO interface. These ferroelectric nanodomains may result from an anisotropic chain conformation and a preferred orientation of local dipoles due to selective H-bond formation between the PVDF macromolecules and the AAO walls. Such relaxor-ferroelectric-like behavior has not been observed for nonirradiated PVDF homopolymer; our findings thus may enable in the future alternative applications for this bulk commodity plastic, e.g., for the production of electrocaloric devices for solid-state refrigeration which benefit from a relaxor-ferroelectric-like response.

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Soliton excitations in multiferroic $LiCuVO_4$

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Broadband dielectric spectroscopy (BDS) is an interesting tool not only to investigate materials where the polarization is a primary order parameter, but also for materials where it is coupled to other properties such as e.g. the magnetization. As these transitions typically occur at low temperatures we use a home-made two-port sample holder based on microstrip design that works in a Quantum Design PPMS as well as an Oxford Kelvinox dilution refrigerator. This setup can be used both with a Novocontrol Alpha-A Analyzer for low frequency measurements and e.g. a Rhode & Schwarz ZNB8 for measurements in the GHz regime in a broad temperature and magnetic field range.

One example where BDS helps to understand the fundamential nature of the material is the magnetoelectric multiferroic $LiCuVO_4$ [1]. In this single-phase multiferroic the polarization is induced by the magnetization of a planar spin spiral ground state below 2.3 K. This coupling is interesting as it offers an additional parameter that can be used to tune the dielectric properties, namely the magnetic field, that in this case can be used to suppress the phase transition at 7.4 T.

Here I present BDS data in a frequency range up to 5 GHz that is used to not only trace this phase transition down to 0.025 K, but also observe a pronounced change in the fluctuation dynamics. Above 0.4 K critical slowing down similar to the dynamics of canonical ferroelectics at their phase transition is observed. Below this temperature the observed Debye-like relaxation changes and we instead see an excitation at approx. 3 GHz (12.5 μeV) as was predicted from theoretical calculations [2].

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Further insights into vapour deposited ultrastable glasses from dielectric spectroscopy

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Vapour deposition (VD) burst into the field of glasses a decade ago due to the ability to produce glasses with exceptionally high density and low enthalpy levels (ultrastable glasses), comparable to those of ordinary glasses aged for thousands of years[1], exhibiting also a particular molecular arrangement[2]. VD glasses became an excellent benchmark to study the dynamical behaviour of glasses, analysing the effect of both density and molecular orientation levels that are not attainable by other means. Here, we study the dielectric properties of vapour deposited molecular glasses of different materials. On one hand, we investigate the effect of ultrastability on the secondary relaxation processes. We show the existence of two clearly differentiated groups of secondary relaxations: those becoming slower in the ultrastable state with respect to the ordinary unaged glass, mimicking the properties of the structural relaxation, and those becoming faster, indicating certain influence of the particular microstructure. In this sense, ultrastable glasses may be the clue to acccess to the properties of the structural relaxation of liquids in the temperature region of ultraslow dynamics, not accesible by conventional routes, and to clearly distinguish the secondary relaxations relevant for their connection to the structural process. On the other hand, we also show the emergence of a new dielectric process in ultrastable TPD, a prototypic organic hole transport material, which is not exhibited in the ordinary glass. We relate this to a Maxwell-Wagner process originated from a heterogeneous structure and the enhancement of charge transfer between molecules due to the particular molecular arrangement of VD. Finally, we explore the effect of molecular orientation on the dielectric properties of different glasses, showing the existance of relaxation and conductivity anistrotopy. In summary, VD emerges as a new exciting tool to get further insights into longstanding issues in glass science such as the classification of secondary relaxations or the inherent heterogeneity of glassy structure, and BDS demonstrates to be an excellent tool to address these issues.

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Asymmetric liquid-liquid criticality in the refractive index and the dielectric constant coexistence curves

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Complete scaling formulation marked a turning point in our understanding of fluid-fluid criticality. It was first introduced by Fisher and coworkers in the year 2000 for describing the asymmetric features of liquid-gas criticality and later extended to binary fluid mixtures [1,2]. Complete scaling maps asymmetric fluid criticality onto the symmetric Ising-model: all relevant physical fields enter symmetrically into all the scaling fields. The nature of the critical behavior in the refractive index n and the dielectric constant ε is revisited for one-component fluids and binary mixtures using this idea [3,4]. A comparison is made with the critical behavior of n as derived from the Lorentz-Lorenz equation. Analogue anomalies to those predicted for the dielectric constant ε, namely, a leading $|t|^{2\beta}$ singularity in the coexistence-curve diameter in the two-phase region and a $|t|^{1-\alpha}$ along the critical isopleth in the one phase region, are expected in both cases. However, significant differences as regards the amplitudes of both singularities are obtained from the two approaches. Analysis of some literature data along coexistence in the two-phase region and along the critical isopleth in the one-phase region provide evidence of an intrinsic effect, independent of the density, in the critical anomalies of n. This effect is governed by the shift of the critical temperature with an electric field, which is supposed to take smaller values at optical frequencies than at low frequencies in the Hz to MHz range.

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The interplay between crystallization and glass transition in nematic liquid crystal 2,7-bis(4-pentylphenyl)-9,9-diethyl-9H-fluorene (5P-EtFLEt-P5)

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This study investigates the crystallization behaviour and molecular dynamics of the supercooled nematic state of the newly-synthesized liquid crystal 2,7-bis(4-pentylphenyl)-9,9-diethyl-9H-fluorene (5P-EtFLEt-P5) using broadband dielectric spectroscopy (BDS). 5P-EtFLEt-P5 is a fragile glass-forming system with a high fragility parameter ($m_f \approx 121$). The particular emphasis is placed on the comparison of the *melt* and *cold* isothermal crystallization processes at several selected temperatures. Our findings reveal that at low temperatures, the crystallization of the Cr1 phase from the nematic melt state occurs more quickly than the *cold* crystallization. The dimensionality of the growing crystallites (*n*), was found to be slightly higher for the *cold* than the *melt* crystallization process, varying from n~5 to n~3 with increasing temperature. In addition, polarized optical microscopy (POM) was employed to exam the isothermal secondary *cold* crystallization (the formation of Cr2 from Cr1), which is inaccessible by BDS measurements due to its very fast crystallization rates. The kinetics of crystallization were analysed by two different approaches proposed by Avrami and Avramov.

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Dynamics in weakly disordered solids

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Several open questions remain to be settled concerning glass-forming materials. Among these, the nature of features appearing in the generalized susceptibility spectra have been the focus of intense debates in the recent past. Specifically, the imaginary part of the susceptibility of typical glass-forming materials displays a strong α-relaxation peak ascribed to processes involving molecular rototranslational movements, and less-intense, higher-frequency relaxations usually referred as secondary relaxations. These features appear either as well defined peaks or as shoulders at the high-frequency flank of the α peak.

A strategy to unravel the physical origin of secondary relaxations and their relation to the α relaxation is to diminish the number of degrees of freedom which become frozen (vitrify) at the glass transition, for example, by studying the glass transition of mesophases which exhibit only partial disorder, such as liquid crystaline phases with long range orientational order, or plastic crystals with long-range translational order. Here we employ broadband dielectric spectroscopy (BDS) to probe the molecular dynamics in systems for which the degree of disorder is even lower [1-3]. These systems include low-temperature “weekly” disordered phases in which the disorder only involves, from the crystallographic point of view, a well-defined occupational exchange of some atoms (or groups of atoms). When such disorder is dynamic, it takes place by means of changes in the orientation of the molecular entities and/or in the molecular conformation, both of which give rise to dipolar relaxations and are therefore observable by means of BDS. In some instances, the interpretation of the relaxation map is carried out with the aid of molecular dynamic simulations [4].

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Dynamics in Mesoscopic Structured Liquids

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The impact of supramolecular structure on dynamics in mesoscopic structured imidazoles, polyalcohols and ionic liquids are probed by broadband dielectric spectroscopy complemented by dynamic-mechanical spectroscopy, vibrational spectroscopy, calorimetry, and quasielastic scattering techniques [1-7]. Slow, sub-α relaxations attributed to dynamics of long-lived aggregates are observed using multiple experimental techniques and employed as probes of the mesoscopic structure in thes4 materials. Detailed analyses reveal (i) a correlation between the slow relaxations and zero shear viscosity as well as the static dielectric permittivity, (ii) an inverse relationship between the average supramolecular chain length and proton conductivity and (iii) no direct correlation between the static dielectric permittivity and proton conductivity in imidazoles. In this talk, the implications of these findings on the interplay between mesoscale structure and dynamics as well as transport in structured liquids will be discussed within the framework of recent theories and models.

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Nonlinear dielectric response beyond structural relaxation in glass-forming materials

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The nonlinear response regime of glass-forming materials has recently revived the interest of a broad scientific community [1,2,3,4]. Despite the wide range of fascinating phenomena unraveled by means of nonlinear dielectric investigations, such studies have been performed so far almost exclusively on "simple" liquids, with non-associating, small-size molecular constituents. Covering a fairly unexplored ground, this contribution reports on nonlinear dielectric effects arising in polymerized ionic melts and hydrogen-bonded liquids, i.e., in the presence of degrees of freedom slower than the ubiquitous ones associated with the structural fluctuations. The results will be discussed within the framework of various theoretical approaches aiming to unravel fundamental details on microscopic dynamics not accessible via linear investigations.

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Third and fifth harmonic responses in viscous liquids

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We review [1] the works devoted to third and fifth harmonic susceptibilities in glasses, namely $\chi_3^{(3)}$ and $\chi_5^{(5)}$. We explain why these nonlinear responses are especially well adapted to test whether or not some amorphous correlations develop upon cooling [2,3]. We show that the experimental frequency and temperature dependences of $\chi_3^{(3)}$ and $\chi_5^{(5)}$ have anomalous features, since their behavior is qualitatively different to that of an ideal gas, which is the high temperature limit of a fluid. Most of the works have interpreted this anomalous behavior as reflecting the growth, upon cooling, of amorphously ordered domains, as predicted by the general framework of Bouchaud and Biroli (BB). We explain why most -if not all- of the challenging interpretations can be recast in a way which is consistent with that of BB. Finally, the comparison of the anomalous features of $\chi_3^{(3)}$ and of $\chi_5^{(5)}$ shows that the amorphously ordered domains are compact, i.e. the fractal dimension d_f is close to the dimension d of space. This suggests that the glass transition of molecular liquids corresponds to a new universality class of critical phenomena.

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Nonlinear electrical and rheological responses of glass formers

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The approach of the glass transition from the supercooled liquid side is characterized by an enormous slow-down of the microscopic fluctuations related to the structural rearrangements. Most experimental studies providing the corresponding response functions carefully ensure that the excitation achieved using external fields and the resulting material response are linearly related [1]. Yet, increasing attention is paid to probing the slow degrees of freedom of monomeric and polymeric glass formers in a nonlinear fashion, for instance using dipolar [2,3] or shear-mechanical degrees of freedom [4,5,6]. This presentation will provide examples from our recent work regarding the application of nonlinear electrical and rheological spectroscopies to various glass forming materials.

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Effect of chain topology on segmental dynamics

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Chain topology exerts a strong influence on segmental dynamics. Here we discuss two such examples in (a) polymers with *cis* and *trans* stereoregular configurations and (b) in cyclic polystyrenes. Altering the stereochemistry of a single double bond in the side group of a polymer resulted in systems with unprecedented local dynamics [1]. These include (i) the appearance of three segmental processes in the *cis*-polymers all with Vogel-Fulcher-Tammann (VFT) temperature dependence, (ii) the low steepness index associated with fragility, *m*, and (iii) the lowest pressure coefficient of T_g, dT_g/dP, reported for polymers. The inability of the *cis*-polymer to pack the side groups efficiently effectively controls the dynamics. The wealth of dynamics reflects the *cis*/*trans* stereochemistry and the presence of different dipoles at specific positions sampling both the side group and backbone dynamics.

In a second more complex topology, the segmental dynamics are investigated in a mono-cyclic and in the corresponding linear polystyrene as well as in a series of multi-cyclic polystyrenes, all with the same total molecular weight [2]. There is a strong reduction of T_g with decreasing molecular weight for linear chains but only a moderate reduction for cyclic chains and this below a certain critical molecular weight. These data contradict the Gibbs-Di Marzio lattice model predicting an increasing glass temperature with decreasing molecular weight of cyclic polymers. In multi-cyclic polystyrenes the results emphasize the role of constrained segments at the coupling sites (linkers) on determining practically all features of segmental dynamics; the exact temperature dependence of relaxation times and associated T_g, the dielectric strength, the distribution of relaxation times and fragility. A nearly linear increase of T_g is found with increasing number of intra-molecular constraints.

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Network formation and molecular dynamics in hydrogen-bonding telechelic polymers: a competition between association lifetime and structural relaxation

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Reversible bonds between polymer chains can form supra-molecular networks which exhibit extraordinary mechanical properties and other functionalities, e.g. self-healing. We study short telechelic polymers with H-bonding end-groups of different interaction strength and backbone flexibility. The glass transition temperature (Tg) of flexible polydimethyl siloxanes (PDMS) does not vary with H-bond strength of the end-groups but differs strongly from Tg in methyl-terminated PDMS [1,2]. At the same time, Tg of the much stiffer telechelic polypropylene glycol (PPG) depends significantly on the H-bond interaction strength [3]. In contrast, viscosity strongly depends on the H-bond strength in the PDMS series while it remains almost the same in PPG with different end groups. Complementary measurements of the shear modulus and dielectric relaxation indicate that these observations can be explained by competing lifetimes of the supra-molecular associations and the structural and chain relaxations. The strength of the chain end association strongly influences the molecular weight dependence of Tg. However, only if the association lifetime exceeds the characteristic chain relaxation time, the viscosity will be affected by the chain associations [3]. We emphasize that dielectric relaxation studies enable estimates of the chain-end dissociation energy, while mechanical relaxation contains an additional contribution due to the probability of the dissociated chain-end to re-associate with the same chain-end [4]. This process does not provide mechanical relaxation, although it shows up in the dielectric spectra.

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Understanding the evolution of entanglements upon the dielectric relaxations in dis-UHMWPE in the presence of Al_2O_3 catalytic ashes

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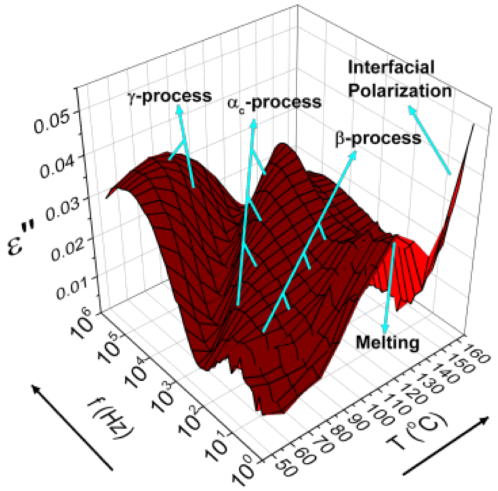
The disentangled ultra-high molecular weight polyethylene (dis-UHMWPE) has proved advantageous in respect to entangled UHMWPE, as solid-state compression moulding and stretching result in highly oriented uni-/bi-axially stretched tapes and films, showing high values of strength/modulus and thermal conductivity [1]. This disentangled state is however metastable once the polymer is brought above its melting temperature (> 140°C), as entanglements start to form due to chain reptations, progressively increasing the viscosity of the polymer [2]. Neat polyethylene is a non-polar material with very small dipole moment from the CH_2 groups so, its dielectric behavior is enhanced by addition of dielectric probes [3]. Polyethylene is known to exhibit three main processes: the α_c-process (crystalline part), the β-process, (amorphous regions) and the γ-process, (amorphous chains very close to the lamellae) [4]. Because of the disentangled nature of the polymer, two β-processes were identified, that we have attributed to the disentangled (β_{dis}-) and entangled (β_{ent}-) amorphous phase. Interfacial polarization between the catalytic ashes and the polymer was identified.



