Online IDS 2021 Workshop

International Dielectric Society

Organizers:

Silvina Cerveny, Catalin Gainaru, Ranko Richert

Workshop dates - September 6 – 9, 2021

WHAT WILL WE FIND AT IDS-2021 online Workshop?

• Eighteen lectures (30 minutes) will be given by Invited Speakers. The lectures will be recorded and available the day after.

• Thirteen short talks (15 minutes) will be given by Young researchers. The lectures will be recorded and available the day after.

• Poster sessions will be continuously open. Exchange of ideas with the presenting author will be possible in the dedicated forums.

• During the break, interaction among the participants will be promoted, through a live chat: if you just want to meet other participants and live chat with them during the break, this is your choice.

• The chat room will be open from (UTC+2) 10:00h to 18:00h, such that you can live communicate there with colleagues and e.g. discuss about your posters… also before and after the lectures.

PROGRAM

SEPTEMBER 6th, 2021 (Monday)

Phoenix (UTC-7)	Washington (UTC-5)	S. Sebastian (UTC+2)	PROGRAM
06:30-06:40	08:30-08:40	15:30-15:40	**WELCOME – Ranko Richert**
			PHYSICAL AGING - CHAIR :
06:40-07:10	08:40-09:10	15:40-16:10	**Birte Riechers.** Direct proof of the existence of a material time in physical aging
07:10-07:40	09:10-09:40	16:10-16:40	**Karolina Adrjanowicz.** Physical ageing, rejuvenation and memory effects studied in nanopore-confinement
07:40-08:10	09:40-10:10	16:40-17:10	**Tina Hecksher.** Time scale ordering in supercooled liquids.
08:10-08:25	10:10-10:25	17:10-17:25	**Farnaz Emamverdi.** Molecular mobility and physical aging of polymers with intrinsic microporosity (PIM-1) revisited: A big glassy world
08:25-08:45	10:25-10:45	17:25-17:45	**Break - 25min**
			DIELECTRIC SPECTROSCOPY COMBINED WITH OTHER TECHNIQUES - CHAIR :
08:45-09:15	10:45-11:15	17:45-18:15	**Jan Swenson.** Mechanism of disaccharide-induced protein stabilization from broadband dielectric spectroscopy and neutron scattering
09:15-09:45	11:15-11:45	18:15-18:45	**Michael Vogel.** Combining BDS with NMR and MDS studies to disentangle complex relaxation patterns of hydrogen-bonded liquids in silica and protein confinements
09:45-10:15	11:45-12:15	18:45-19:15	**Riccardo Casalini.** Dynamics of physical networks studied by dielectric and mechanical spectroscopy
10:15-10:30	12:15-12:30	19:15-19:30	**Till Böhmer.** The origin of the apparent slow solvent dynamics in binary mixtures

SEPTEMBER 7th, 2021 (Tuesday)

Phoenix (UTC-7)	Washington (UTC-5)	S. Sebastian (UTC+2)	PROGRAM
			HYDROGEN BONDED AND BIO-SYSTEMS - CHAIR :
06:30-07:00	**08:30-09:00**	**15:30-16:00**	**Larisa Latypova.** The balance between bulk and bound water in methemoglobin solutions: Dielectric spectroscopy study
07:00-07:30	**09:00-09:30**	**16:00-16:30**	**Airat Khamzin.** The microscopic model of dielectric relaxation of ice with impurities.
07:30-07:45	**09:30-09:45**	**16:30-16:45**	**Lara Röwekamp.** Predicting dielectric properties of deeply supercooled pharmaceutical liquids from shear rheology
07:45-08:00	**09:45-10:00**	**16:45-17:00**	**Jorge H. Melillo.** Dynamics crossovers in the fast water relaxation in solutions of biological and non-biological solutes
08:00-08:15	**10:00-10:15**	**17:00-17:15**	**Cindy Galindo.** Role of water in the response to glucose uptake in red blood cells; is it specific?
08:15-08:45	**10:15-10:45**	**17:15-17:45**	**Break - 30 min**
			CHARGE TRANSPORT AND RELAXATION PHENOMENA - CHAIR :
08:45-09:15	**10:45-11:15**	**17:45-18:15**	**Philipp Münzner.** The relation between charge and mass transport in coupled and decoupled conductors
09:15-09:30	**11:15-11:45**	**18:15-18:45**	**Ciprian Iacob.** Correlating ionic conductivity and nanoscale morphology of polymerized imidazolium-based ionic liquids
09:30-09:45	**11:45-12:00**	**18:45-19:15**	**Florian Pabst.** The generic alpha relaxation in supercooled liquids

SEPTEMBER 8th, 2021 (Wednesday)

Phoenix (UTC-7)	Washington (UTC-5)	S. Sebastian (UTC+2)	PROGRAM
			DIELECTRIC TOPICS - CHAIR:
06:30-07:00	**08:30-09:00**	**15:30-16:00**	**Simone Capaccioli**. Space-time heterogeneity of Johari-Goldstein β-relaxation in supercooled and glassy systems and its relation to α-relaxation dynamics
07:00-07:30	**09:00-09:30**	**16:00-16:30**	**Thulasinath Raman Venkatesan**. Non-linear dielectric spectroscopy for detecting and evaluating structure-property relations in a P(VDF-TrFE-CFE) relaxor-ferroelectric terpolymer
07:30-07:45	**09:30-09:45**	**16:30-16:45**	**Wenkang Tu**. Effect of high electric field on the kinetics and product properties of free radical polymerization of 2- hydroxylethyl methacrylate initiated by 2, 2'- azobisisobutyronitrile
07:45-08:15	**09:45-10:15**	**16:45-17:15**	**Erik Thoms**. A new experimental approach to the field dependence of the static dielectric constant
08:15-08:45	**10:15-10:45**	**17:15-17:45**	**Break - 30min**
			NANO/COMPOSITES / CONFINEMENT - CHAIR:
08:45-09:15	**10:45-11:15**	**17:45-18:15**	**Daniel M. Tong.** Local measurements of molecular dynamics and transport properties in polymer thin films
09:15-09:45	**11:15-11:45**	**18:15-18:45**	**Malgorzata Jasiurkowska-Delaporte.** Molecular dynamics and crystallization of smectic liquid crystals under hard and soft confinement
09:45-10:00	**11:45-12:00**	**18:45-19:00**	**Anna Z. Szeremeta.** The reversible dielectric switching at ambient and high pressure conditions in selected hybrid perovskite structure
10:00-10:15	**12:00-12:15**	**19:00-19:15**	**Jan Philipp Gabriel.** Polyamorphism in vapor-deposited 2-methyltetrahydrofuran: A broadband dielectric relaxation study

SEPTEMBER 9th, 2021 (Thursday)

Phoenix (UTC-7)	Washington (UTC-5)	S. Sebastian (UTC+2)	PROGRAM
			POLYMERS I- CHAIR:
06:30-07:00	**08:30-09:00**	**15:30-16:00**	**Koji Fukao.** Dielectric relaxation and glassy dynamics in poly(diisopropyl fumarate) and its copolymers
07:00-07:15	**09:00-09:15**	**16:00-16:15**	**Tiberio Ezquerra.** Relaxation behavior and free volume of bio-based poly(trimethylene terephthalate)-block-poly(caprolactone) copolymers as revealed by broadband dielectric and positron annihilation lifetime spectroscopies
07:15-07:30	**09:30-09:45**	**16:15-16:30**	**Numera Sahfqat.** Calculating the calorimetric glass transition trace of simplified industrial polymer mixtures from the neat components and the modeling of dielectric relaxation
08:15-08:45	**10:15-10:45**	**17:15-17:45**	**Break - 30min**
			POLYMERS II - CHAIR:
07:30-08:00	**09:30-10:00**	**16:30-17:00**	**Mohamed Kolmangadi.** Molecular dynamics of Janus polynorbornenes: Glass transitions and nanophase separation
08:00-08:15	**10:00-10:15**	**17:00-17:15**	**Panagiotis Kardasis.** Layers of distinct mobility in densely grafted dendrimer arborescent polymer hybrids
08:15-08:30	**10:30-10:30**	**17:15-17:30**	**Angelika Wrzesińska.** Molecular dynamics of poly(dimethylsiloxane) coordinated by metal-ligand complexes.
08:30-08:45	**10:30-10:45**	**17:30-17:45**	**CLOSING**

POSTERS

1. Roksana Winkler, Wenkang Tu, Lukasz Laskowski, Karolina Adrjanowicz
The Influence of surface polarity on the segmental dynamics of poly(phenyl methyl siloxane) confined in alumina nanopores**.**

2. Daniel Duarte, Ranko Richert, Karolina Adrjanowicz
How AC Electric Field Frequency Influences the Crystallization of a Molecular Liquid

3. Claudia Borredon, Luis A. Miccio, Anh D. Phan, Gustavo A. Schwartz
Estimating molecular relaxation dynamics of amorphous drugs based on their chemical structure: a numerical and theoretical approach.

4. Katarzyna Chat**,** Wenkang Tu, Aparna Beena Unni, and Karolina Adrjanowicz
Effects of Polymer Tacticity on the Segmental Dynamics of Poly(methyl methacrylate) (PMMA) under Elevated Pressure and Geometrical Nanoconfinement

5. Yael Beilinson, Anna Greenbaum (Gutina), Jiri Prusa, Tatiana Antropova, Yuri Feldman
The nature of low-temperature relaxation crossover of water in confinement

6. Shinian Cheng, Małgorzata Musiał, Zaneta Wojnarowska, Marian Paluch
The role of entropy in the description of the relaxation dynamics of ionic liquids

7. Yuima Kawatani and Ryusuke Nozaki
Dielectric α-relaxation of supercooled sugar alcohols near the glass transition temperature

8. Beibei Yao, Z. Wojnarowska, M. Paluch
Effect of aromaticity on molecular dynamics of glass-forming liquids

9. Antonela Ananiadou, George Papamokos, Martin Steinhart, and George Floudas
Effect of Confinement on the Dynamics of Monohydroxy Alcohols

10. Chien-Hua Tu, Hans-Jürgen Butt, George Floudas
In Situ Monitoring the Imbibition and Adsorption Kinetics of cis-1,4-Polyisoprene in Nanopores by Nanodielectric Spectroscopy

11. Marianna Spyridakou, Manos Gkikas, Martin Steinhart, George Floudas
Effects of nanometer confinement on the self-assembly and dynamics of Poly(γ-benzyl-L-glutamate) homopolymers and its copolymers with polyisobutelene

12. Pipertzis, A., Papamokos, G., Sachnik, O., Allard, S., Scherf, U., Floudas, G.
Ionic Conductivity in Polyfluorene-Based Diblock Copolymers Comprising Nanodomains of a Polymerized Ionic Liquid and a Solid Polymer Electrolyte Doped with LiTFSI

LECTURES ABSTRACTS

Direct proof of the existence of a material time in physical aging

Birte Riechers[1,2*], Lisa A. Roed[1], Saeed Mehri[1], Trond S. Ingebritsen[1], Tina Hecksher[1], Jeppe C. Dyre[1], Kristine Niss[1]

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Physical aging deals with small property changes over a long time resulting from structural rearrangements. Understanding this type of aging is crucial for applications of non-crystalline materials like oxide glasses, polymers, metallic glasses, and more. Describing and predicting physical aging has been a focus of materials science for many years, but the subject still presents fundamental challenges [1]. We here address the concept of a material-time controlled aging, which was proposed by Narayanaswamy in 1971 [2]. While the material-time concept rationalizes several striking aging phenomena [2, 3, 4, 5], the existence of a material time has never been validated in direct experiments. We do this here by long-time dielectric experiments on a glass-forming molecular liquid, 4-vinyl-1,3-dioxolan-2-one (VPC), demonstrating with the fundamental material-time prediction that linear-response aging data determine the highly nonlinear aging behavior.