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Molecular dynamics of novel poly(pentamethylene 2,5-furanoate): Exploring a complete landscape of molecular dynamics and finding unexpected results

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In the last decade, there has been an increased interest toward the development and application of bioplastics, to contribute to the sustainable economy and to help reducing environmental problems. Among bioplastics, particular attention is devoted to biobased polymers synthesized from 2,5-furan dicarboxylic acid (2,5-FDCA). Furan-based polymers with an even number of methylene units are able to crystallize, leading to the formation of a phase-separated material, *i.e.* a semicrystalline polymer. This is the case of poly(ethylene 2,5-furanoate) (PEF), poly(butylene 2,5-furanoate) (PBF), and poly(hexamethylene 2,5-furanoate) (PHF), where broadband dielectric spectroscopy (BDS) studies have been carried out by different groups and changes in both local and segmental relaxations were observed as the system crystallized [1]. In this work, we explore the molecular dynamics of poly(pentamethylene 2,5-furanoate) (PPeF), a furan-based polyester with an odd number of methylene groups. Surprisingly, while differential scanning calorimetry and wide-angle X-ray scattering results showed no evidences of PPeF crystallization, BDS experiments showed changes in both local and segmental dynamics. By BDS, we observed an overall dependence of the PPeF dynamics with thermal history, characterized by the dissapearance of one component describing the local relaxation, and the slow down of the segmental relaxation without significant changes in its shape. These BDS results in PPeF suggest the development of unusual structural features in this material, different from those of a semicrystalline state, as a "frustrated" crystallization or even the possible formation of a mesophase.

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Dynamics of raw and vulcanized rubbers. What can we learn from dielectric spectroscopy studies?

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Styrene-butadiene (SBR) and natural rubber (NR) are both general-purpose rubbers mainly used in the tire industry. For converting into more durable materials, rubbers have to be vulcanized. Vulcanization is a chemical process which in its simplest forms it is brought about by heating rubber with sulphur. In addition, other chemical products are added to improve further the quality of the compounds. Vulcanization modifies the polymer by forming crosslinks between individual polymer chains.

The deep comprehension of the dynamics of rubber compounds is a key factor to further improve the material properties and therefore the tire performance. However, the dynamics of vulcanized rubbers is still far from being understood. In the literature, we can observe that the α-relaxation of vulcanized SBR splits into two different contributions (the α-relaxation and an additional process at lower frequencies which is not observed in the raw material). On the other hand for NR compounds and even in the raw polymer, the dielectric response also showed two components in the temperature region corresponding to the α-relaxation. The presence of this additional peak, in both SBR and NR, has been related to different phenomena such as the existence of an immobilized layer around surfaces (zinc oxide [1] or silica particles for filled compounds). Also, the occurrence of a Maxwell-Wagner-Sillars (MWS) process has been reported [2]. In the case of NR the presence of stearic acid/lipids was reported the origin of this slow process [3].

Here, we discuss the influence of the vulcanizing additives on the dynamics of both SBR and NR compounds by broadband dielectric spectroscopy. Our results indicate that the molecular origin of the slow processes in SBR and NR are of different nature. In the case of SBR, the type of accelerant is the key to describe the slow process [4] whereas for NR the presence of lipids is the cause of this slow contribution to the dielectric spectrum.

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Straightening effect of the polymer chains around nanoparticles.

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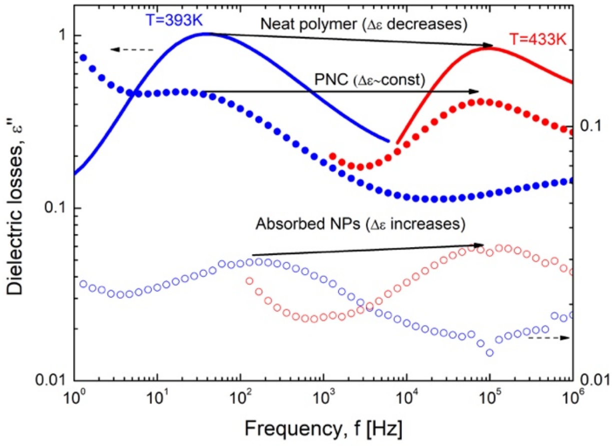
Polymer nanocomposites (PNC), a class of hybrid materials composed of polymers with dispersed nano-sized particles, can produce desirable structural and functional properties without compromising other valuable properties of polymers. In this study we focus on PNCs with dispersed silica core nanoparticles (NPs) with radius ~10nm. The functional groups on the surface of the NPs provide good interaction wth the polymer chains via hydrogen bonding, enabling good NP dispersion.



Temperature dependence of the dielectric losses for three system: neat polymer, PNC and PNC consisted of absorbed polymer chains only

In the current study, we examine the unusual dielectric behavior of the interfacial polymer layer surrounding NPs in PNCs. While in the neat polymer the dielectric strength obeys the Curie-Weiss law, the amplitudes of the dielectric losses appear almost independent of temperature in PNCs. Furthermore, in the PNC consisted of NPs with absorbed polymer chains only, the dielectric strength growths with temperature increase. This effect was attributed to the stretching and ordering of the polymer chains absorbed around NPs [1]. A theoretical model is proposed to explain this effect, which allows obtainment of the energy of interaction between the polymer chains.

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Dramatic effect of the slower component topology on the matrix dynamics in polymer mixtures

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Single-chain nano-particles (SCNPs) [1] are polymeric soft nano-objects consisting of individual linear macromolecules collapsed to a certain degree by means of intramolecular cross-linking. These new nano-particles are attracting increasing interest due to their intriguing physical properties toghether with potential applications. In particular, they can be used as components of all-polymer nanocomposites, i.e., systems formed by a polymeric matrix and polymeric nano-particles instead of hard inorganic nano-particles [2]. Since SCNPs are soft particles, all-polymer nano-composites can be compared with conventional nanocomposites. Moreover, as any SCNP is made of only one macromolecule, the Polymer/SCNPs mixture should also be compared with traditional polymer blends [2].

In this contribution, the dynamics of Polymer/SCNPs blends studied by means of dielectric relaxation methods is presented. Mixtures of poly(vinyl methyl ether) (PVME) and poly(styrene) (PS), either in linear chain form or as SCNP, with different relative concentrations have been investigated. These systems show a strong dynamic asymmetry due to the huge difference in the glass transition temperatures of the components. Moreover, the dielectric response of the PVME/PS mixtures is largely dominated by the fluctuation of the molecular dipole moment associated to PVME. Thus, using dielectric relaxation techniques the molecular mobility of the matrix has been characterized in detail highligting the dramatic effect of the SCNP topology on the segmental dynamics of the PVME matrix.

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Rigid Amorphous Phase in Polymer Nanocomposites as Revealed by Relaxation Spectroscopy

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In inorganic/polymer nanocomposites the polymer matrix region near a filler surface, termed as the interphase, is of topical interest due to its possible influence on the macroscopic properties of the material. The segmental dynamics of this interphase is expected to be altered, as compared to the pure matrix, which might percolate into the entire system. It was found that a so-called Rigid Amorphous Phase (RAF) is formed in the interfacial region by adsorption of the polymer segments onto the nanoparticles, yielding in their immobilization. Here, we employed a combination of two relaxation spectroscopy techniques (Broadband Dielectric Spectroscopy (BDS) and Specific Heat Spectroscopy (SHS) in a form of Temperature Modulated DSC (TMDSC)) to investigate the structure and molecular mobility of Epoxy/Inorganic nanofiller composites with different nanoparticles geometries and contents. The two techniques show different perspectives on the glassy dynamics; BDS is sensitive to dipole fluctuations, whereas SHS senses entropy fluctuations.

First, our dielectric relaxation investigations proved an existence of an additional process in nanocomposites, which is not present in the pure material. Due to the increasing intensity of the process with increasing filler content it was assigned as the α-process related to the segmental dynamics of polymer chains adsorbed onto the nanoparticles. Considering the expected high conductivity effects of the material, the dielectric data were analyzed by fitting a derivative of the HN function to a “conduction-free” loss spectra: $\varepsilon''_{\mathrm{deriv}} = -\frac{\partial \varepsilon'}{\partial \log\omega}$.

Second, TMDSC measurements were used to study the specific heat capacity of nanocomposites in its nanofiller content dependence. Assuming that RAF is proportional to the decrease of the specific heat capacity step (Δc_p) in the glass transition region of the nanocomposites, comparing to the pure material, the inorganic/polymer interphase was quantitatively analyzed and the amount of RAF estimated.

Analyzing the interfacial layer properties in polymer nanocomposites by broadband dielectric spectroscopy

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There is a growing of evidence showing the presence of an interfacial layer between the polymer matrix and the surface of nanoparticle in polymer nanocomposites (PNCs), which exhibits distinguishing dynamics from the bulk polymer. [1] However, probing the properties of the interfacial layer in polymer nanocomposites (PNCs) remains a challenging task. Recently, broadband dielectric spectroscopy has been actively applied to study the dynamic features of the interfacial layer in PNCs, despite the complex spectra of the multi-component system of nanocomposites. In this contribution, we quantitatively compare three different methodologies that have been proposed in the literature on analyzing the dielectric spectra of PNCs, namely, a single Havriliak-Negami (HN) function fit, a two HN functions fit, and the heterogeneous model analysis (HMA). We find the HMA presents the most accurate analysis on both the thickness and dynamics of the interfacial layer, in comparison to the other two methods. In addition, the dielectric spectra at low temperatures reveal unexpectedly non-monotonous changes in the secondary relaxation of the polymer with nanoparticle loadings. These results clearly demonstrate that dielectric spectroscopy is an easy and robust method to study a wide range of dynamic properties of the interfacial layer in PNCs, and the HMA show the best performance among so far proposed methodologies. [2]

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Water and its dielectroc signature. New markers for biosensing

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Whenever the 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 [1]. The parameters of the main water peak define a trajectory that can clarify the nature and rate, at which water interacts with the solute. In this paper, we extend this approach from comparatively simple solutions to the complexity of Red Blood Cells (RBC) suspensions by monitoring the RBC cytoplasm under different external conditions [2]. 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. The conclusion is that the dielectric response of the cytoplasm in microwaves is due to the water therein and its interaction with physiological active components in cytoplasm. This opens a window of opportunity to exploit this for the non-invasive monitoring of diabetes or to non-invasive control of the quality of Stored RBC in a Blood bank in order to manage the inventory.

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Depolarized Dynamic Light Scattering and Dielectric Spectroscopy: Two Perspectives on the Debye-Relaxation in Monohydroxy Alcohols.

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The slow Debye-like relaxation in the dielectric spectra of monohydroxy alcohols is a matter of long standing debate. While the Debye relaxation for a long time was mainly considered as a dielectric phenomenon, its signature was recently reported to also appear in the shear modulus and many features were explained by a model of transient chains, which form due to H-bonding [1]. Considering that background one would also expect a signature of such transient chain formation to be visible in depolarized dynamic light scattering (DDLS), which also probes molecular reorientational dynamics. But, although Debye-like processes were reported in several lightscattering experiments, their existence in the case of monohydroxy alcohols was only shown recently [2]. In the present work, we probe reorientational dynamics in a series of monohydroxy alcohols, with broadband dielectric spectroscopy (BDS) and DDLS in the supercooled regime down to the glass transition, with a particular focus on a quantitative comparison between the dielectric and DDLS manifestation of the Debye-like contribution. It turns out that in DDLS the Debye-like contribution is slightly faster and weaker by orders of magnitude compared to the α-process. Moreover, the process is significantly broadened in DDLS, while α- and β-relaxation are basically identical in both methods. Based on these observations, it is also possible to identify a Debye contribution in a series of phenyl-alcohols, where it is debated, if steric hindrance due to the additional phenyl group at all allows for a formation of transient chains [3].Altogether the observations of the Debye contribution by BDS and DDLS in different monoalcohols support the picture of transient chains: While the Debye process in BDS represents fluctuations in the end-to-end vector dipole moment of these chains, its occurrence in DDLS shows a more local signature and is related to residual correlations which occur due to a slight anisotropy of the α-relaxation caused by the chain formation.

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Advantages of examining alcohols containing a phenyl group by the means of Broadband Dielectric Spectroscopy

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Most monohydroxy alcohols investigated by the means of broadband dielectric spectroscopy exhibit in the dielectric spectra, beside the common observed structural relaxation, a slower Debye relaxation process which is assigned to hydrogen bonded chain-like structures [1]. This encourages a discussion, whether or not this two relaxation processes does influence each other. Through an addition of a phenyl group to the alcohol structure, we are able to hinder the creation of chain like structures responsible for the Debye process. This gives us a possibility to study the behaviour to temperature and pressure diversification of the structural relaxation solely. Moreover we have an expanded opportunity to study the influence of variation of the molecular architecture of these alcohols on the relaxation dynamics by elongating the alkyl backbone, changing the position of both the OH group and the phenyl group, and also by adding a methyl group to the phenyl member at different positions on the phenyl ring. Thus it was possible to find some pairs of alcohols with almost identical temperature behaviour of α-relaxation times i.e. 1-(4-methylphenyl)-1-propanol – 1-phenyl-2-butanol and 2-phenyl-1-butanol – 4-phenyl-2-butanol. This enabled us to make an extended analysis of the molecular behaviour of phenyl-alcohols at different p-T conditions, extracting the effect of temperature and pressure. In this presentation we show the results of the analysis of dielectric data measured in alcohols containing a phenyl group collected at ambient and elevated pressure conditions, what will provide, in combination with rheological studies, essential information on the molecular dynamics of alcohols containing a phenyl group.

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How various strength of the H-bonds is reflected by relaxation dynamics of associated liquids

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One of the longlasting problem in case of hydrogen-bonded materials is meaning of their strength and architecture for molecular dynamics of the liquids. Influence of difference of the architecture of the H-bonded supramolecualr structure were thoroughly studied, especially during last few years [1]. Dielectric studies in combination with other experimental methods, performed in the case of monohydroxy alcohols exhibited that terminal or non-terminal position of the OH group results in creation of chain-like and ring-like H-bonded structures, respectively. It was obsereved that amplitude of the so-called Debye relaxation visible in the dielectric spectra of many of these alcohols, related to these transient chains, strongly depends on the architecture of associated structures [2]. On the other hand, comparison of results from temperature and pressure investigations of these alcohols enabled to show that compression can strongly modified supramolecular structures [3].

However, up to now investigations were focused mainly on strongly H-bonded systems with hydroxyl groups, like varios alcohols. But, size and shape of associated structures should also depend on ability of varios groups to create H-bonds with different strength. Eg. it was showed in the case of 2-Ethylo-1-hexanol that replacing the –OH group by $-NH_2$ or –SH group changes the strength and morphology of the supramolecular structures [4]. Unfortunately, these investigations were performed only as a function of temperature at ambient pressure.

In this presentation we will show how another thermodynamic variable, pressure, influence properties of these three components, studied by the dielectric spectroscopy. Especially, we try to related changes of the quantities like fragility or activation volume with variation of the strength of the H-bonds.

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Dynamics of hydration water in Gelatin – Hyaluronic Acid hydrogels

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Hydrogels based on natural polymers have become especially attractive in the field of tissue engineering because they have unique properties such as good biodegradability, biocompatibility and high water retention capacity, they allow transport of nutrients and metabolic wastes and they provide a three dimensional environment for the proper differentiation of cells. In this work we investigate the hydration properties of a family of injectable hydrogels that mimic the composition of the extracellular matrix, with a homogeneous distribution of gelatin (Gel) and hyaluronic acid (HA) chains by enzymatic gelation of aqueous solutions of different mixtures of both polymers. Protein (Gel) and polysaccharide (HA) have been combined in an injectable crosslinked hydrogel with controlled Gel–HA ratio, anticipating that synergistic effects would promote the differentiation of encapsulated cells, since HA provides resilience, due to the stiffness of its chains in the hydrated state, and higher hydration levels [1].