An ideal aging experiment involves a temperature jump that starts from a state of thermal equilibrium, changes temperature rapidly compared to the response time scale of the material and monitors the system's gradual approach to equilibrium at the new temperature [6]. Doing this requires a setup that allows for fast temperature changes and has a precise temperature control with minimal long-time drift. Moreover, very accurate measurements are needed because the long-time-tail of physical aging and the entire aging response to a small temperature step involve minute changes of material properties. We performed several temperature-jump experiments around a reference temperature on VPC including single temperature jumps, double-jumps similar to Kovacs' cross-over protocol [7], and multi-jumps resembling a sinusoidal temperature modulation. High thermal stability and quick temperature changes were assured by a Peltier element with direct contact to a thin-sample plane-plate capacitor. The dielectric response of the sample was tracked with an Andeen-Hagerling ultra-precision capacitance bridge. Based on a single-parameter material-time formalism inspired by Narayanaswamy's description of physical aging, these linear and nonlinear experimental aging responses were successfully predicted from linear response data.

[1] G. B. McKenna and S. L. Simon, Macromolecules **50**, 63333-6361 (2017).

[2] O. S. Narayanaswamy, J. Am. Ceram. Soc. **54**, 491 (1971).

[3] G. W. Scherer, Relaxation in Glass and Composites (Wiley, New York, 1986).

[4] A. Q. Tool, J. Am. Ceram. Soc. **29**, 240-253 (1946).

[5] G. B. McKenna, Rubber Chem. Technol. **93**, 79-120 (2020).

[6] T. Hecksher, N. B. Olsen, K. Niss, and J. Dyre, J. Chem. Phys. **133**, 174514 (2010).

[7] A. J. Kovacs, J. J. Aklonis, J. M. Hutchinson, A. R. Ramos, J. of Polymer Sci. **17**, 1097-1162 (1979).

Physical Ageing, Rejuvenation and Memory Effects Studied in Nanopore-Confinement

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When spatially constrained at the nanoscale level, the glass transition dynamics of molecular liquids and polymer materials reveal pronounced out-of-equilibrium features. This includes deviation from the bulk-like mobility that in many cases can be partially or even eliminated with time. Since out-of-equilibrium phenomena in nanopore-confinement are observed only below the glass-transition temperature of the interfacial layer (located well below T_g of the bulk material) we have a unique opportunity to follow how the structure recovers in the experimental window provided by the dielectric spectroscopy. In this work, by performing a series of typical one and two-step experiments used in physical aging studies we discuss the kinetics of structural recovery in nanopore-confined glass-former, especially on the importance of the distance from the equilibrium state, the vitrification temperature of the interfacial layer, and the pore size. We also think of the pressure effects that need to be eliminated upon the evolution of the structural relaxation towards the bulk-like mobility.

Time scale ordering in supercooled liquids

Birte Riechers, Lisa A. Roed, Jeppe C. Dyre, Kristine Niss, and Tina Hecksher

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The question of what controls the temperature dependence of the alpha relaxation time is central in glass science. Relaxation time can however be defined in different ways from a given spectrum, from different experimental probes and even from different representations of the same data, what makes the concept somewhat ill-defined. It is for instance well-known that the time scale for dielectric relaxation is slower than that of shear mechanical relaxation and that susceptibility and modulus representations have different characteristic times.

We discuss different definitions of relaxation time. Previous results [1] show that for "simple" liquids time scales from five different response functions are different but have the same temperature dependence. Recent results [2] show the same to be the case for some "non-simple" systems, hexanetriol (a hydrogen-bonded liquid) and squalane (van der Waals-bonded liquid with a prominent secondary relaxation process). The latter displayed a decoupling of time scales when comparing loss peak positions, but temperature-independent time-scale ratios were restored when comparing terminal relaxation times. Interestingly, the same ordering of response-function-specific time scales is observed which - from fast to slow dynamics - is: shear modulus, bulk modulus, dielectric permittivity, longitudinal thermal expansivity, and longitudinal specific heat. These findings indicate a general relation between the time scales of different response functions and, as inter-molecular interactions apparently play a subordinate role, suggest a rather generic nature of the process of structural relaxation.

[1] Jakobsen *et al.*, J. Chem. Phys. **136**, 081102 (2012)

[2] Roed *et al.*, J. Chem. Phys. **154**, 184508 (2021)

Molecular Mobility and Physical Aging of Polymers with Intrinsic Microporosity (PIM-1) Revisited: A Big Glassy World

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Polymeric membranes represent a cost- and energy-efficient solution for gas separation. Recently Polymers of Intrinsic Microporosity (PIMs) have been in a great interest because of their outstanding BET surface area larger than 700m^2/g and pore size smaller than 1 nm [1]. PIMs are a promising candidate in gas separation with high permeability and appealing selectivity due to their inefficient packing derived from a combination of ladder-like rigid segments with sites of contortion [2]. However, it is recognized this class of polymers suffer from decrease in performance with time due to physical aging. The initial microporous structures approach a denser state via local chain rearrangements, leading to a dramatic reduction in permeability. As chain packing during film casting and physical aging are the key factors determine the performance in separation applications, characterization of the molecular mobility in these materials has been proved to provide valuable information. In recent researches on PIM-1 the archetypal PIM, a molecular relaxation process with high activation energy together with a significant conductivity in the glassy state has been found and explained with the formation of local intermolecular agglomerates due to interaction of π-electrons in aromatic moieties of the polymer backbone [3]. In this work, the dielectric behavior of the polymeric films and their response upon heating (aging) were measured by isothermal frequency scans during different heating/cooling cycles in a broad temperature range down to 133K for the first time. Multiple dielectric processes following Arrhenius behavior were observed. Local fluctuations, Maxwell-Wagner-Sillars (MWS) polarization and structural relaxations were discussed correlating to structural-properties of PIM-1. Up to now, no other work has studied the role of porosity and thermal history of PIM-1 film in dielectric processes. The goal is by eliminating thermal history and considering storing conditions provide better understanding on aging and plasticizing in high free volume glassy polymer PIM-1.

[1] P. Budd et al., Advanced Materials **16.5**, 456-459 (2004).

[2] N. McKeown, P. Budd. Macromolecules **43.12**, 5163-5176 (2010).

[3] N. Konnertz et al., ACS Macro Lett. **5**, 528-532 (2016).