The glass transition and the molecular dynamics of water in the hydrogels have been studied by using an experimental approach which combines differential scanning calorimetry (DSC) technique with dielectric relaxation spectroscopy (DS) and also with water dynamical sorption - desorption measurements. Our results enable us to follow the evolution of the observed dynamics with hydration level. Regarding the dielectric relaxation processes, the emphasis has been given to those related to hydrogen bond network of uncrystallized water molecules organized in clusters (with and without crystalline ice phase). The relationship between the protonic conduction mechanism and the recorded relaxation processes is in the focus of this work. Additionally, we investigate miscibility issues for the two components, while the hydrogels offer a great opportunity to study comparatively the water dynamics in proteins and polysaccharides.

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Dynamics of freeze-dried solvated proteins revealed by broadband dielectric spectroscopy

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We present extensive broadband dielectric spectroscopy (BDS) studies of dynamics in freeze-dried, de-hydrated, binary mixtures of lysozyme and excipients. The latter have been selected among hydrogen bonding glass-formers, with different viscosity and molecular mass, spanning more than 150 K in glass transition temperatures T_g. We followed measurement methods and analysis protocols shown in recently published enlightening BDS studies of hydrated [1] or solvated [2] proteins.

Beyond interfacial relaxation and Maxwell–Wagner (MW) polarization effects that are present in freeze-dried powder samples, we found the ubiquitous existence of three relaxation processes: one has a Vogel-Fulcher-Tamman temperature behavior, it is strongly influenced by the type of solvent and it share the same timescale of the process, revealed by calorimetry, that brings the system to vitrify; the other two processes are faster and active also in the glassy state. The intermediate process shows activated dynamics independent on the excipient present in the mixture but it appears to evolve on ageing.

Combining BDS data with calorimetry and neutron scattering experiments [3] a complex scenario emerges, where some dynamic processes of proteins appear to be coupled to solvent dynamics in the range from ns to ks, as predicted also for faster dynamics by the “slaving” assumption [4], but other processes seem to have a more peculiar behavior.

The presented results suggest that freeze-drying proteins in presence of a cosolvent could not guarantee that relaxation motions are suppressed in the glassy state. The relation between this scenario and the implication for stability of biopharmaceuticals [5] will be discussed.

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Application of BDS to follow cis to trans isomerism in photoswitchable molecule Aberchrome 670

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Recent studies on the supercooled pure saccharides as well as some active pharmaceutical ingredients (API) clearly indicated that Boadband Dielectirc Spectroscopy can be succesfully applied to follow mutarotation and tautomerization in these compounds [1,2]. Herein, we will show that BDS can be also very useful to follow cis (Z) to trans (E) isomerism, which is a classical chemical conversion, in very important photoswitchable fulgide Aberchrome 670. It was found that during this kind of conversion structrual relaxation process shifts to the lower frequencies. It was connected to the difference in the viscosity of E and Z isomer. Just to remind that gerenally both isomers differ significantly even by more than 50 K. Moreover, from the kinetic curves constructed from the time evolution of the structural relaxation process constant rates as well as activation barrier E_a =16 kJ/mol of cis to trans isomerism in supercooled pure Aberchrome 670 has been calculated. Interestingly, the estimated activation barrier was close to that evaluated in stilbenes. That simply means that in fact structrual relaxation time can be another importat parameter to monitor cis to trans isomerism. Therefore, completely new ways to explore this chemical conversion appeared. Just to mention that application of dielectric spectrscopy provides an uniqe opportunity to study cis to trans isomerism at high pressures, under 1D and 2D confinement and at high electric fields. Consequently, we expect to gain a better understanding of the mechanism and how to control this process by manipulation in extenal conditions. *E. K., A. M., and D. H. are thankful for the financial support from the National Science Center based on decision DEC 2016/22/E/NZ7/00266. M.T. and K.K acknowledge the support received from the National Science Centre (decision no DEC-2015/18/E/ST4/00320)*

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BDS and TSDC measurements on $Ca_{10}(PO_4)_6(OH)_2$, β-$Ca_3(PO_4)_2$ and biphasic bioceramics

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Synthetic hydroxyapatite-based [Hap, $Ca_{10}(PO_4)_6(OH)_2$] bioceramics have been highlighted over the past four decades due to their structural and compositional analogousness with the biologic Hap [1,2], which occurs naturally in human bones, comprising 65 to 70 wt% of their mass. These bioceramics display a bioactivity process in which, when placed in contact with the physiological media, inside the human body, they promote the growth of new biologic bone along their surface forming strong bond with it [2]. However, their bioactivity level has still the potential to be considerably improved. Among the methods being researched to enhance their bioactivity, the electrical polarization is the one with the most remarkable results, both in-vitro and in-vivo, which promotes an acceleration in the biologic bone growth [3]. On the other hand, the electrical polarization of beta-tricalcium phosphate [β-TCP, β-$Ca_3(PO_4)_2$] bioceramics is a recent subject, with the first reports dating back to 2010. Curiously, the few publications are contradictory and not clear: it is stated that β-TCP is not electrically polarizable, yet, it is also reported that β-TCP has a suitable composition and structure for ionic conduction and a large electric charge storage ability [4,5].

In the present work, the electrical polarization of pure Hap, β-TCP, and biphasic (75Hap-25β-TCP, wt%) bioceramics was analyzed by measuring thermally stimulated depolarization currents (TSDC). The samples, thermoelectrically polarized at 500 ºC, revealed stored charge densities in the order of 10^{-4} - 10^{-2} C/cm^2. The dielectric characterization of the samples was carried out by broadband dielectric spectroscopy (BDS) measurements, between room temperature and 1000 ºC and in the frequency range of 100 Hz – 1 MHz. The BDS results were correlated to the TSDC results.

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Scaling behavior of electric conductivity and structural relaxation in supercooled ionic liquids

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Over the last decade, ionic liquids (ILs) have received a considerable amount of scientific attention. An appropriate combination of cations and anions makes them attractive electrolytes for fuel cells and batteries. One the most desired feature of these media is their high electric conductivity (σ). Therefore, in the last years many efforts have been dedicated to understanding the conductivity mechanism in ion-containing systems and consequently to predict the σ behavior under various thermodynamic conditions. According to recent reports, the electrical conductivity (or any other dynamic property of ILs) measured at different temperatures and pressures, can be analyzed together in terms of the thermodynamic (or density) scaling concept. According to this idea, both isobaric and isothermal data can be expressed as a single universal curve if they are plotted against $(TV^{\gamma})^{-1}$. It has been confirmed several times that the density scaling concept is satisfied for various ionic conductors. However, in most of these studies it was tested using the data measured only over a narrow temperature range around T_m.

In this talk we examine the thermodynamic scaling concept both in the vicinity of the liquid-glass transition as well as in the normal liquid state of several protic and aprotic ionic systems characterized by different charge transport mechanisms (Grotthuss vs vehicle). To determine the value of scaling exponent γ, the highpressure dielectric, DLS and PVT data were analyzed. Having the γ parameter determined for a number of ionic systems one can state that generally the same value of exponent can not be used to rescale electric conductivity and viscosity data if there is decoupling between these two transport properties. In addition, one can observe a clear relation between the values of exponent *k* in DSE relation and the ratio $\gamma_\sigma/\gamma_\eta$,

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On Protonic and Electronic Charge Transport in Eumelanin

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Eumelanin, nature's black-brown pigment [1], has emerged as a model material for bioelectronic devices [2]. Its biocompatibility, processibility into thin films, its hydration dependent charge transport and apparent mixed ionic/electronic charge transport properties have all been utilised in the creation of the first reported all solid-state Organic Electrochemical Transistor or OECT [3]. OECT devices are at the forefront of the bioelectronics revolution that promises to yield new devices for medical applications [4]. With the advent of a solid-state version of the device platform, in large part due to eumelanin's properties, there is now a greater likelihood for miniaturization and the potential to create bioelectronic logic.

However, eumelanin's charge transport properties are not fully understood. It is known that the conductivity of the biopolymer is regulated by a redox reaction, the comproportionation reaction, which yields both free radicals and excess hydronium [5]. What has not been reported is any quantification or disentangling of the protonic and electronic contributions to long-range current conduction. Understanding the relative contributions to charge transport should give insight to potential materials engineering considerations for enhancing eumelanin's device capabilities. Presented in this talk is a systematic hydration controlled electrical study on synthetic eumelanin thin films utilizing impedance/dielectric spectroscopy. The results indicate that the hydration dependent charge transport is due to proton currents and that there is no apparent electronic current contribution contra to previous suppositions. Results show a real dielectric constant for hydrated melanin of order ~ 1×10^3. Surprisingly, this very high value is maintained over a wide frequency range of ~ 20 Hz to 10^4 Hz. Overall, melanin should be considered a protonic conductor (with a probable charge density of ~ 10^{19} cm^{-3}), and not as previously suggested, a mixed protonic/electronic hybrid.

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Charge Transport and Glassy Dynamics in Polymeric Ionic Liquids as reflected by its Inter- and Intramolecular Interactions

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Polymeric Ionic Liquids (PILs) form a novel class of materials in which the extraordinary properties of Ionic Liquids (ILs) (e. g. wide thermal and electrochemical window, high conductivity, non-flammable, non-explosive) are combined with the macroscopic stability of polymeric systems making them promising candidates for multifold applications. In the present study, Broadband Dielectric Spectroscopy (BDS), Fourier Transform Infrared Spectroscopy (FTIR), AC-Chip Calorimetry (ACC), and Differential Scanning Calorimetry (DSC) are employed in order to analyze the impact of *inter*- and *intra-molecular* interactions on charge transport and glassy dynamics. On the basis of a systematic variation of anionic or cationic moieties of the low molecular weight ILs as well as in their polymerized systems it is demonstrated that charge transport can be comprehended as dynamic glass transition assisted hopping conduction. By analyzing the IR spectra one observes concurrently for all PILs distinct changes of specific *intramolecular* vibrations at temperatures where the thermal activation of the DC-conductivity changes from a Vogel-Fulcher-Tammann- into an Arrhenius-dependence, whereas other molecular units are not affected. This leads to the identification of charge transport responsive (CTR) as well as charge transport irresponsive (CTI) moieties and paves the way to a refined molecular understanding of electrical conduction in PILs.

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Impact of Mesoscale Organization on Charge Transport and Dynamics in Ionic Liquids

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Mesoscale aggregates arising from the solvophobic separation of ionic and alkyl groups into polar and non-polar regions have been observed in a variety of ionic liquids (ILs).[1] The existence of these distinct regions provides ILs with the ability to solvate both polar and non-polar molecules and has important implications for applications such as energy storage, nanoparticle growth, biomass processing, and organic synthesis.[1] It has been found by computational studies and x-ray scattering that the morphology of the mesoscopic structure is highly sensitive to the alkyl chain length, however, the lifetimes of the aggregates and their influence on physicochemical properties, such as ionic conductivity, viscosity, and static dielectric permittivity, is not yet well understood. In this study, a series of imidazolium and phosphonium ionic liquids as well as binary IL mixtures are investigated by broadband dielectric spectroscopy, shear-mechanical spectroscopy, small angle x-ray scattering, and differential scanning calorimetry to elucidate the impact of alkyl chain length and solvophobic aggregation on charge transport and dynamics. It is observed that systematic ordering of ILs into complex polar and non-polar domains results in the emergence of slow, sub-α dynamics in both the dielectric and dynamic-mechanical spectra linked to fluctuations of the mesoscale aggregates.[2,3] These findings confirm the existence of long-lived mesoscale aggregates in neat ionic liquids and provides a new route to tune transport properties in these mesostructured fluids.

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Coupled electrical/mechanical investigations on elastomeric composite materials

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A recently developed experimental approach is applied to carry-out coupled electrical-mechanical investigations on elastomeric composite materials upon mechanical deformation. The goal of the study is to develop a platform that allows one to detect, by means of in-situ electrical measurements, the impact of thermal and mechanical fatigue on the functionality of elastomeric composite materials (natural rubber, nitrile-butadiene rubber and EPDM rubber filled with carbon black). Two orthogonal directions are accessible for the electrical measurements, carried-out by means of Broadband Dielectric Spectroscopy: parallel and perpendicular to the direction of the mechanical stretching. For the perpendicular direction, a non-conventional approach to measure the conductivity value without employing a direct contact between the electrodes and the samples under investigation has been developed and implemented. Large variations in conductivity, for both the parallel and the perpendicular directions, were detected (Figure 1), proving the sensitivity of this approach in assessing the effects of the thermal and mechanical fatigue on the properties of the elastomeric materials. Our study brings, for the first time, a direct experimental evidence for a strong anisotropy in the evolution of conductivity upon mechanical stretching.

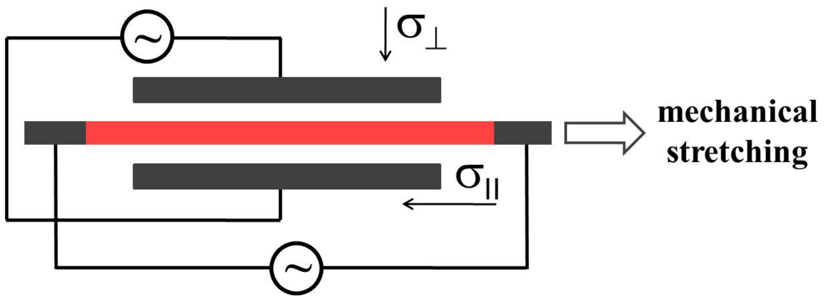

Figure 1: coupled mechanical/electrical measurements.

Dielectric properties of jute fibres reinforced Poly(lactic acid)/Poly(butylene succinate) blend

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Biodegradable polymers can potentially be combined with plant fibres to produce green composite materials. In our research, dielectric properties of jute fibres reinforced PLA/PBS blend was investigated in the temperature range from 20°C to 140°C and frequency range from 10^{-1} Hz to 10^{6} Hz. For the PLA/PBS blend three dielectric relaxations were identified. These were associated with the α mode relaxation associated with the glass transition of the PLA, β relaxation which appeared with the addition of the PBS and Maxwell-Wagner-Sillars (MWS) relaxation due to the semi-cristalline character of the PLA. Dielectric analyses of the composite revealed the existence of the water dipoles polarization caused by the hydrophilic character of jute fibres. Analyses of the MWS relaxation in the composite using the Havriliak-Négami model allowed probing the interfacial adhesion of the reinforcement in the blend matrix taking into account of the addition of the black carbon in the untreated composite.

BDS as a novel tool to probe phase separation in compatibilized polymer blends

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We demonstrate the ability of BDS as a more sensitive toolbox compared to bulk rheological and optical methods to probe phase separation in polymer blends using the lower critical solution temperature PMMA/PαMSAN blend in the presence of various copolymers as a representative case. Thermodynamically driven phase separation was monitored by probing the interfacial entrapment of the PαMSAN charges at the PMMA/(co)polymer inter-face [1] as a function of temperature.

Phase separation could be detected once the structure dimension, i.e. the average width of the co-continuous structures (chord length - L_C) was similar to the Debye length (L_D). The kinetics of phase separation was then monitored at equal quench depths by measuring the dielectric interfacial properties using successive dielectric frequency sweeps. From the evolution of the interfacial relaxation time (τ_{HN}), the intrinsic length scale, i.e. the ratio of L_C to L_D, was mapped during phase separation (Fig. 1a). In the neat blend, a monotonous increase in L_C, determined using optical microscopy, is observed due to pronounced coarsening.

By combining both results, a threefold increase followed by a constant behavior of L_D is derived at early (shaded area) and late stages, respectively, o-wing to a rapid de-crease and subsequent saturation of the charge density (n_0). The dielectric interfacial strength ($\Delta\varepsilon$) was propor-tional to L_C/L_D at early (Fig. 1b) and late stages (inset of Fig. 1b). Upon incorporation of (co)polymers that rapidly diffuse to the blend's interface and generate a larger contrast in dielectric interfacial properties, over fivefold reduction of both L_C and L_D was obtained. The characteristic time for the evolution of interfacial properties was in agreement with the copolymer's Rouse diffusion to the interface.

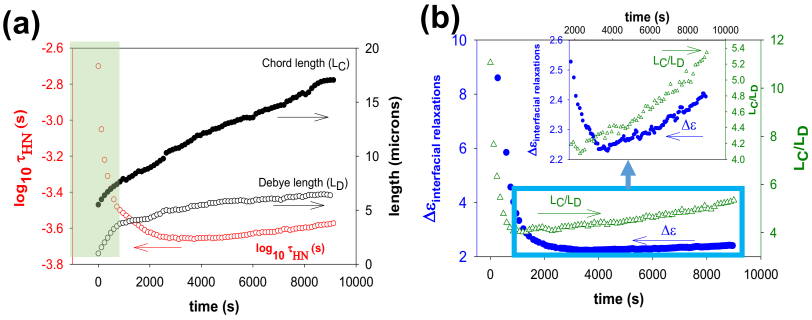

Fig. 1: Time evolution of (a) interfacial relaxation time, chord length (L_C) and Debye length (L_D), and (b) dielectric interfacial strength and L_C/L_D of neat blend during phase separation at 213 °C

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BOOK OF ABSTRACTS:

POSTER

contributions

Molecular dynamics of PDLLA and its α-cyclodextrins complexes investigated by thermostimulated depolarization currents

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Poly(D,L-lactic acid) (PDLLA) is a well-known biodegradable polyester that has been widely employed in biomedical devices. Inclusion complexes formed by the combination of amorphous PDLLA with α-cyclodextrins (CDs) result a material with a well-organized channel-type crystalline structure [1]. Such organization at nanometric scale has a marked influence on the conformational dynamics of PDLLA. In fact, it was previously shown as two secondary relaxations are clearly distinguished in the inclusion complex (β and γ) while only one was detected in bulk PDLLA (β). Additionally, the cooperative α process of neat PDLLA comes out with an accentuated decrease of intensity and shifted to higher temperatures in the IC system. [2]
In the present work, the thermostimulated depolarization currents (TSDC) technique has been applied to deep understanding the molecular dynamics of PDLLA in bulk and incoporated in the α-CD complexes. In bulk PDLLA, TSDC results put in evidence the existence of the normal mode process which was not detected by DRS in our previous work [2]. The resolution of the normal mode was possible due to the very low equivalent frequency of TSDC, that sometimes is able to separate processes overlapped in DRS. The thermal sampling procedure in which a very narrow set of dipolar modes are selected in each experiment, allows estimating the characteristic relaxation times of the relaxations detected from a large temperature range below and above the glass transition temperature for the bulk and the inclusion complexes of α-CDs.

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Chirality impact on molecular mobility of chiral amorphous compounds: An original case study

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Chiral molecules are coumpounds non-superimposable to their mirror images. For example, couples of enantiomers (or antipodes) are couples of 3D objects that differ from their image through inversion symmetry [1]. The stereochemical, structural and thermodynamic implications of such molecular property play an important role in many biological and physico-chemical processes [2]. In particular, more than half of the commercialized Active Pharmaceutical Ingredients (API) are chiral. However, the impact of chirality on the amorphous state of organic molecules remains a scientific field still poorly understood. The few cases reported in the literature illustrate different crystallization kinetics from the amorphous state dependent on the enantiomeric excess (ee) [1, 3-4].

The present work deals with the investigation of the molecular mobility of a chiral molecule (namely N-acetyl-α-methylbenzylamine) below and above Tg as function of the ee. For this purpose, the amorphous state of the model compound has been studied by broadband dielectric spectroscopy coupled to molecular dynamic simulations.

The first results highlight an unexpected Debye process (already observed in the case of monohydroxy-alcohols, secondary amides and other small organic molecules [5]) taking place concomitantly with the structural relaxation process α. So far, the impact of the ee seems to be mainly expressed in this Debye relaxation, by contrast to α and secondary relaxation processes. The Debye relaxation may be related to supramolecular hydrogen bond aggregates, which can remain even in the amorphous state. The latter bond chains are traduced by the giant value of the dielectric strength in the supercooled liquid region and is function of the ee.

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Correlation between molecular dynamics and physical stability of two milled anhydrous sugars: lactose and sucrose

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The focus of this study is the propensity of two anhydrous disaccharides (lactose and sucrose) to amorphize on ball milling and the physical stability of the resultant amorphous phase. The amorphous content in these milled sugars (estimated by DSC) increases with milling time and is greater for lactose than sucrose with 60% and 35% of an amorphous phase forming, respectively, after 60 min milling. The amorphous phase stability was measured in terms of the tendency to devitrify (determined as onset temperatures by broadband dielectric spectroscopy BDS). At the same degree of amorphization of both sugars, the sucrose devitrifies at temperature which is ~15 °C higher than that of milled lactose, indicating higher stability of the amorphous sucrose phase than lactose. The relationship between the de-vitrification temperatures and moisture content also suggests that the amorphous lactose is more susceptible to moisture, as similar devitrification temperatures are observed for sucrose but at much lower moisture contents. Another finding of this study is the greater stability of long milled samples, the reasons for this include i) less moisture in long milled samples ii) fewer nucleation sites in the long-milled samples. An attempt was also made to evaluate the molecular dynamics of the amorphous phase, using BDS to evaluate the characteristics of the beta relaxation process associated with segmental motion of sugars. The values of activation energies for the beta process were comparable to the amorphous phases of these sugars obtained by other methods suggesting that the intermolecular bonding within the amorphous phases do not change with milling. However, in making a comparison between the sugars, it was noted that the activation energies of milled sucrose are higher than those in lactose by ~9 kJ mol^{-1} and the β-relaxation time of sucrose was longer than that of lactose. All these observations support the suggestion of a greater susceptibility of lactose to devitrify and hence a greater stability of amorphous sucrose [1], probably as a consequence of the differences in molecular packing/ molecular structure of both sugars. However, on extended milling when the moisture content decreases, lactose was seen to become relatively more stable.

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The impact of chemical modification on the torsion rotations of carboxyl group and conformational changes in ibuprofen in the bulk and under confinement

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Earlier studies on IBU showed a slow Debye process of small amplitude connected with rotations of this moiety in the dielectric spectra.[1,2,3] To better understand this phenomenon Broadband Dielectric, Raman and Nuclear Magnetic Resonance spectroscopies were applied to study molecular dynamics in the bulk as well as under confinement of four ibuprofen esters, in which the hydrogen atom from the hydroxyl group was substituted by the methyl, isopropyl, hexyl and benzyl moieties (Met-IBU, Iso-IBU, Hex-IBU, Ben-IBU). We found that an additional process (slow mode, SM), broader than typical Debye relaxation, appears in dielectric spectra in all examined compounds except for benzyl derivative of ibuprofen (for this ester, NMR measurements demonstrated that the rotation around O=C-O-R group is significantly slowed down or completely suppressed). Moreover, with an increasing molecular weight of the substituent, the relaxation times of the SM become longer and its activation energy clearly increases, which indicates that the substituent of a various size and mobility has a different impact on the torsion rotations of the carboxyl group. What is more, isothermal time-dependent experiments on the samples having different thermal history revealed an ongoing equilibration (the strongest in the case of Hex-IBU, but absent in Ben-IBU) manifested by the continuous shift of the structural process until it finally reached its equilibrium position. Raman investigations demonstrated that observed effect may be due to conformational equilibration of the long hexyl moiety. Furthermore, we carried out isothermal time-dependent measurement on Ben-IBU incorporated into porous anodic aluminum oxide of two sizes (d=20 and 80 nm). Unexpectedly, there was a shift of the structural relaxation process indicating ongoing conformational equilibration in this compound. In fact, Raman studies supported by DFT calculations confirmed that. Obtained results clearly suggest that the spatial restriction imposed by nanochannels may enforce conformational variation of the molecules. *Financial support from the Polish National Science Centre based on Dec: 2016/22/E/NZ7/00266 is acknowledged.*

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The Impact of Interfacial Energy and Specific Interactions on the Molecular Dynamics of series of Poly(propylene glycols) under 2-Dimensional Confinement

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Molecular dynamics and thermal properties of native and chemically modified poly(propylene glycol) (PPG) with molecular weight M_n=4000 g/mol was investigated in bulk and in AAO templates of varying pore diameter by means of BDS and DSC techniques, supported by Surface Tension and Contact Angle measurements. To influence on the intermolecular interactions between nanoporous matrix and polymer terminal units -OH has been replaced by the $-NH_2$ and $-OCH_3$ moiety. Analysis of the loss spectra revealed that there is a clear kink in the temperature dependence of the segmental relaxation times that shifts to higher temperature with the increasing degree of confinement. Interestingly this crossover (T_c) in segmental dynamics corresponds very well to the high glass transition temperature registered during calorimetry studies. In view of the two layer model by McKenna et al. it can be interpreted as connected to the vitrification of the interfacial polymers. On the other hand low glass transition temperature from calorimetry measurements agrees very well with the temperature at which $\tau_\alpha(T)$=100 s. That means that at this condition core polymers vitrified. By comparing shift in the T_c with respect to the bulk T_g in the studied polymers it was found it varies dependently to the ability of H-bonds formation in the following order: PPG → PPG-NH_2 → PPG-OCH_3 for the constant interfacial energy γ_{SL}.[4] Interestingly no such relationship was noted for the evolution of the glass transition temperature of the core macromolecules. Anyway our data strongly points out that reduction in the glass transition temperature is directly related to the vitrification of the interfacial polymers that may be tuned by modification of the specific interactions between host and guest material. However, the relationship between T_g and T_c under confinement seems to be more complicated since thermal history of the sample, annealing processes as well as sensitivity of the segmental dynamics to the density fluctuations may affect the results.[1,2,3,4,5]

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Interfacial dynamics in two-layered thin polymer films investigated by BDS and Neutron Reflectivity measurements

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Amorphous materials can be transformed into glassy state which has random molecular structure when they are cooled from high temperature. The dynamics of glass transition is affected by the molecular mobility of surfaces and/or interfaces. In this study, we used BDS measurements and neutron reflectivity (NR) measurements of two-layered thin polymer films in order to clarify the annealing effects on the interfacial interaction.

The polymer samples used in this study were atactic h-PMMA for BDS measurements, and atactic h-PMMA and d-PMMA with two different molecular weights) for NR measurements. Stacked thin films of PMMA were prepared as follows: single thin films were prepared on glass substrate by spin coating from a toluene solution. The film was floated onto the surface of water and transferred onto the top of the substrate or previously stacked thin films on the substrate. For DRS measurements, the first layer is prepared onto Au-deposited glass substrate, and Al was vacuum-evaporated as the upper electrode. For NR measurements, two kinds of d-PMMA was mixed to make sample which has various Tg s. For DRS measurements, an LCR meter (HP4284) was used, and the temperature of sample was changed between 273 and 418K, and the frequency range was 20Hz to 1MHz. NR measurements were performed on BL-16 in J-PARC), and the temperature of samples was kept at 409K for annealing measurements.

DRS measurements show that there are two loss peaks can be observed, α-process and β-process. It can be observed that the relaxation rate of the alpha process is decreased and the mobility of molecules changes from thin film-like one to bulk like one by annealing. NR measurements shows the roughness of the interface between thin layers increases with annealing. This indicates that the diffusion of polymer chains near the interface of polymer layers was activated during annealing process. Furthermore, the dependence of the thickness of each layer on the annealing time strongly changes depending on T_gs and thickness of h-PMMA and d-PMMA layers.

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Exceptional secondary relaxation in fluorinated ultrathin polymer films

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We investigated the molecular dynamics of bulk melts and capped thin films of a fluorinated polymer currently used by industry. In this system, in addition to a well pronounced peak attributed to segmental motion, we observed one secondary process separated from the former by five frequency decades at the glass transition temperature, T_g. This process shows an unusual behavior within a narrow temperature window near T_g, where the relaxation rate decreases – rather than increasing – with increasing temperature. This trend is an anomaly in the typical behavior observed for secondary processes, characterized by a constant activation energy. Remarkably, this unsual phenomenon gradually vanishes upon reduction of the thickness at the nanoscale level. For films as thin as 10 nm the commonly Arrhenius behavior is observed.

We have analysed our results by means of the Minimal Model [1], according to which secondary relaxations can be described by an asymmetric well potential. The anomaly observed increases with the asymmetry of the relaxation potential, and is imputable to a network of directional bonds which hinders rotational motion above T_g. Our results, indicate that confinement at the nanoscale level affects the stability of such network, probably due to the symmetry break introduced by the presence of adsorbing interfaces.

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Experimental test of the Cooperative Free Volume (CFV) rate model under 1D confinement: the interplay of free volume, temperature, and thickness in driving segmental mobility

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We show that the Cooperative Free Volume (CVF) rate model [1,2] can be employed to successfully describe the temperature (*T*) and thickness (*h*) dependence of the segmental time (τ) of polymers confined in thin films (1D confinement). The CVF model is based on an activation free energy that increases with the number of cooperating segments (n^*), wherein, it is the system's free volume that determines n^*. CFV describes pressure dependent dynamics, $\tau(T,V)$, for bulk systems, and now we test its natural extension to $\tau(T,h)$ for films. The system's thermodynamically characterized free volume leads to the volume contribution in bulk, and similarly, it leads to the thickness contribution in films.

Here, we apply the CVF model to new experimental results on the segmental relaxation of 1D confined poly(4-chlorostyrene), P4ClS, a model system to study the impact of free volume on dynamics [3]. By using bulk data to characterize the pressure dependence of the segmental time and the isothermal thickness dependence of the segmental time at a single temperature as input, the CVF model could reproduce the outcome of experiments over the whole temperature range investigated.

The remarkable agreement with experimental data further validates the robustness of the model and supports the idea that confinement effects originate from local perturbations in free volume content.

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Substrate roughness speeds up segmental dynamics of thin polymer films

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We show that the segmental mobility of thin films of poly(4-chlorostyrene), a polymer whose glassy dynamics is particularly sensitive to changes in volume, gets enhanced in proximity of rough substrates. This trend is in neat contrast to predictions of molecular dynamics simulations which propose roughness as a universal source of slower dynamics. Our experimental evidence indicates that faster interfacial dynamics of spincoated films originate from an increase in interfacial free volume content, due to the non-complete filling of asperities. Importantly, our results are in line with Doolittle equation, the bulk scaling, holding in isothermal conditions, correlating segmental mobility to an exponential term of free volume content.

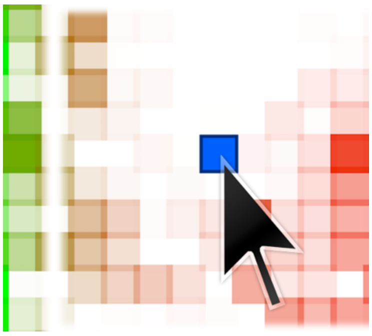
Limited Mobility Live! : interactive macOS software for exploring facilitated dynamics in glassy soft matter

Nicholas B. Tito

Theory of Polymers and Soft Matter, Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands.

This poster presents a visual computer application for carrying out live simulations of facilitated glassy dynamics on a lattice.

Facilitated molecular motion is at the heart of the glass transition in liquids and polymers.[1] Relaxation at one locality in a glassy material is contingent on cooperative motion of the surrounding molecules. Local dynamics are therefore enslaved to large kinetic barriers, and “facilitation” at the microscale is how a glass makes the slow trek across its energy landscape. A variety of facilitated kinetic lattice models have been devised over the years, to examine the consequences that local kinetic barriers have on the structure, dynamics, and trajectories of a frustrated glassy system at, moving towards, or far from equilibrium.