Mechanism of disaccharide-induced protein stabilization from broadband dielectric spectroscopy and neutron scattering

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Proteins are an important component in many medical and food products, and the long-time properties of these products are directly dependent on the stability of their proteins. To enhance this stability it has become common to add disaccharides in general, and trehalose in particular. However, the mechanisms by which disaccharides stabilize proteins and other biological materials are still not fully understood, and therefore we have used broadband dielectric spectroscopy (BDS), neutron diffraction and quasielastic neutron scattering (QENS) in combination of molecular modeling to investigate the stabilizing role of the disaccharides trehalose and sucrose on myoglobin. Our aim was to enhance the general understanding of the role of disaccharides and to obtain specific insights into why trehalose exhibits extraordinary stabilizing properties. The diffraction results show that both disaccharides are preferentially excluded from the protein surface, but that this effect is more pronounced for trehalose than sucrose. Hence, the disaccharide molecules are generally not affecting the protein by direct interactions [1]. Instead, the BDS and QENS results show that the protein dynamics is slowed down by a slowing down of the protein hydration water, caused by the disaccharide molecules [1,2]. Thus, the disaccharide molecules interact with the protein hydration water, causing a slowing down of this water dynamics, which in turn slows down the protein dynamics by the "slaving mechanism" [3,4]. Since the structural (α) relaxation of the trehalose solution and the motions of the hydration water are slower than for the corresponding sucrose solution, the protein motions are slower in the trehalose solution, which explains the more efficient stabilizing effect of trehalose on proteins.

[1] C. Olsson, S. Genheden, V. Garcia Sakai and J. Swenson. Mechanism of trehalose-induced protein stabilization from neutron scattering and modeling. J. Phys. Chem. B 123, 3679-3687 (2019).

[2] C. Olsson, R. Zangana and J. Swenson. Stabilization of proteins embedded in sugars and water as studied by dielectric spectroscopy. Phys. Chem. Chem. Phys. 22, 21197-21207 (2020).

[3] P. W. Fenimore, H. Frauenfelder, B. H. McMahon and R. D. Young, Bulk-solvent and hydration-shell fluctuations, similar to a- and b-fluctuations in glasses, control protein motions and functions. Proc. Natl. Acad. Sci. USA 101, 4408–14413 (2004).

[4] H. Fraunefelder et al. A unified model of protein dynamics. Proc. Natl. Acad. Sci. USA 106, 5129–5134 (2009).

Combining BDS with NMR and MDS Studies to Disentangle Complex Relaxation Patterns of Hydrogen-Bonded Liquids in Silica and Protein Confinements

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Generally, confined hydrogen-bonded liquids show very complex relaxation spectra. Therefore, we combine broadband dielectric spectroscopy (BDS) with nuclear magnetic resonance (NMR) and molecular dynamics simulations (MDS) studies to determine the microscopic origin of various observed relaxation processes. Our combined approach shows that the main structural (alpha) relaxation of the confined liquids can readily be identified, which allows us to analyze, e.g., the glass transition of confined water, whereas other relaxation processes are more difficult to assign. In silica pores, we find that slow relaxation processes can stem either from an interfacial layer with retarded dynamics or, e.g., for water, from a distorted crystal in the confinement center. Moreover, it is shown that NMR and MD studies allow us to ascertain the exchange between such dynamically distinguishable subensemles and its effects on the BDS results. In soft confinements, the situation is even more complicated because the dielectric spectra receive further contributions from the flexible matrix. In the literature, particular attention was given to the glass transition of proteins in water or another appropriate solvent. While various BDS studies argued that a prominent slow relaxation can be assigned to glassy protein dynamics, our NMR studies reveal that this process does not meet the criteria of an alpha relaxation. Finally, it is shown that cross terms play a crucial role for the interpretation of BDS spectra of dynamically asymmetric mixtures such as aqueous protein and peptide solutions. Specifically, our MDS studies unravel that the decay of inter-component cross terms can feign the existence of a coupled dynamical process of the components, which does not exist in their single-particle correlation functions.

Dynamics of physical networks studied by dielectric and mechanical spectroscopy

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The presence of side chemical groups able to form ionic or hydrogen bonding between polymer chains allow the formation of physical networks. Unlike in chemical networks where covalent bonds are fixed, in physical network the bonds are dynamic and have a characteristic lifetime related to the strength of the bond.

In this presentation, we report an investigation of the dynamics of physical networks by a combination of broadband dielectric spectroscopy and rheology. These two techniques complement well each other and allow the determination of the nature of the observed dynamic processes. In particular, we show how the number and type of physical bonds affects the dynamics of the physical networks.

The Origin of the Apparent Slow Solvent Dynamics in Binary Mixtures

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In dynamically asymmetric but fully miscible binary mixtures characteristic relaxation times of solute and solvent can be separated by several orders of magnitude. Nevertheless, a relaxation process, which is caused by the solvent and occurs on the timescale of the much slower dynamics of the solute has been observed in various binary mixtures. This leads to the notion that, while solvent relaxation is fast on average, a fraction of very slow solvent molecules exists in the vicinity of the solute.[1] By combining broadband depolarized dynamic light-scattering and dielectric spectroscopy with molecular dynamic simulations we show that in contrast to this notion long-lived cross-correlations between solvent molecules cause the slow solvent contributions. These cross-correlations originate from the fact that via solute-solvent interactions the solute imprints an energy landscape to the neighboring solvent, which leads to enhanced correlations between the positions and orientations of different solvent molecules until the solute relaxes. This mechanism explains discrepancies found between results of techniques probing collective and single-particle dynamics, like light-scattering and dielectric spectroscopy on the one side and nuclear magnetic resonance spectroscopy on the other.

[1] T. Blochowicz, S. Schramm, et al., Phys. Rev. Lett., 2012, 109, 035702

The Balance between Bulk and Bound Water in Methemoglobin Solutions; Dielectric Spectroscopy Study

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In this work, based on the symmetrical broadening of the dielectric response of water, we consider the solutions of methemoglobin (MetHb) both in pure water and in phosphate-buffered saline (PBS). The universal character of the Cole-Cole dielectric response enables the interpretation of the dielectric data of these solutions in a unified way using the previously developed 3D trajectory method driven by protein concentration [1]. It was shown that protein hydration is determined by the interaction of water dipoles with the charges and dipole residues located at the surfaces of the protein macromolecule. In the case of the buffered solution, the transition from a dipole-ion to a dipole-dipole interaction with protein concentration is observed [1].

A new approach is proposed for hydration water molecules bounded to the macromolecule evaluation. The theoretical model describes the change in the free to bound water ratio as a function of MetHb concentration in ion-containing and ion-free aqueous solutions. It takes into account the number of positive and negative charges at the protein surface, the number of bound water molecules in its hydration shells and the participation of inorganic ions as well as MetHb in binding the water. The theoretical evaluation of the ratio of free and bound water for the hemoglobin concentration in the absence of ions corresponds with the experimental results and shows that MetHb binds about 1400 water molecules. For the solution of MetHb the amount of bound water does not change as hemoglobin concentration increased from 15 to 30 g/dL remaining at the level of ~20% of total intracellular water pool. These observations suggest that within concentration range close to physiological (35g/dL) MetHb molecules are so close to each other that their hydration shells interact [2]. To prove the reliability of the theoretical model dielectric measurements of the solution of MetHb at concentrations close to physiological (30g/dL) in the low frequency range (10^{-2} – 10^{6}) were carried out in cooled state.

[1] Dielectric spectra broadening as a signature for dipole-matrix interactions. V. Water in protein solutions, L. Latypova, A. Puzenko, E. Levy and Y. Feldman, *J. Chem. Phys.*, **2020**, 153, 045102;

[2] Hydration of methemoglobin studied by in-silico modelling and dielectric spectroscopy, L. Latypova, A. Puzenko, Y. Poluektov, A. Anashkina, I. Petrushanko, Y. Feldman, submitted to J. Chem. Phys.

The microscopic model of dielectric relaxation of ice with impurities

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In nature, impurities are always present in water and their effect on the electrical properties of water is not fully understood. In this work, a microscopic model of dielectric relaxation of ice with impurities has been developed, which was successfully tested by describing the temperature dependence of the dielectric relaxation time of ice in partially crystallized water-gelatin mixtures of low concentration. The model is based on the concept of proton hopping, which is controlled by traps from orientation defects generated by impurity molecules. Fig. 1 shows a schematic representation of the temperature dependence of the relaxation time of ice with impurities and relaxation mechanisms in all characteristic temperature ranges. Here E_{LD}, $E_{\pm}$ are the activation energies of the orientation and ionic defects, respectively, $\Delta E = E_C - E_L$ is the depth of the trap, E_C, E_L are the energies of the conduction band and the trap, respectively, $T_{C1,2}$ are the crossover temperatures. The non-Arrhenius behavior of the ice relaxation time at high and low temperatures and its suppression with increasing impurity concentration are described. The increase of the impurity concentration leads to an growing of the number of orientation defects in ice and, accordingly, to an increasing in the concentration of traps. This, in turn, leads to an increasing in localized protons in the system and suppression of the relaxation mechanism caused by mobile ionic defects. As a result of the suppression of the ionic mechanism, the Arrhenius behavior of ice relaxation through orientation defects is restored. Fig. 2 shows the results of a numerical fitting of the experimental temperature dependences of the relaxation time of ice in water-gelatin mixtures with gelatin concentrations 1–4 wt % from [T. Yasuda et al., J. Phys. Chem. B 121 (2017) 2896–2901], using the model. The developed model can be successfully applied to aqueous mixtures with various types of impurities (soluble and insoluble) in a wide range of concentrations.

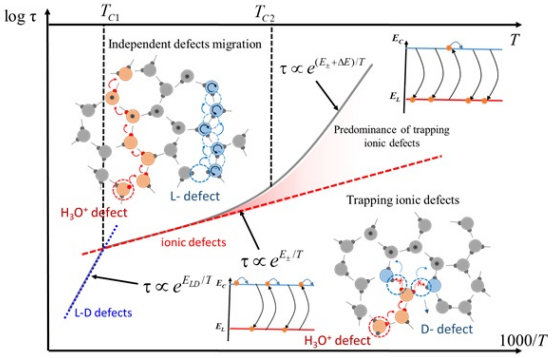

Fig. 1. A schematic representation of the temperature dependence of the relaxation time of ice and explanatory diagrams of the mechanisms of relaxation in each part of the dependence. At high temperatures ($T > T_{C1}$), the relaxation mechanism through orientation L–D defects predominates. In the region of intermediate temperatures ($T_{C2} < T < T_{C1}$), the relaxation mechanism through ionic defects begins to dominate; in this case, ionic and orientational defects or move independently, or the intensity of the processes of trapping ionic defects is comparable to the intensity of emission from them. At low temperatures ($T < T_{C2}$), the number of events of capture of ionic defects in traps from orientational defects increases, and capture processes prevail over the processes of release from them.

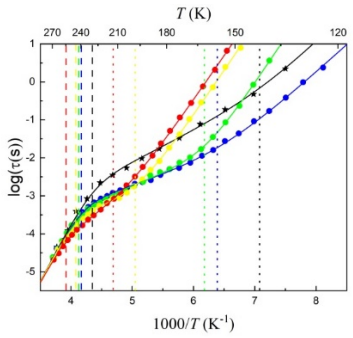

Fig. 2. Graphical presentation of the results of the numerical fitting of the experimental temperature dependences of the dielectric relaxation time of ice in pure water (black stars) and in water-gelatin mixtures with gelatin concentrations of 1 wt% (blue circles), 2 wt% (green circles), 3 wt% (yellow circles), 4 wt% (red circles) from [T. Yasuda et al., J. Phys. Chem. B 121 (2017) 2896–2901], using theoretical dependence (solid curves of the corresponding color) obtained within the developed model. The vertical lines show the position of the crossover temperatures (the dashed lines correspond to the temperature T_{C1}, the dotted lines correspond to the temperature T_{C2}, the color of the straight lines corresponds to the color of the curve).

Predicting dielectric properties of deeply supercooled pharmaceutical liquids from shear rheology

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Broadband dielectric spectroscopy as well as shear mechanical measurements can yield invaluable insights regarding the molecular mobility and physical stability of amorphous pharmaceuticals in their supercooled states [1,2]. Previous studies on small-molecular glass formers have shown how the model of Gemant, DiMarzio, and Bishop (GDB) [3,4] or modifications thereof [5,6] can be used to predict dynamical information of one spectroscopic method from the other.