"Limited Mobility Live!" implements the mathematics for two kinetic lattice models into a live and interactive Monte Carlo simulation on your Mac. Watch a system based on the Fredrickson-Andersen (FA) model[2] or Limited Mobility (LM) model[3] evolve before your eyes, subject to a variety of parameters and boundary conditions that can be changed, enabled and disabled in real-time.

Stop by to try it out, and "paint" a glassy system yourself!

Website and download link to get your own copy of the software will be provided at the poster.

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Soft Confinement Effects on Relaxation Dynamics of Polymers

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Soft materials under nanoscopic confinement display a range of fascinating properties owing to the reduced degrees of freedom and modified molecular interactions [1]. Here, we report the *structural relaxation dynamics* (α-relaxation) of the biopolymer gelatin dissolved in water (bulk form) and under soft spatial confinement probed using *dielectric relaxation spectroscopy* over a wide frequency range starting from 1 Hz up to 2 GHz [2]. The soft confinement of hydrated gelatin is achieved by enclosing the polymer inside the droplet core of water-AOT-n-decane reverse microemulsions, where the fluctuating surfactant shell constitutes the *soft confining boundary* [3, 4]. Herein, the stability of the droplet phase of microemulsion loaded with polymer is confirmed by the small-angle neutron scattering (SANS) experiment. The α-relaxation of hydrated gelatin in bulk as well as in confinement is modeled using *Havriliak-Negami function*. Notably, the gelatin in soft confinement exhibit faster relaxation dynamics in comparison to its bulk counterpart and it further gets accelerated with reduction in the confining volume. We conjecture that the enhancement in the dynamics of the gelatin polymer chain subjected to increased spatial confinement may arise from its *proximity induced cooperativity* with the enclosing surfactant boundary [2]. Our combined results imply that the properties of confining boundary strongly influence the dynamics of the enclosed material.

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High Molecular Weight *cis*-1,4-Polyisoprene confined in Nanoporous Alumina: Dynamics over the Entanglement limit

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The effect of confinement on polymer dynamics and the associated liquid-to-glass temperature, T_g, has been an issue of great interest in polymer physics [1]-[6]. In this study, we investigate the effect of nanometer confinement on the dynamics of *cis*-1,4-polyisoprene with molecular weights above the entanglement limit (M_w=8500-100000 g/mol). As confining medium we employ self-ordered nanoporous alumina (AAO) with diameters, *d*, ranging from 400 nm to 25 nm and explore the range $0.01<2R_g/d<0.82$. An earlier study [1] investigated the effect of confinement in PI with $M<M_e$ and found a sligthly faster segmental dynamics under confinement with respect to the bulk. Subsequently, the role of interfacial energy on the segmental dynamics for different polymers confined in AAO was explored [2]. Herein we employ Broadband Dielectric Spectroscopy (BDS) and Temperature-Modulated Differential Scanning Calorimetry (TMDSC) to examine the effect of confinement on molecular dynamics. BDS measurements revealed consistently faster segmental dynamics under confinement with respect to the bulk, leading to a decrease in T_g with increasing degree of confinement ($2R_g/d$). The cooling traces (equilibrium curves) obtained from MDSC showed a decreased T_g under confinement in accordance with DS. In addition, we provide evidence for an intermediate process with an Arrhenius temperature dependence whose dielectric strength increases with increasing degree of confinement ($2R_g/d$). This is attributed to a "dead layer" consisting of partially immobilized chains next to the interface, discussed in recent imbibition studies of polymers in nanopores and confirmed by theory [3], [4]. We further report on the effects of annealing and quenching on the thermodynamics and dynamics [7].

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Dynamics of Nanoscopically Confined PVME in Thin Films of an Asymmetric Miscible PVME/PS Blend

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In recent years, substantial efforts have been devoted to investigating nanoscopic confinement of polymers, and its effect on glassy dynamics. Broadband Dielectric Spectroscopy (BDS) was used to study the dynamics of ultra-thin films of PVME/PS 50/50 wt% blend, employing a novel nano-structured capacitor sample arrangement. The investigated system shows a complex dynamic behavior. First, an α-relaxation, related to a bulk-like layer was found. Second, an α'-relaxation was observed, characteristic for dynamically asymmetric blends, where the out of equilibrium dynamics is attributed to weakly-cooperative PVME segments relaxing within a frozen environment of PS segments. Third, for thinnest films, an Arrhenius-like process was dominant in the dielectric spectra, indicating localized fluctuations of the segments. Relaxation rates of this process resembled that of the degenerated α-relaxation of the adsorbed layer, found for pure PVME [1], thus it was assigned accordingly. For thinnest films, this process undergoes a further confinement, due to the topological constraints, introduced by PS. Such multiple confinement effect has not been reported for ultra-thin films of polymer blends, before this study [2].

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Molecular Dynamics of an Asymmetric PVME/PS Blend Investigated by Broadband Dielectric and Specific Heat Spectroscopy

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Over the past decades research on the molecular dynamics of miscible polymer blends are of topical interest in the literature, in an attempt to understand the segmental mobilty of individual components, as it is affected by blending. In general, miscible polymer blends exhibit a complex behavior of the molecular mobility. For an A/B blend the relaxation times of component A and component B are affected by the spatial local compositional heterogeneity, present in binary systems on a microscopic level, regardless of the macroscopic homogeneity. Here, a combination of broadband dielectric and specific heat spectroscopy was employed to study the dynamically asymmetric PVME/PS blend with seven different compositions, focusing on samples with high PS contents. Considering that PS is dielectrically invisible, BDS is a powerful technique to study the response of PVME, as it is affected by PS segments. In this work the well-known binary relaxation times distribution of PVME in a blend, originating from the spatial local heterogeneity, was studied over ten decades in frequency, for the first time in literature. Secondly, one of the detected processes, α'-relaxation, shows a crossover from high-temperature behavior (system in equilibrium) towards a low temperature regime, where PS undergoes the thermal glass transition, resulting in confined segmental dynamics of PVME within a frozen network of PS. Here, we introduce a precise mathematical tool to distinguish between the temperature dependency regimes of the process, and examine the composition dependence of the crossover temperature, detected by dielectric spectroscopy. Moreover, the dielectric data was compared in detail with results obtained by specific heat spectroscopy. This comparison provides new insights in the dynamics and dynamic heterogeneity of the PVME/PS blend system.

Molecular Dynamics of Dipole Functionalized Triphenylene-based Discotics

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Since discovery of discotic liquid crystals (DLCs), consisting of a disklike rigid aromatic core and flexible alkyl chains attached to the core, dating back to Chandrasekhar's work in 1977, they have been extensively investigated to reveal their fundamental properties and potential for applications.[1] The researches on DLCs in last decades showed that DLCs can be considered as promising materials for organic electronic applications since they exhibit one dimensional high charge mobility along the column axis in a columnar mesophase.[2] The mobilies of the rigid aromatic core and the flexible alkyl chains can influence their application properites, e.g. the charge carrier mobility, therefore, it needs to be explored in detailed. [3]
In this study, a series of dipole functionalized triphenylene-based discotics, forming a columnar mesophase, were investigated to reveal the influence of the functionalization on phase behavior, molecular dynamics and as well as conductivity. The molecular mobility of the discotics was probed by broadband dielectric spectroscopy (BDS). In addition to conductivity and localized dynamics, glassy dynamics were also observed. The phase behavior of the material was explored by a power-compansated differential scanning calorimetry (DSC). Beside the phase transition temperatures and enthalpies, thermal glass transitions were found for all the materials. Moreover, the glassy dynamics were further investigated by Flash DSC, which is a chip-based calorimetry technique allows fast heating and cooling rates as high as 10000K/s.

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Collective Orientational Order and Phase Behavior of a Discotic Liquid Crystal under Confinement

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Discotic liquid crystals (DLCs) are a promising class of soft matter for electronic applications. This is due to their ability to self-organize into columns in a hexagonal columnar mesophase, driven by the overlapping of the π orbitals of their aromatic cores. This leads to a high charge-carrier mobility along the column axis. Embedding liquid crystals into nanopores of anodic aluminum oxide (AAO) results in a 2D nanoconfinement of these materials. This confinement affects their properties, compared to the bulk, such as phase transition temperatures and enthalpies, molecular mobility, and crystallization [1,2,3].
In this study, 2,3,6,7,10,11 hexakis[hexyloxy] triphenylene (HAT6) was confined into parallel aligned cylindrical nanopores of AAO membranes by melt infiltration. The membrane as confining hosts used have varying pore diameters, from 10 nm to 160 nm, covering a broad pore size range, thus, a better understanding of the confinement effect on phase behavior and molecular configuration in the pores. Furthermore, it is aimed to obtain axial ordering or to increase degree of axial ordering by chemically modifying the surfaces of the pores. Therefore, the pore surfaces the membranes were chemically modified, resulting in a more hydrophobic pore surface than the unmodified ones. The phase behavior was explored by a power-compensated DSC allowing the detecting of small changes in the phase behavior. In the literature, dielectric spectroscopy was demonstrated as a method to monitor molecular order inside the pores. [4] Here, we also investigate the collective orientational order, corresponding to dominating molecular ordering, by dielectric spectroscopy.

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Molecular dynamics in 4-(2,3-difluoro)-pentylphenyl-trans-4-(2,3-difluoro)-pentylcyclohexylbenzoate nematic liquid crystal

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Negative dielectric anisotropy is quite rarely observed in nematic liquid crystals. Newly synthesized 4-(2,3-difluoro)-pentylphenyl-trans-4-(2,3-difluoro)-pentylcyclohexylben-zoate shows negative dielectric anisotropy. Molecular dynamics studies were carried out at temperatures from 173 to 410 K and frequencies 10^{-1}-10^{7} Hz on sample cooling and heating by broadband dielectric spectroscopy. Investigated substance shows monotropic system of phases. Isotropic, nematic and crystalline phase CrI were observed on cooling, while on sample heating additionally the so-called cold crystallization of CrII was found. Kinetics of crystallization of both partially ordered crystals was analyzed by isothermal and non-isothermal methods. The kinetics parameters, dimensionality of crystal growth and energy of the process were found using Avrami and Avramov approaches.

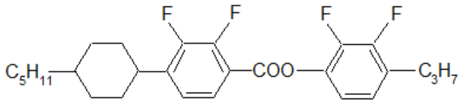

Fig.1 Chemical structure of 4-(2,3-difluoro)-pentylphenyl-trans-4-(2,3-difluoro)-pentylcyclohexylbenzoate.

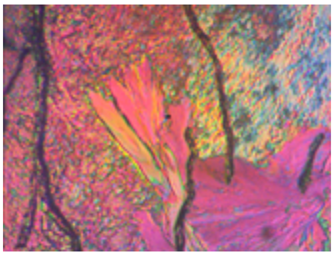

Fig.2 Cold crystallization of CrII phase.

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The dedicated simulator for soft matter systems dynamics - ARUZ

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Dynamic Lattice Liquid (DLL) algorithm [1] is designed to simulate dynamics in complex liquid systems, like polymer solutions, melts, multi-phase systems, etc. The DLL was an inspiration for construction of dedicated FPGA-based device, called ARUZ (Analyzer of Real Complex Systems) [2, 3], in BioNanoPark, Lodz (Poland). ARUZ is a scalable, fully parallel data processing system equipped with low-latency communication channels, dedicated for simulations involving interactions among huge amount of relatively simple elements working in parallel. The device is composed of almost 26 000 FPGAs interconnected in a 3D network. ARUZ can be used in research of complexity in chemistry of macromolecules and variety of physical phenomenon. Some exemplary results are presented concerning synthesis of polymer stars and dynamical investigation of their properties, as well as solvent dynamics, as a function of star arm number, arm length and concentration. The device performance is also presented and compared with classical computing architectures.

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BDS as an analytical tool for the analysis of polyethers with different architectures

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Synthesis of polymers with well-defined architectures has been among the top aspects in polymer science in recent years, in great part driven by the dependence of the physical properties on the defined molecular structure. Here, BDS has played a very important role in the study of molecular dynamics and chain structure in different polymer systems. In this study, we have placed our attention into poly(glycidyl phenyl ether) (PGPE), a polyether with pendant methoxyphenyl groups that is characterized by large dipole moments.[1,2] In its linear and regioregular form, PGPE exhibits a dielectric relaxation highly sensitive to the net dipole moment of the whole chain, generally called normal mode We have exploited this dielectric relaxation to verify the success in cyclization reactions and in the formation of symmetric two-arm chains. Cyclic regioregular polymers are expected to have net zero dipole moment due to the cancellation of the dipole moment vectors parallel to the chain contour. This has been confirmed in our BDS measurements through the disappearance of the normal mode relaxation after cyclization. This signature of the dielectric spectra was very useful for evaluating the cyclic purity of synthesized cyclic topologies, highlighting the importance of BDS as an additional tool for verifying cyclization over traditional gel permeation chromatography and MALDI-ToF techniques [2]. Moreover, since the normal mode relaxation is highly sensitive to the net dipole moment of the whole chain, we also have used BDS in this study to verify the formation of linear PGPE chains containing two symmetric arms with net dipole moments pointing in opposite directions and to characterize their cyclic topologies. The obtained results highlight again the value of BDS in the synthesis lab for structural verification, an information not readily accessible by complementary techniques.

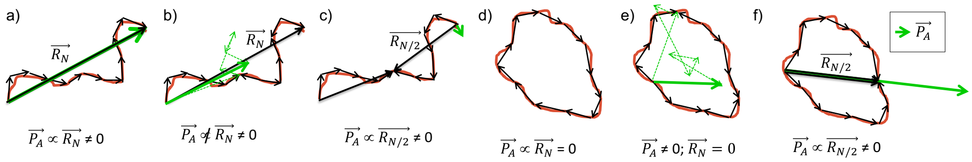

Figure 1. Characteristic dipole moment of a chain ($\overrightarrow{P_A}$) with linear (a-c) and cyclic (d-f) architectures, and with isoregic (a, d, c, f) and aregic (b, e) microstructures.

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Molecular mobility in highly piezoelectric P(VDF-TrFE) copolymer: dielectric and mechanical correlation

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The calorimetric, dielectric and mechanical responses of highly piezoelectric 70/30 P(VDF-TrFE) displaying homogenous d_{33} of -19 pC.N^{-1} are studied.

This work aims at better understanding the influence of poling on the mechanical properties of this copolymer. In order to explain the one decade mechanical modulus drop observed across the Curie transition, a stiffening process of the amorphous phase due to the local electric fields in the ferroelectric crystals is proposed. In poled P(VDF-TrFE), these fields are preferentially aligned resulting in a more stable and higher modulus below the Curie transition. This hypothesis accounts for the lower dielectric signals obtained with the poled sample. Through the Curie transition, the vanishing of these local electric fields, stemming from progressive disorientation and conversion of ferroelectric crystals to paraelectric ones, releases the constraints on the amorphous phase, leading to a storage modulus drop typical of a viscoelastic transition.

Broadband dielectric spectroscopy evidenced the γ (local mobility), β (free amorphous phase), T_{g-u} (constrained amorphous phase) and α_c (most likely fusion of secondary crystals at the surface of the main crystals) relaxations as well as the dielectric manifestation of the Curie transition. The dielectric response of the poled material was found to be globally reduced compared to the depoled one below the Curie transition.