In the light of the GDB model, we present shear rheological measurements of pharmaceutical liquids such as acetaminophen, ibuprofen, indomethacin, lidocaine hydrochloride, and nicotine and discuss them in relation with published dielectric results of these substances. Apart from lidocaine hydrochloride, where the dielectric and mechanical degrees are dynamically "decoupled", we find that with one free parameter (related to the molecular size) the shape and peak position of the dielectric loss spectra can be predicted from rheological data on the basis of the GDB model. The frequency dependent dielectric response of lidocaine hydrochloride is dominated by charge transport phenomena rather than by the structural relaxation [7], so that here the model was not expected to be applicable.

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Dynamics crossovers in the fast water relaxation in solutions of biological and non-biological solutes

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The dynamics of water in biological and synthetic materials have enormous importance in several technological, biological and basic research fields. The characteristics of the water dynamics when it is mixed with proteins or with synthetic materials is not usually related because it is commonly thought that water in protein solutions is exceptional when compared with water in non-biological solutes. Recently, we have shown that water in peptides and water in some non-biological solutes share the same type of dynamics in the supercooled region[1, 2]. The condition for observing the same characteristics in both types of solutions (proteins and synthetic solutions) is that the variation of the glass transition temperature (T_g) with water concentration is very large (more than 100 degrees) considering water contents[2] from ~ 0 to 50 wt%.

In this talk, we will concentrate on the fastest water relaxation observed in these solutions (called fast water relaxation in previous works) previously detected by BDS[1,2] and NMR[3]. This relaxation shows an unequivocal crossover at T_g. The question is whether this relaxation shows other crossovers at lower temperatures. By combining broadband dielectric spectroscopy and calorimetric measurements, we will discuss the temperature dependence of this process with emphasis on the temperature where the crossovers are produced. In addition, we will compare amorphous and semi-crystalline solutions to determine if the level of crystallization affects the temperature dependence of the fast water relaxation.

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Role of water in the response to glucose uptake in red blood cells; is it specific?

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It was shown recently that dielectric relaxation of water in the microwave frequency band is sensitive to glucose concentration changes in red blood cells (RBC) suspension [1]. Hence, dielectric spectroscopy has been actively used in the study and development of non-invasive glucose monitoring (NIGM) sensors including microwave frequencies [2-4]. However, the mechanism behind the sensitivity of dielectric spectroscopy (DS) to glucose concentration in the RBC environment is not yet entirely clear [5]. To clarify the issue, we measured the dielectric spectrum of RBCs suspension supplemented with various concentrations of D-glucose in the medium (from 0 up to 20 mM). The behavior of the cells that were treated with an inhibitor of D-glucose uptake (Cytochalasin B, CCB) was compared with the control untreated RBCs.
In this paper, we are presenting the study, using the microwave dielectric spectroscopy (MDS) in the frequency band from 500 MHz to 40 GHz, to investigate the impact of glucose transmembrane transport RBC on the dielectric response of the cytosol water. The results revealed that after incubation of RBCs with CCB the dielectric response of water in the cytoplasm and specifically, its relaxation time demonstrate minimal sensitivity to glucose concentration in the medium. This, together with the behavior of the relaxation time of cytoplasmic water in the absence of the inhibitor, adds a further piece to the overall picture of the underlying mechanisms and use of MDS to follow the effects of glucose uptake and metabolization in RBC. Finally, we can further hypothesize that the main mechanism of sensitivity of MDS associates with post-uptake glucose utilization (i.e., glycolysis) and/or associated cellular processes.

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The relation between charge and mass transport in coupled and decoupled conductors

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The present contribution analyses the relation between the dynamics of charge carriers and the rearrangements of their matrix for two categories of highly concentrated electrolytes, namely ionic liquids (ILs) and aqueous acid solutions. These materials exhibit different mechanisms of their conductivities, on the one hand of a vehicular type (charge transported by molecules), while governed by proton transfer on the other.

Regarding the former class of conductors, our results demonstrate that the OH-functionalization of ionic liquids can change their local dynamics by several orders of magnitude [1], even though the Coulombic interaction is usually considered to dominate their energy landscape [2]. Also interesting is that all investigated ILs (no matter whether they support H-bonding) exhibit similar spectral signatures in their dielectric and shear mechanical responses. Since their corresponding time scales are also method-independent, this demonstrates that in ILs the charge transport is well coupled to the structural rearrangements in the entire dynamical range defining their conductivity (σ-) and their main rheological (α-) relaxations [1].

The same techniques have been employed to access the charge and structural rearrangements of viscous sulfuric acid tetrahydrate and phosphoric acid monohydrates [3] in both protonated and deuterated forms [4]. Our analysis reveals that the viscoelastic response of phosphoric acid hydrates is bimodal, comprising the structural relaxation and an additional, faster relaxation process. The time constants of this fast mechanical feature agree with those of the (dielectrically probed) conductivity process, indicating that by means of shear rheology one can gain information regarding the dynamics of charge carriers in systems with decoupled conductivity. In addition, we found that the conductivity responses of acid hydrides in general closely resemble those exhibited by classical ionic electrolytes (including ILs), enabling the transfer of knowledge previously gained from the descriptions of ionic conductivity to the case of proton transport [4].

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Correlating ionic conductivity and nanoscale morphology of polymerized imidazolium-based ionic liquids

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The impact of the chemical structure on ion transport, nanoscale morphology, and dynamics in polymerized imidazolium-based ionic liquids is investigated by broadband dielectric spectroscopy and X-ray scattering, complemented with atomistic molecular dynamics simulations [1, 2, 3]. Anion volume is found to correlate strongly with Tg-independent ionic conductivities spanning more than 3 orders of magnitude. In addition, a systematic increase in alkyl side chain length results in about one decade decrease in Tg-independent ionic conductivity correlating with an increase in the characteristic backbone-to-backbone distances found from scattering and simulations. The quantitative comparison between ion sizes, morphology, and ionic conductivity underscores the need for polymerized ionic liquids with small counterions and short alkyl side chain length in order to obtain polymer electrolytes with higher ionic conductivity.

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Disentangling different dynamic contributions in the dielectric response of ionic liquids

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Molecular dynamics of ionic liquids (ILs) in an electric field can be decomposed into contributions from translational motions of ions, rotational motions of permanent dipoles and – in the case of ions equipped with long alykl-chains – motions of ionic aggregates. The discrimination of these contributions in the dielectric spectrum is quite involved, resulting in numerous controversies in the literature. We show here that in ILs where only a conductivity relaxation is present, this contribution can be modeled with the MIGRATION model, resulting in a better data description than by using the random barrier model.[1] We attribute a second, slower relaxational contribution, which is observed in some ILs, to dipolar reorientations, since it appears on the same time scale as probed by depolarized dynamic light scattering, which is sensitive to the reorientation of optical anisotropic molecules only.[2] We could not confirm another explanation for the microscopic origin of the slower process, as put forward in the literature,[3] namely the motion of aggregated ions, by comparing high pressure dielectric results with high pressure X-ray scattering data from the literature. This comparison shows that the pressure dependence of the X-ray scattering pre-peak, which is attributed to the formation of supramolecular aggregates, is different from the pressure dependence of the slow dielectric relaxation.

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Space-time heterogeneity of Johari-Goldstein β-relaxation in supercooled and glassy systems and its relation to α-relaxation dynamics

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Since at least two decades, evidence has been given that the Johari-Goldstein (JG) β-process is strongly coupled to the structural α-relaxation [1-3]. Nevertheless, its dedicated role in the glass-transition remains under debate: in particular, few studies have dealt with the microscopic length scale of JG β-process and with its time evolution from very short times to those characteristic of the α-one. Therefore, even the nature of the heterogeneity of (JG) β-dynamics is still unclear. Recently [4], thanks to a novel technique, nuclear resonance time-domain-interferometry (TDI), structural and dynamical information has been made available by means of microscopic density correlation function in a wide time range (from ns to hundreds of μs) and scattering vector q range (4–40 nm−1). A new scenario for the JG β-dynamics in supercooled systems emerges: the molecules participating in it are highly mobile and spatially connected in a system-spanning, percolating cluster, while the slowest molecules coordinate into low mobility islands related to the α-process; the JG β-process is not limited to a short length scale but it has a continuous space-time evolution, as confirmed by its observation in vicinity of the maximum q of the static structure factor S(q). Moreover, TDI data obtained in the glassy state give evidence that a change of temperature dependence for the non-ergodicity factor occurs at $T_{g\beta}$, the temperature where JG β-relaxation times exceed the experimental time window, in agreement to what already shown for cage dynamics amplitude in molecular glass formers [5].

In this talk, data from TDI, dielectric spectroscopy and neutron scattering will be compared and discussed. The experimental results show the JG β-relaxation observed by dielectric spectroscopy is intrinsically heterogeneous, since comprised of processes with different length- and time-scales, that explains the reason of the broad relaxation time distribution usually shown by β-process. Motions with longer length-scale have longer relaxation time up to merging into those of α-process. TDI data also make clear the relation of the primitive relaxation time τ_0 of the Coupling Model [1] to the q-dependent distribution of relaxation times of the JG β-relaxation, and this explains why the experimental τ_β is approximately equal to τ_0 as found in many glass-formers.

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Non-Linear Dielectric Spectroscopy for Detecting and Evaluating Structure-Property Relations in a P(VDF-TrFE-CFE) Relaxor-Ferroelectric Terpolymer

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Relaxor-ferroelectric (RF) fluoropolymers receive increasing attention due to their unique properties that allow for the design of flexible and stretchable electronics with high electromechanical activity, which is only possible with soft polymers [1]. Non-linear dielectric spectroscopy (NLDS) allows us to measure the non-linear permittivities, which can give additional information that is otherwise not detected in conventional dielectric relaxation spectroscopy (DRS) [2]. Hence, NLDS is employed as an effective tool to study relaxation processes and phase transitions of a poly(vinylidenefluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) RF terpolymer in combination with thermally stimulated depolarization (TSDC) and dielectric hysteresis techniques. From the application point of view, the impact of polarity and the poling temperature on the polarization of the terpolymer is investigated by measuring the $\varepsilon_2/(3\varepsilon_0^2\varepsilon_1^3)$ ratio (proportional to the remanent polarization P_r in the sample) as a function of time.

NLDS reveals that the sign of ε_2' changes from positive to negative at the Curie-transition temperature (T_C), implying that the terpolymer undergoes a second-order transition. ε_2' measurements show two new peaks at 30 and at 80 °C that cannot be observed in conventional dielectric spectroscopy experiments. The former peak is associated with the mid-temperature transition found in all other vinylidene fluoride-based polymers [3], which can explain the non-zero ε_2' values detected in the paraelectric phase of the terpolymer. The latter peak is interpreted as a result of conduction and space-charge polarization at the electrode-sample interface. Since RF terpolymer shows a very low P_r at room temperature, they were poled at a lower temperature at which it exhibits a broader hysteresis loop. On the other hand, poling the sample with a positive voltage yields a higher P_r than with negative voltage. $\varepsilon_2/(3\varepsilon_0^2\varepsilon_1^3)$ *vs.* time measurements show that the polarization of a RF terpolymer at -25 °C is stable for more than 2 hr, indicating its suitability to be used in memory applications.

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Effect of high electric field on the kinetics and product properties of free radical polymerization of 2- hydroxylethyl methacrylate initiated by 2, 2′-azobisisobutyronitrile

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Synthetic polymer materials are playing an indispensable role in people's daily life due to their widespread applications in clothing, household goods, automobiles, and etc. Throughout the past hundred years, researchers have been devoting their efforts to the development of novel polymers and the exploration of new synthetic technologies. One of the hot research topics is the modulation/control of polymerization via applying external physical regulators, such as light, pressure, ultrasonic waves and electric field.[1]

In this study, we focused on the free radical polymerization (FRP) of 2- hydroxylethyl methacrylate (HEMA) with 2, 2′- azobisisobutyronitrile (AIBN) used as the initiator at T= 343 K, and examined the impacts of external electric fields (which are homogenous and in the range from 14 kV/cm to 140 kV/cm) on the polymerization kinetics and the properties of the resultant polymers. Broadband dielectric spectroscopy is a powerful tool allowing the precise real-time tracking of the polymerization reactions in the presence/absence of electric fields.[2] Analysis of the structure and macromolecular properties such as molecular weight and its dispersity for obtained polymers were conducted by using the techniques of nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC).