A study on molecular dynamics and thermal properties of linear and cyclic oligosaccharide derivatives

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In this work, we thoroughly characterized dynamical and thermal properties of representative modified linear and cyclic oligosaccharides, which unlike traditional ones (H-bonded systems) are typical van der Waals materials. For this purpose, two experimental techniques, i.e. Broadband Dielectric Spectroscopy (BDS) and Differential Scanning Calorimetry (DSC) were applied. It was shown that in dielectric spectra of acetylated linear carbohydrates (acTRE, acRAF, acSTA) as well as cyclodextrins (ac-α-CD, ac-β-CD, ac-γ-CD), measured above the glass transition temperature (T_g), the dc conductivity and the structural (α)- relaxation peak of nearly the same shape can be detected. In contrast to linear compounds, the α-process in acCDs was not well separated from the conductivity. Therefore, to calculate the relaxation times (τ_α) we used a derivative method based on the Kramers-Kronig (KK) relation. Then, the T_gs of all examined compounds were determined. It turned out that the estimated values are close to the ones obtained from calorimetric studies. Interestingly, the glass transition temperatures as well as isobaric fragilities (m) determined for linear acetylated saccharides increased with increasing molecular weight (M_w) of the material. Note that the same behavior has been generally reported for polymers [1,2,3]. On the other hand, completely different scenario was observed for the modified cyclodextrins. Namely, the T_g was practically independent of M_w, while m decreased with M_w. One can suppose that the drop in m may be due to some strains in cyclodextrin rings, which get smaller with increasing size of acCD molecule. In the glassy state of the investigated carbohydrate derivatives, one: γ (linear acSACCH) or two: β and γ (cyclic acCDs) well-resolved secondary relaxations were detected. Interestingly, in the case of modified cyclodextrins, the widtht of the faster γ-process, as well as its activation energy were almost identical, regardless of the molecular weight of compound. In turn, the γ-peak of acSACCH became broader with increasing M_w. What is more, the position and the shape of the slower β-relaxation in acCDs were similar at nearly the same temperature. However, activation barrier for this process decreased with increasing M_w. Obtained results enabled us to elucidate the differences in molecular dynamics of acetylated saccharides characterized by various topologies (linear and cyclic). *Financial support from the Polish National Science Centre based on Dec: 2016/22/E/NZ7/ 00266 is acknowledged.*

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Secondary relaxation in D-mannitol under liquid-liquid transition

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The liquid-liquid transition (LLT) has been attracting many researchers because of its scientific importance especially on the scientific fields of water -the most ubiquitous and also anomalous liquid-. It has been hypothesized that LLT and the critical point of LLT (liquid–liquid critical point: LLCP) could be the key to understand anomalous features of water. This is based on experimental results that show existence of the two distinct amorphous states, low density amorphous (LDA) and high density amorphous (HDA) states, at temperatures around 77 K. [1] According to LLCP hypothesis, origin of plenty of anomalies of water seems to be understood as fluctuation of liquid structure around LLCP. However, unfortunately, at temperatures around LLCP, water crystallized suddenly and detailed studies of water in a liquid state are prevented. Therefore, an alternative material is needed to investigate LLT of hydrogen-bonded (HB) system.

Recently, LLT of sugar alcohol, D-mannitol as the alternative material, has revealed by differential scanning calorimetry, X-ray, Raman spectroscopy, and near infrared spectroscopy. [2] LLT of D-mannitol has classified as equilibrium 1st order phase transition from super-cooled-liquid (SCL): HDA to phase X: LDA at around 290 K and at ambient pressure.

In this study, the relationship between the secondary relaxation process and LLT in D-mannitol was revealed by broadband dielectric spectroscopy. The origin of the secondary process in sugar alcohol has known as universal HB dynamics because of its relaxation time that is independent on the number of carbon atoms of the backbone and the conformation. Our results show that the secondary process in D-mannitol depends on LLT in contrast to the LLT-independent secondary process in triphenyl phosphite [3] that is well known material for investigations of LLT. Therefore, our findings are important for understanding the LLT of HB materials such as water. [4]

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Dielectric relaxation of novel biodegradable aliphatic-aromatic block copolymers

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Thermoplastic elastomers are copolymers composed of a hard block, typically a polyester, and a soft block, typically a polyether. While the hard segment provides mechanical stability and processabillity the soft one is responsible for the elastomeric properties [1]. Depending on the hard/soft block ratio copolymers with a wide range of mechanical and biodegradation properties can be prepared. Until recently, most commercially available poly(ether-ester) thermoplastic elastomers have been produced based on petrochemical monomers. The increasing necessity of eco-friendly polymers has driven the interest for the production of thermoplastic elastomers fully or partially based on monomers from renewable sources [2]. Poly(lactic acid) (PLA) is a biodegradable aliphatic polymer which can be obtained from natural products. PLA has appeared as a promising building hard block for thermoplastic elastomers with attractive properties for medical applications especially when combined with poly(ethylene oxide) (PEO) as soft block. The knowledge of the relaxation behavior of this type of materials may play an important role in order to better understand the final mechanical properties which, in addition to biodegradability and biocompatibility, are of importance for medical applications. In this contribution we present dielectric relaxation results of a series of thermoplastic elastomers based on poly(tetramethylene oxide), as soft segment, and on a multiblock of poly(buthylene terephthalate) (PBT) and poly(lactic acid) (PLA) as hard segment. The main aim of the study was to investigate the influence of PBT/PLA hard block ratio on the relaxation behavior. The results indicate the existence of a single α-relaxation, associated to the segmental motions above the glass transition temperature, regardless of the PBT/PLA ratio of the hard segment. This result points towards an absence of phase segregation between the two blocks within the hard segment. In addition, different local dynamic processes are revealed below the glass transition temperature contributing to a multimodal β-relaxation. The different contributions to this multimodal β-relaxation can be assigned to different bonds of both hard and soft blocks. These results are in line with previously reported data in aromatic polyesters in which the multimodal character of the β-relaxation was discussed on the basis of intrachain local dynamics.

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Influence of processing conditions on restricted amorphous fraction (RAF) formation: Characterization by DSC, Flash DSC and dielectric spectroscopy

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The presence of interphase has been already evidenced in the case semi-crystalline polymers but also in the case of inorganic/polymer nanocomposites. In fact, it is recognized that the molecular mobility of some fraction of the amorphous phase may be restrained by the crystalline phase and by the inorganic filler. This fraction is called the rigid amorphous fraction (RAF). Then, the "three-phase model" can be followed, where the nanocomposite consists of the crystalline fraction (CF), the mobile amorphous fraction (MAF) and the RAF. The existence of a RAF in PA6-montmorillonite nanocomposite films is available from specific heat capacity measurement at the glass transition region of the nanocomposites using calorimetric analysis method, and from focusing on segmental dynamics by dielectric relaxation spectroscopy. The aim of this study is to correlate correlation between thermal and dielectric analysis and especially the role played by the RAF.

Structural, morphological and dielectric properties of $LiFe_5O_8$ prepared by different methods

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Lithium ferrite ($LiFe_5O_8$) is a ceramic material with very interesting properties such as high Curie temperature, low magnetic losses, presenting a square hysteresis loop and high magnetization, high electrical resistivity and low eddy current losses [1–3]. This material has several technological applications in magnetic recording, microwave devices, transformer cores, rod antennas and could be applied in the biomedical field. It is also a promising candidate to be used in rechargeable lithium batteries such as cathode materials or as low-cost substitutes for garnet materials in microwave frequency applications.

In the present work, amorphous $Li_2O–Fe_2O_3$ powders were prepared by sol-gel and solid state reaction methods. The obtained mixture of these powders was pressed into pellets and then heat-treated at temperatures between 400 and 1200 ºC.

The structure of the obtained samples was studied by X-ray diffraction and by Raman spectroscopy. The surface morphology was characterized by scanning electron microscopy. The dielectric properties were analyzed in the temperature range between 200 and 400 K and frequencies between 10^2-10^6 Hz.

The samples prepared by the sol-gel method, the single crystalline phase of lithium ferrite was obtained for lower heat treatment temperatures when compared with the solid-state reaction method. The dielectric properties were related to the structure and morphologic characteristics. For energy storage applications, the samples prepared by sol-gel at 800 ºC ($\varepsilon'=22.79$; $\tan\delta=0.10$ at 1 kHz and 300 K) and by solid-state reaction, at 1100 ºC ($\varepsilon'=53.64$; $\tan\delta=0.83$ at 1 kHz and 300 K) are the most promising.

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Relative Permittivity Properties of Hydrated Polymers for Desalination Membrane Applications

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Providing sustainable supplies of purified water and energy is a critical global challenge for the future, and polymer membranes will play a key role in addressing these clear and pressing global needs for water and energy. Polymer membrane-based processes dominate the desalination market because they are more energy efficient than thermal desalination processes. Much remains unknown about the influence of polymer chemistry on even basic intrinsic water and ion transport properties, and these relationships must be developed to design next generation polymer membrane materials.

For desalination, polymers with simultaneously high water permeability and low salt permeability are desirable to prepare selective membranes that can efficiently desalinate water. A tradeoff relationship between water/salt selectivity and water permeability suggests that both sorption (thermodynamic) and diffusion selectivity properties contribute significantly to water/salt permeability selectivity. The sorption component of this tradeoff has been modeled using an electrostatic (or dielectric) exclusion approach [1].

Microwave dielectric spectroscopy measurements were made on hydrated polymers based on poly(glycidyl methacrylate), pGMA [2]. Relative permittivity properties are linked to ion sorption properties that are critical for desalination applications, but little is known about the influence of polymer chemistry and water sorption on relative permittivity. The pGMA-based materials considered in this study had lower relative permittivity compared to Nafion®, which is a perfluorosulfonic acid polymer considered for fuel cell applications, at comparable water content. This result favors ion exclusion and demonstrates the importance of polymer chemistry in engineering polymers for desalination membrane applications.

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Dielectric response of LAGP-based polymer-in-ceramic electrolytes

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The development of clean and highly efficient energy storage systems is one of the frontier goal. Inorganic-ceramic- and organic-polymer-based solid electrolytes (SE) could revolutionize battery and supercapacitor technology because of their nontoxicity, stability during operation and enhanced safety. Of particular interest are electrolytes, which contain high concentrations of ion charge carriers with a minimum polymer concentration required for good flexibility and allowing the major ion-conduction path through the inorganic material.

A novel thin-film polymer-in-ceramic composite electrolyte with high ion-conduction properties was prepared by electrophoretic deposition. Commercial nanoparticles of lithium aluminum germanium phosphate ($Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, LAGP) material were used as a ceramic matrix. Polyethyleneimine (PEI) and polyethylene glycol dimethyl ether (PEO) were tested as binders and lithium-ion-conducting media.

Dielectric properties of LAGP and LAGP-based quasi-solid electrolytes, containing different concentration of LiTFSI-based Pyr14 ionic liquid were studied using the BDS 80 (NOVOCONTROL) with automatic temperature control by a QUATRO Cryosystem. The measurements were performed in the wide frequency (10^{-2}-10^{6} Hz) and temperature (-140^{o}C – $+100^{o}$C) ranges. The samples were hermetically sealed in coin cells, which contain blocking nickel electrodes with a deposited electrolyte or a powder between them.

The complex non-Debye dielectric response of electrolyte can be described in terms of several distributed relaxation processes separated by different frequency and temperature ranges. While at low temperatures the main contribution comes from LAGP, at the middle- and high-temperature regions the superposition of few non-Arrhenius processes are observed. Relaxation is perturbed by clear phase transition related to melting of the ionic liquid. Different scales of the ionic transport and corresponding relaxation of the apparent dipole moment in the materials are discussed. The correlation of ion transport phenomena with XRD, DSC and ESEM data is presented in details.

Structural relaxations in Polyvinylidene fluoride/Polymethyl methacrylate blends in presence of graphene oxide assessed using BDS

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The intermolecular coupling and segmental dynamics influence the structure and properties of polymeric systems. Incorporation of nanoparticles in the polymer causes chains to be confined in narrow spaces and this influences the relaxations and segmental dynamics at the cost of both configurational and conformational entropy [1]. The aim of this study is to analyze the mobility of polymer chains in semicrystalline poly(vinylidene fluoride)/Poly methylmethacrylate (PVDF/PMMA) blends in the presence of graphene oxide using broadband dielectric spectroscopy. Three distinct relaxations namelyα_c due to relaxations in the crystalline phase of PVDF, α_m originating from the amorphous miscible PVDF/PMMA phase, and αβ concerning the segmental dynamics of PMMA,were observed in the blends in the temperature range $T_g < T < T_c$ [2]. The dynamics as well as the nature of the relaxations were observed to be dependent on the blending concentation and surface functionalities of the nanoparticles. The peak position and width of the α_m relaxation allows to quantify the miscibility in PVDF/PMMA blends in presence of graphene oxide. In addition, the low temperature α_c peak allowed to unravel the effects of PMMA and nanoparticles on the crystallinity of PVDF. The orientation of dipoles is faster in blends containing nanoparticles, and henceforth all the structural relaxation shifted to higher frequencies. The structural relaxations thus suggest that nanoparticles induce dynamic heterogeneities in PVDF/PMMA blends and influence the specific interactions between PVDF and PMMA. In conclusion, this study provides insight in the miscibility and heterogeneities developed in semicrystalline blends in presence of nanoparticles.

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Dielectric properties ofoil extracted from vegetation involved in wildland fires

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In general, forest fires exhibit unexpected behaviors that play bad turns on fire operatives. Among these behaviors, generalized conflagration observed in various configurations of the fuel in wildland fires. Despite the fact that the mechanisms leading to generalized conflagration are not fully understood, it appears that the ignition of a cloud of volatile organic components released by vegetation heated by a fire explains the appearance of an accelerated forest fire [1],[2].

The aim of this work is the use dielectric spectroscopy to determine the oxygenated and hydrocarbons Monoterpene composition of a selection of vegetation involved in forest fires. In each fuel, majority terpenes are responsible for its ignition. The flammability limits of these terpenes define the ignition conditions of the fuel (time and temperature of ignition). There are other techniques which can be used to determine these chemical composition [3], such as liquid and gas phase chromatography. Dielectric spectroscopy appears to be cheaper.

Essential oils are extracted from selected vegetations involved in wildland fires (*Rosmarinus officinalis*, *Pinus halepensis*, *Eucalyptus* and *cypressus*). Dielectric spectra of these oils, are measured from 10 mHz to 10 MHz, and their relaxation distribution frequencies are determined as a function of temperature in the range 100-300 K, and the activation energies are deduced [4]. The relaxations frequencies and activation energies are then compared to those of a selection of Monoterpenes(α-pinene, β-pinene and limonene).The activation energies obtained by these oils are also compared to the energies of phase transitions obtained from DSC Calorimetry***.***

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Molecular Dynamics of Fluorinated Methacrylate/Clay Nanocomposites investigated by Dielectric Relaxation Spectroscopy

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In the present work, the dielectric properties of nanocomposites based on 2,2,2-trifluoroethyl methacrylate copolymer (PMATRIF) and montmorillonite (MMT) nanoparticles were studied. The effect of varying amounts of (MMT) filler (in weight ratios of 1%, 3%, and 5%) on the molecular dynamics and polarization of PMATRIF was investigated using broadband dielectric spectroscopy from 10^{-1} to 10^{6} Hz and at temperatures between 20 to 170°C. For PMATRIF matrix, the real part ε' and the imaginary part ε'' of the dielectric permittivity curves revealed four dielectric processes β, α, $\beta\alpha$ and ionic conduction phenomenon. Furthermore, it was found that incorporating MMT led to an increase in the dielectric losses and generated additional relaxation processes known as Maxwell –Wagner- Sillars (MWS) polarization. Calculation of the activation energy for the different processes revealed that α relaxation followed the Vogel–Fulcher-Tammann–Hesse (VFTH) dependency while the other processes were suitably fitted with the Arrhenius law. In order to probe matrix/MMT interface properties, dielectric strength $\Delta\varepsilon$ of MWS polarization was also analyzed with the sum of Havriliak-Negami (HN) functions.

The dielectric performance of phenolic nanocomposites based on treated sugar palm fibres as reinforced materials

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Polymer/natural fiber nanocomposites have attracted great interest due to their improved some properties not only in mechanical behaviour, but also in physical and thermal properties compared to neat polymer or polymer-polymer blends. Nevertheless, there are some limitations on using natural fibres in nanocomposites especially when it comes to the compatibility of the fiber with the matrix. Fiber-matrix adhesion is one of the main issues that affect the behaviour of these biocomposites. Therefore, much work has been done to overcome this problem. In this present work, we propose to investigate the effect of sea water and alkaline treatments of the sugar palm fiber (SPF) on the dielectric properties of the phenolic (PF) composites. The dielectric study was performed using the broadband dielectric spectroscopy (BDS), covering the temperature range of the molecular and high-temperature relaxation processes and over the frequency range from 0.1Hz to 0.1MHz. Our analysis suggests that interfacial adhesion in the case of alkaline treated composite is higher than those of untreated and sea water treated composites. It was shown that dielectric permittivity and dielectric loss factor were decreased when adding alkaline treated SPF in PF matrix indicating that we have a good adhesion between the reinforcement (SPF) and the matrix. Whereas, dielectric relaxation strength increases after sea water treatment.

Characterizations and properties of poly (acrylonitrile-co-2,2,2-trifluoroethylmethacrylate) copolymer/organomodified Moroccan Beidellite clay lamellar structure nanocomposites

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Aiming to develop new dielectric nanocomposites containing CN and F groups with strong dipole moments, the nanocomposites based on acrylonitrile-co-2,2,2 trifluoroethylmethacrylate and CTA-BDT (lamellar structure) nanoclay was successfully prepared by in situ radical polymerization with different weight percentages (1 %, 2 % ,3 % and 5 %) of CTA-BDT. Using the Broadband Dielectric Spectroscopy (BDS), the nanocomposites were dielectrically characterized over a frequency range from 10^{-1} to 10^{6} Hz, and in a temperature range from 293(K) to 373(K) . For the matrix , the real part ε' and the imaginary part ε'' of the dielectric permittivity curves disclosed three dielectric process which are : β , α and ionic conduction phenomenon . The addition of nanoclay generated addiotional relaxation process which named Maxwell –Wagner- Sillars (MWS) polarization and affect the ionic conduction. According to the dielectric results ,three major sections will be studied. Firstly, the glass transition temperature for each composite will be evaluated using the Vogel–Fulcher-Tammann–Hesse (VFTH) law fit. Secondly, the fragility of the composites will be estimated (deviation from the Arrhenius law). Finally, the matrix/CTA-BDT interface properties will be investigated (calculation of the dielectric strength Δε and the activation energy of MWS polarization) to identify the most reliable composite in the field of application.

Bionanocomposites based on biodegradable aliphatic polyesters / beidellite Moroccan clay prepared by in situ polymerization: Structures and dielectric properties

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Beidellite (BDT) minerals, extracted from Moroccan clay, were used as a reinforcing agent for Polybutylene succinate biopolymers (PBS). Investigation of electric properties of (PBS) and its nanocomposites was carried out by means of dielectric spectroscopy. The measurements took place on a wide range of temperature [-50°C-90°C] and frequency [0.1 Hz-1MHz]. The obtained results highlighted different segmental dynamics as well as the mechanisms of conductivity for various amounts of nanofillers. Interfacial dynamics were also considered as one of the major phenomenon while interpreting the variation of distinct electrical quantities (dielectric primitive, conductivity… etc) whether in isochronal or isothermal spectra.

Preparation and Characterization of Nanocomposite films based PVA for Fuel Cell Application

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Over recent years, an important interest was giving to the proton conducting polymers owing to their potential uses in different areas of science and technological applications like batteries, sensors, fuel cells, solar cells. Among these polymers, the Poly (vinyl alcohol) (PVA) has been widely used for electronic applications in the reason of their interesting properties.

In this framework, this present work deals firstly with the study of structural, thermal, and dielectric properties of polyvinyl alcohol (PVA) films by varying the molecular weight (Mw) and the hydrolysis degree (HD). Indeed, the XRD analysis showed the improvement of the crystallinity degree by the enhancement of HD or the decrease of Mw. In addition, the dielectric measurements revealed different dielectric processes attributed to electrode/ sample polarization, αa-relaxation, αc-relaxation, and β-relaxation. Based on this study, our choice for low-cost electrolytes will be directed to the PVA based nanocomposites with high hydrolysis degree and low molecular weight.

In this context, nanocomposite polymer films based polyvinyl alcohols with different weight ratios of nanoparticles TiO_2 were prepared secondly with the aim of enhancing the dielectric properties of PVA. In fact, the SEM analysis showed that TiO2 nanoparticles were well dispersed in the PVA matrix below 30 wt % where aggregates were found to be observed. Infrared spectroscopy evidenced the presence of interactions between the PVA and TiO_2. Dielectric permittivity and loss tangent reveal seven relaxation processes ascribed to electrode polarization, conduction phenomena, Grain–Boundary–Relaxation, MWS relaxation, and (αa, αc and β) relaxations. The activation energy values Ea associated with DC conductivity confirm the protonic type of the conductivity and present a lower value for the PVA with 5% amount of TiO_2.

Dielectric and electric properties of poly (ε-caprolactone)/ organomodified clay bionanocomposites prepared in open air by *in situ* polymerization

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Dielectric and electric properties of bionanocomposites based on poly (ε-caprolactone) (PCL) in the presence of a commercial organomodified montmorillonite clay (MMT-ODA) at different concentrations PCL/ MMT-ODA were investigated by broadband dielectric spectroscopy (BDS) in the frequency range from 1Hz to 1MHz and in the temperature range from -100 to 25°C. The originality of the work is that the polymerization was carried out in open air by using titanium alkoxide as a catalyst. Due to the semicrystalline nature of PCL, the higher number of modes and its overlap, the relaxation patterns observed in dielectric spectra measured are complicated. These relaxation data were modeled using the H-N empirical equation with the contribution of the conductivity. The local dynamics of PCL are unaffected by the increase of nano-clay amount, in agreement with DSC values of glass transition temperature. The PCL/MMT-ODA 3wt% showed the lowest value of the dielectric strength, indicating the strongest adhesion between PCL matrix and organo-modified clay. While for PCL/MMT-ODA 5 wt%, the presence of agglomerate makes the adhesion between PCL and MMT-ODA very weak, in good agreement with FTIR analysis. The Jonscher’s law was used to analyze the electrical conductivity of PCL. To interpret the ac conductivity mechanism, the exponent s values give evidence for several models.

Dielectric relaxation study on nanocomposite of polyurethane based on polycaprolactone with nanowhiskers cellulose

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In this work, we present a study on nanocomposite pure polyurethane (PU) films based on polycaprolactone diol to molecular weight of 4000 g/mol (PCL_{4000}) reinforced with cellulose nanocrystals or nanowhiskers (NCC/CW) extracted from the rachis of date palm tree. The thermal and dielectric properties of nanocomposite films have been studied using differential scanning calorimetry (DSC) and dielectric relaxation spectroscopy (DRS). The thermal study give us information on the glass transition temperature (T_g) which is of the order of -55 ° C for the pure polyurethane matrix (PU) and clearly indicates changes during the addition of cellulose nanowhiskers (CW). Broadband dielectric spectroscopy was used to study the dielectric properties of PU and nanocomposites over a wide frequency range of 10^{-1} to 10^{6} Hz and in the temperature beach of -100 °C to 40 °C. The dielectric relaxation processes associated with different molecular motions and the conductivity phenomena are discussed and related to the content of cellulose nanowhiskers (CW). The α, α_c and β relaxations are probably associated with (i) glass transition temperature (ii) molecular motions in crystalline phase (iii) reorientational motions of water molecules. The micro-phase separated morphology associated with soft and hard domains is reflected in the dielectric spectra, at high temperatures (low frequencies), by the presence of the Maxwell-Wagner-Sillars (MWS) interfacial polarization process.

Non-Invasive Monitoring of Red Blood Cells in Blood Banks

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Maintaining an appropriate inventory of packaged blood products is critical, and so is monitoring the quality of stored red blood cells (sRBC) in blood banks. Hydration of red blood cells (RBC) is controlled by factors such as RBC age, osmolarity, mechanical stress, and pathological conditions. At the same time regulation of ion and water content itself is a parameter defining the functionality of RBC and their lifespan. Pathological alterations in hydration state related to aging, mutations in cytoskeletal protein components, ion channels or hemoglobin (Hb) are associated with dramatic reduction RBC longevity. sRBC undergo these aging processes during storage, and are collectively called storagelesions. Our study aims to gauge the effect of storage lesions on the dielectric response of the packaged suspensions of leukofiltrated RBC stored under 4°C in SAGM solution. We present a comprehensive broadband (1 MHz - 40 GHz) study of the lesion kinetics which includes spectroscopy of the processes linked to deformations of the cellular membrane (β-dispersion), and of the cytoplasmic water in sRBC (γ-dispersion), during 35 days of storage. For a qualitative characterization of the storage lesions, we measured the deformability of fresh and stored RBC as expressed by their elongation ratio (ER) achieved under a shear stress of 3.0 Pa; this method is a gold standard for characterizing RBC vitality. The extracted dielectric parameters are sensitive to the age of the cells and, in particular, to the critical moment of transition from discocyte to echinocyte. Analysis of the dielectric relaxation as a function of storage duration revealed alteration in the delicate interplay between bound and bulk water in the cellular interior of the cells during storage. We hypothesized that these changes modulated by alteration of Hb state. Our results open a possible new avenue for the noninvasive inspection of stored red blood cells, permitting a true inventory system for the modern blood bank.

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Dielectric relxation of hydarted water in microcrytalline cellulose of different origin

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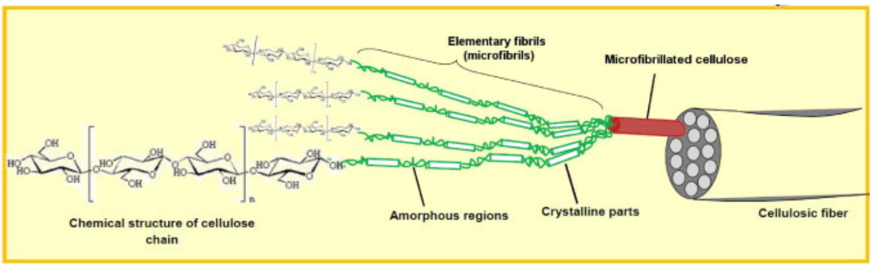

Fig.1.Details of the cellulosic fiber structure with emphasis on the cellulose microfibrils [1].

Today cellulose is the most common renewable polymer, and its use for the functional composite materials is an emerging task. The type of the source material affects the morphology and properties of the final product due to the presence of different non-cellulose components such as lignin or hemicellulose. However, despite the importance and numerous studies, dielectric properties of microcrystalline cellulose of various origins are still remains unclear [2,3]. Mechanisms of dielectric relaxation should be clarified in such systems in terms of dissimilarities in the morphology of specimens.

In this work, the results of dielectric measurements of hydrated micro cellulose films of various origin (cotton, linen, wood) with different levels of hydration are presented. Measurements are carried out in a wide frequency (10^{-2} -10^{6} Hz) and temperature (138 -250K) ranges. Three types of different relaxation processes were observed for all the studied samples depending on the hydration level. Based on the dielectric relaxation and existence of critical points in its temperature behavior we can assign one of the processes with the interface water on the porous surface in a glassy state. At high hydration levels, a relaxation of bulk ice can be considered. Other relaxation processes are probably related to the presence in the structure of micro fibril lignin and hemicellulose.

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A combined study of modulated calorimetry and dielectric spectroscopy on freeze-dried solvated proteins

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We present a comparison of Broadband Dielectric Spectroscopy (BDS) and Temperature Modulated Calorimetry (TMC) studies of dynamics in freeze-dried, de-hydrated, binary mixtures of lysozyme and excipients. The latter have been selected among hydrogen bonding glass-formers, with different viscosity and molecular mass, spanning more than 150 K in glass transition temperatures T_g. We followed measurement methods and analysis protocols shown in recently published enlightening BDS and TMC studies of hydrated or solvated proteins [1-3].

Beyond interfacial relaxation and Maxwell–Wagner (MW) polarization effects that are present in freeze-dried powder samples, we found the ubiquitous existence of a relaxation process in vicinity of the glass transition temperature of the system. It has a Vogel-Fulcher-Tamman temperature behavior, it is strongly influenced by the type of solvent and it share the same timescale of the process, revealed by calorimetry, that brings the system to vitrify.

Being BDS and modulated calorimetry data related to different observables, the information on this relaxation process coming from both techniques is invaluable. In particular, we compared, using the two techniques, for the mixtures and the pure solvents: the distribution of relaxation times, the static quantities (heat capacity step, dielectric strength), the temperature dependence of relaxation times.

A complex scenario emerges, where the effects of “solvent-slaving” and nanoconfinement play a different role.

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Local dynamics in monohydroxy alcohols: New insights with triplet state solvation dynamics

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The relaxation behavior of hydrogen-bonded liquids, especially of monohydroxy alcohols, is a long-standing topic [1]. There is an ongoing debate on the microscopic origin of the so-called Debye process showing a prominent peak in dielectric spectra. The recently proposed model of transient chains [2] linking the Debye process to an average end-to-end dipole vector reorientation seems to be a promising explanation.

Now an interesting question is whether information about those transient supramolecular structures can be gained by investigation with a *local* measurement technique.

By means of the triplet state solvation dynamics (TSD) technique, it is possible to gain local insight into the relaxation dynamics [3]. In TSD a dye is dissolved at low concentration in the sample and is excited followed by an intersystem crossing into the metastable long-lived triplet state by a UV laser pulse. Due to the relaxation of the surrounding solvent molecules, the phosphorescence spectrum of the dye is modified over time. These changes can be quantified by calculating the Stokes shift from the spectra in a range from milliseconds up to seconds revealing the local relaxation of the solvation shell. Depending on the dipole moment change of the dye on excitation, a local dielectrical or mechanical experiment can be performed [3, 4].

With our improved experimental setup [5] we extend the existing TSD data of the monohydroxy alcohol 1-propanol [4], measure 5-methyl-2-hexanol and compare our data with data from dielectric spectroscopy and depolarized light scattering [6, 7]. Thereby, we gain insight into α, β and the Debye process from a local point of view. Consistent with the model of transient chains and contrary to previous conclusions [4], one of our results shows that the dynamical signature of the Debye process only weakly contributes to the local Stokes shift correlation function.

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Probing the Dielectric-Debye-Process in Monohydroxy Alcohol 5-Methyl-2-Hexanol by Depolarized Light Scattering

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While the Debye relaxation previously was mainly considered as a dielectric phenomenon, its signature was recently reported to also appear in the shear modulus and many features were explained by a model of transient chains, which form due to H-bonding. Considering that background one would also expect a signature of this transient chain formation to be visible in depolarized dynamic light scattering (DDLS), which also probes molecular orientational dynamics. However, although Debye-like processes were recently reported in several DDLS experiments, in the case of monohydroxy alcohols a Debye like contribution has been elusive so far.

Recent improvments of the DDLS technique [1] enable us to present the reorientational dynamics of 5-methyl-2-hexanol not only with dielectric spectroscopy but also whith DDLS in the supercooled regime. While in a previous study of a primary alcohol no indication of the Debye peak in the DDLS spectra was found [2], we now for the first time report clear evidence of a Debye contribution in a monoalcohol in DDLS [3]. A quantitative comparison between the dielectric and DDLS manifestation of the Debye peak shows that in DDLS it is slightly faster and weaker by two orders of magnitude. Moreover, it is significantly broadened in DDLS, while α-and β-relaxation are basically identical in both methods. All of these observations indicate that while the Debye process in BDS represents fluctuations in the end-to-end vector dipole moment of the transient chains, DDLS locally probes residual correlations which occur due to a slight anisotropy of the α-relaxation caused by the chain formation.

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The effect of organic co-solutes on local water structure and dynamics

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We investigate the effect of the organic co-solutes ectoine, trimethylamine N-oxide (TMAO), urea, and guanidinium chloride (GdmCl) on water dynamics by means of Molecular Dynamics (MD) simulations at different, low co-solute concentrations (0 - 2mol/l). In our analyses, we compute dielectric spectra [1] as well as hydrogen bond (HB) numbers and life times [2], and assess the structural tetrahedrality of water using two different order parameters [3]. Our spectroscopic data are compared to experimental measurements, thereby validating the employed MD force fields (see also [4]).

Our findings exhibit distinct effects for protein stabilizers and denaturants, complementing previous experimental findings [5].

For the protein stabilizers ectoine and TMAO, we observe significantly slowed-down bulk-water dynamics, whereas the effect of urea is much weaker, and GdmCl does not alter the bulk-water dielectric relaxation time. The tetrahedral structure of water, however, is perturbed by ectoine and TMAO to a certain extent, while urea shows almost no disturbance. Surprisingly, even though GdmCl does not affect water dynamics much, it affects tetrahedral order the most. Hydrogen bond (HB) life times strongly increase with rising ectoine or TMAO concentration, while this effect is much weaker for the denaturants urea and GdmCl. Even though the tetrahedral water structure and sphericity is disturbed by the protecting osmolytes, we observe a pronounced strengthening of the structure in terms of dynamics.

Our findings indicate that changes in water structure alone provide a rather ambiguous picture, while changes in dynamics might allow a distinction between possible water structure-breaking or -making behavior.

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Fractional Power Dielectric Loss Spectra Observed in the Composite of "Ideal" Conductor and Insulator

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Dielectric loss in lowest frequency regime generally shows dc-conductivity which follows $\varepsilon''{\sim}\omega^{-1}$. On the other hand, dielectric loss following fractional power law ($\varepsilon''{\sim}\omega^{-\nu}$) is also seen in a variety of complex solids, such as ceramics, ice, polymers, and glasses. Especially the power law behavior with ν close to zero is called near constant loss (NCL) and it is often found in vitrified liquids.

Despite the numerous efforts, a general principle of the fractional power law is still mystery. Since materials studied so far mostly composed of complicated components, effects from complex dynamics within the component materials and that from complex conduction pathway due to intricate structure were not disentangled. In order to understand the latter effect, we examined the composite of ideal conductor and ideal insulator in which each component is treated as conventional resistor or capacitor component.

We use carbon fine powder as the ideal insulator and paraffin as the ideal insulator. It is expected that complex dynamics such as side-group dynamics, grain boundary effect, and complex ionic hopping motion do not appear in these components.

We found that dielectric loss spectra of carbon-paraffin composites showed fractional power law behavior in a wide composite ratio around its percolation threshold. Obtained exponents ν were in the range 0.1 – 0.6. Especially NCL behavior is seen at low carbon fractions. This result highlight that even only the effect of complex conduction pathway can cause power low dielectric loss spectrum.

Charge carrier localization in doped polyaniline composite with polyacrylic acid and bentonite

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Temperature dependence of complex conductivity of polyaniline-dodecylbenzene-sulfonic acid and its composite with polyacrylic acid and bentonite clay have been investigated using terahertz-time domain spectroscopy. Using Drude-Smith model we observed that charge carriers in polyaniline composites become more localized (insulating) with increasing charge carrier density [1, 2]. The relaxation time also decreased when charge carrier density was increased. The nonlinear changes are attributed to multiple scattering mechanisms [1-3] intrinsic to polyaniline and interaction with polyacrylic acid and bentonite. We observed that increasing temperature decreases the charge carrier density. The introduction of polyacrylic acid after polymerization of doped polyaniline resulted in significant decrease in the temperature profiles of the scattering rate, plasma frequency, and charge carrier density compared to doped polyaniline. Partial delocalization and mobility, on the other hand, were found to increase. These effects of polyacrylic acid are attributed to its electron-donating capability and its electrostatic interaction through the carboxylic group [6]. Polyacrylic acid also acted as stabilizer of doped polyaniline in aqueous dispersion. Effect of bentonite in the conduction properties depends on the amount and order of its introduction into the solution. Generally, the introduction of bentonite decreased the conduction properties of the polymer composite. Both polymers are involved in bentonite intercalation as seen from XRD data. Hydration of bentonite also played an important role in charge carrier localization at terahertz range. All samples show dc conductivities linearly dependent on temperature contrary to the prediction by the variable range hopping model [3].

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Charge Transport and Molecular Orientation in P3HT as model semiconducting Polymer

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Conjugated semiconduting polymers have obtained significant attention, due to their soft matter properties such as flexibility and convenient adaption of shape joint with semiconducting characteristics, which allow their application in organic field effect transistors or solar cells, for instance. [1] Because the devices' macroscopic properties arise from the materials' molecular organization, detailed understanding of the microscopic structure is essential for targeted developments.

In order to analyze the charge transport and molecular organization in thin films of the model polymer *poly(3-hexylthiophene)* (P3HT) the experimental techniques of *broadband dielectric spectrsocopy* (BDS) and *infrared transition moment orientational analysis* (IR-TMOA) are combined. On the basis of the former the DC-conductivity and its temerpature and frequency charateristics are revieled. [2] In the case of the latter the spectral absorption is recorded depending on the polarization of the IR light *and in addition* on the inclination of the sample film relative to the propagation direction of the incident light. This enables to determine the three dimensional tensor of absorption and hence the spatial orientation and order of particular molecule segments. [3,4]

As a consequence of thermal annealing the DC-conductivity drops which reflects structural re-organization into a more edge on alignment of the thiophene rings in the polymer backbone and the aliphatic side chains pointing in the direction of the electrical field. Thus, the. charge transport along the *out-of-plane direction* is hindered, whereas a general increase is published regardless of the directionality. [5]

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Maxwell-Wagner-Sillars interfacial polarization in composite materials: characteristic frequencies and scaling laws

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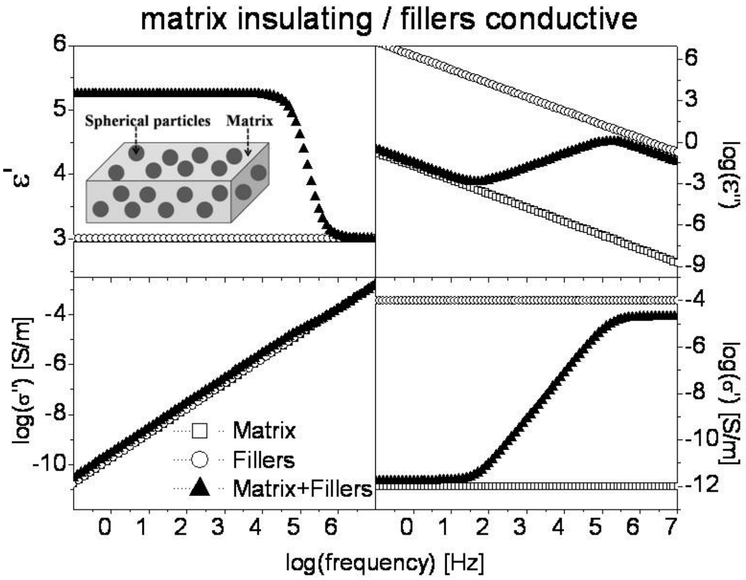
A general strategy to enhance the electrical performance of polymeric materials represents the composite approach, when fillers of different morphologies, sizes and electrical properties are embedded into a polymer matrix. The resulting macroscopic properties of the composite material depend on the volume fraction and the spatial distribution of the fillers as well as on their interaction with the polymeric material. The current contribution aims to develop a complete theoretical description of the Maxwell-Wagner-Sillars interfacial polarization in multiphase composite materials in systematic dependence on morphology, volume fraction, form factor, orientation, volume distribution of the fillers and interphases. Three scientific challenges are addressed: (a) Understanding the impact of internal interfaces and interphases on the dielectric response of composite materials; (b) Detailed quantitative analysis of the impact of heterogeneity on the spectral dependence of existing molecular relaxation processes; (c) To develop and propose a criterion which enables one to distinguish, in the case heterogeneous materials, true relaxation processes from dielectric dispersions caused by the phenomenon of interfacial polarization.



Electrode polarization process in imidazolium-based ionic liquid crystals

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Ionic liquids have attracted a strong interest because of excellent physical properties including low melting point, almost no vapor pressure, incombustibility, high ion density, and high ionic conductivity. Ionic liquid crystals have anisotropy and can be expected to be applied for new electrical device developments. In this study, salts of imidazolium group and tetrafluoroboric acid, $[C_{16}mim]BF_4$, which exhibit liquid crystal phase, were investigated using BDS. In previous studies, dielectric relaxation measurements show that two kinds of relaxation processes are observed in $[C_{16}mim]BF_4$; one is considered as the α process due to the molecular motion of alkyl-chains and the other is electrode polarization process (EP process) due to charge carrier motion [1]. During the cooling process, $[C_{16}mim]BF_4$ changes from a smectic phase (Sm phase) to a higher-ordered smectic phase at lower temperature through a supercooled Sm phase [1]. Here, the latter phase is called as the low-temperature smectic (LtSm) phase. In this study, BDS measurements have been performed for $[C_{16}mim]BF_4$ in order to elucidate whether the origin of the observed relaxation process can be really assigned to the EP process and, furthermore, to evaluate the dynamics in the LtSm phase. For this purpose, we measured the dependence of relaxation time and strength of the process on the distance between electrodes, *d*, because a standard theory of the EP-process predicts the strong *d*-dependences of the time and the strength. Furthermore, the BDS and X-ray scattering measurements have been done during the ramping processes in order to investigate the temperature change in the dynamics of the EP process and α process and the change in structure, through the phase transition.

As a result, it was confirmed that both relaxation time and strength are proportional to the distance between the electrodes. Hence, it was found that the observed relaxation process is EP process due to charge carriers. In our poster, the effect of molecular orientation on the dynamics of the EP process and α process will also be discussed.

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DC bias assisted negative permittivity of a magnetic nanofluid based on transformer oil

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Magnetic nanofluids (MNF) are colloidal suspensions of magnetic nanoparticles (MNP) in a liquid carrier. Those based on transformer oils constitute an attractive cooling and insulating medium for electrical power apparatus. Besides the enhanced heat transfer, the dispersed MNP can increase the electric breakdown field strength of transformer oils [1]. This phenomenon is probably associated with charge trapping on the nanoparticles and resulting streamer propagation velocity reduction [2]. Moreover, it is known that the permittivity of MNF is controllable by external magnetic fields. The resulting effect of magneto-dielectric anisotropy originates in the MNP assembly formation induced by the applied magnetic field [3]. The particle assembly in MNF can be induced even by a DC electric field [4]. Then, analogously to the magneto-dielectric effect, a question arises concerning the effect of the DC bias electric field on the nanofluid permittivity in a wide frequency range. In this paper, we present dielectric spectra (1 mHz – 1 MHz) measured on a transformer oil-based MNF at various temperatures. Electrode polarization and an interfacial relaxation process are analyzed. We show that the applied DC bias voltage results in permittivity sign switching at low frequencies. The critical frequency depends on the nanofluid temperature and the DC voltage level. We describe a mechanism leading to the observed phenomenon and propose its utilization in the study of nanofluid selfassembly.

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Conductivity percolation and electrochromic properties in carbon nanotube/poly(pyridinium triflate) composites

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Electrochromic polymers represent the class of smart materials that are capable of modulating their absorption spectrum after the application of external potential. These systems are intensively studied due to a number of promising applications in various fields, such as smart windows and other optoelectronic devices [1]. One of the proposed methods to obtain enhanced properties is the formation of electrochromic composites with carbon nanotubes (CNTs) [2]. The incorporation of nanotubes promises significant improvement of the charge transport in polymer systems due to the excellent electronic properties of the CNTs. Our research is devoted to the study of the electrochromic properties and electrical percolation behavior of the composite material based on poly(pyridinium triflate) (PV) and MWCNTs with different PV and MWCNT concentrations. Noncovalent interaction between polymer and CNTs allows to obtain stable dispersion of CNTs, which in turn affects the charge transport properties of polymer.

The improvement of electrochromic properties is demonstrated by the hysteresis decrease between the redox peaks and by the advanced switching kinetics between the redox states of electrochromic PV. Conductivity measurements demonstrate an increase in the electronic conductivity of PV/MWNTs composite films by 5 orders of magnitude in comparison with pure PV films. It is found that the electrical percolation threshold occurs above 0.3% and 0.4% MWNTs for PVs of concentrations 5 mg/ml (PV5) and 8 mg/ml (PV8) respectively. Corresponding critical exponents t were found to be be 2.8 ± 0.4 for PV5 and 3.1 ± 0.3 for PV8. The t values are close for both PV concentrations and are higher than the "universal" one (t=2). The "non-universal" percolation behavior can be explained by changes in conductivity properties at tube-tube contacts [3]. We can suppose that interaction between polymer and MWCNTs results in the formation of non-random composite structure.

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New superprotonic crystals with dynamically disordered hydrogen bonds: conductivity studies

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Single crystals $(K_{1-x}(NH_4)_x)_mH_n(SO_4)_{(m+n)/2}\cdot yH_2O$ are of special interest for their unique properties, especially high proton conductivity. This makes them promising materials for various electrochemical devices, including proton exchange membranes in fuel cells [1]. One specific feature of this class of hydrogen-containing compounds is the partial or complete disordering of hydrogen bonds at phase transitions, which leads to high proton conductivity close to that of the melts of these salts (10^{-3}–10^{-1} S/cm). These crystals are grown in $K_3H(SO_4)_2$–$(NH_4)_3H(SO_4)_2$–H_2O system which end members are known to undergo superprotonic phase transitions with essentially different kinetics. The use of $K_3H(SO_4)_2$ and $(NH_4)_3H(SO_4)_2$ solutions with a K:NH_4 concentrations ratio 3:7-1:9 led to growth of single crystals of the same structure type as the high-temperature superprotonic phase of $(NH_4)_3H(SO_4)_2$ [2].
The aim of this study was to investigate the new single crystals grown from solutions with K:NH_4 concentrations ratio 3:7, 2:8, 1:9 by means of dielectric spectrosopy in wide frequency and temperature range (0.1 Hz – 10 MHz, 223 – 353 K). AC conductivity data were analyzed within complex dielectric permittivity and electic modulus formalisms. Investigations revealed high values of conductivity of grown crystals comparable with conductivity of known superprotonic compounds at high temperatures, and an anomaly corresponding to a transition to the phase with low conductivity upon cooling.

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Electrophysical properties of doped ferroelectric films

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Ferroelectric polymers based on vinylidene fluoride (VDF), due to their specific properties and biocompatibility, are widely used in technology and medicine [1-4]. One of the applications of dye-doped PVDF is an "optode", which allows to detect a change in the absorption or luminescence spectrum of a material under the action of external reagents in a clinical analysis.

In this paper, changes of the electrical properties of VDF copolymer with hexafluoropropylene (HFP) are studied when porphyrin dye -tetraphenylporphyrin (TFP) - is introduced into it. It was found that even at a TFP concentration 0.005 wt. %, the dc conductivity σ_{dc} increases by more than an order of magnitude. This is accompanied by a shift of the dielectric dispersion associated with the Maxwell-Wagner polarization by two orders of magnitude into higher frequency region. An analysis of the temperature dependence of σ_{dc} shows that for both films there are several temperature regions where the data follow Arrhenius laws with different activation energies. DSC data show that the temperatures where the activation energy changes fall on the main region of crystal melting (in both films) and melting of the secondary crystals (in doped film). It is concluded that the TFP is located in amorphous regions and promotes the formation of secondary crystals increasing their fraction by 30%.

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