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A new experimental approach to the field dependence of the static dielectric constant

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Since Debye's recognition of the field dependence of the static dielectric constant, experiments have been performed to quantify this nonlinear dielectric effect (NDE). A common metric for this field dependence is the Piekara factor, the field induced change of the dielectric constant divided by the square of the electric field. The numerous obstacles to a reliable determination of the Piekara factor will be discussed, and an experimental approach to measuring this NDE in the static limit over a range of temperatures is presented. For the case of propylene glycol (PG), it is shown that applying a sequence of various field amplitudes within several milliseconds reveals time invariant levels that scale with field square. These features are indicative of the absence of heating or chemical degrading effects, and consistent with the quadratic field dependence implied in the definition of the Piekara factor. For the case of PG, we find that the Piekara factor is reduced by a factor of about two as a result of raising the temperature from 204 K to 235 K.

Local measurements of molecular dynamics and transport properties in polymer thin films

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Broadband dielectric spectroscopy (BDS) allows probing the dipole reorientations and/or charge motions taking place inside a sample; however, it lacks spatial resolution, as many macroscopic techniques. To overcome this issue, during the past years we have developed Atomic Force Microscopy (AFM) methods to perform local BDS measurements allowing for a lateral resolution < 100 nm. Our approach allows for direct access to the frequency-dependent dielectric permittivity of polymer thin films. Here, we present our recent advances in probing the molecular dynamics and charge transport properties of polymer thin films by local dielectric spectroscopy. First, we present experiments on poly(ethylene oxide) (PEO) thin films. PEO is a semicrystalline polymer that at room temperature shows a dielectric relaxation signal related to charge trapping between amorphous/crystalline interfaces. This phenomenon is connected to the ionic conductivity of the amorphous phase of the material. Using our AFM-based approach, we obtained topography images and dielectric spectra of PEO at room temperature, with 40 nm lateral resolution, and in a humidity range of 15 – 60%. We modeled our results following the Maxwell-Wagner-Sillars theory and obtained relevant physical parameters such as the DC-conductivity of the amorphous phase, and its dependence with relative humidity [A]. Second, we investigated thin films of novel polymer blends based on 2,5-furan dicarboxylic acid (2,5-FDCA), in particular using poly(pentamethylene 2,5-furanoate) (PPeF) and poly(hexamethylene 2,5-furanoate) (PHF). Our results showed a clear phase separation in the topography images, which was dependent on the blend ratio, thermal history, and time. To gain further information about the chemical nature of each phase, we probed the molecular relaxations at different zones of the films via local dielectric spectroscopy measurements. The AFM-based approach allowed probing the actual miscibility of the components in the blends; an information that is not directly evidenced by topographical imaging alone, and which is of utmost important for possible applications of these materials.

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Molecular dynamics and crystallization of smectic liquid crystals under hard and soft confinement

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The first part of the talk will focus on the effect of confinement imposed by nanopores on the molecular dynamics and phase behaviour of BBOA liquid crystal [1]. The phase transition temperatures of bulk BBOA and enclosed in napores show linear dependence as a function of inverse pore diameter. The BDS investigations revealed new relaxation processes associated with gradual paranematic-to-nematic transition in nanopores. Special emphasis is given to the influence of geometrical restriction on the non-isothermal crystallization process upon cooling. The impact of spatial constraint on intramolecular dynamics in the course of crystallization will be discussed in the context of Fourier transform-infrared spectral data. It was revealed that the process of gradual crystallization in pores is also reflected in vibrational dynamics of alkyl chains.

The second part of the talk will present the behaviour of 6BT liquid crystal under soft confinement, deriving from the interactions between polymer and guest 6BT molecules in composite electrospun poly(ε-caprolactone)/6BT fibres, and hard confinement, imposed by the rigid pore walls [2]. Differential scanning calorimetry, broadband dielectric and Fourier-transform infrared spectroscopy were employed to gain detailed insights into the effects of both forms of confinement on 6BT. BDS studies identified the similarities and differences in the relaxation dynamics of the 6BT compound under *soft* and *hard* confinement. The crystallization process of 6BT was found to be enhanced in the composite fibres, but fully suppressed for the material confined in pores. Two-dimensional correlation spectroscopy (2D-COS) analysis of infrared spectra confirmed that soft and hard confinement have different impacts on the intramolecular dynamics of 6BT.

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The reversible dielectric switching at ambient and high pressure conditions in selected hybrid perovskite structure

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The pyrrolidinium-templated cyanide $[(CH_2)_4NH_2]_2[KCo(CN)_6]$ is one of the representatives of organic-inorganic hybrids with a perovskite structure that exhibit switchable dielectric properties. The electric impedance was measured by using broadband dielectric spectroscopy. At ambient pressure, the first-order type of phase transition was registered at T = 243 K. After the applied high hydrostatic pressure, representing isotropic stress, the phase transition temperature increased. The temperature-pressure dependence for observed phase transition responsible for the switching mechanism enabled the phase diagram for two different thermodynamic paths. The pressure-temperature coefficient for the switching "upwards" is equal dT_C/dp = 73(1) K GPa^{-1}, and for switching "downwards": 54(1) K GPa^{-1}. The obtained results indicate that combined control of switching using pressure and temperature can reduce dielectric switching time.

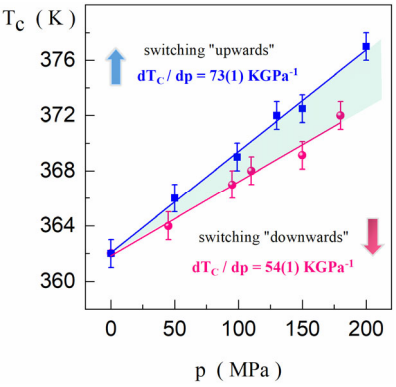

Fig. 1. The temperature-pressure $T_c(p)$ phase diagram of PyrKCo pellet [1].

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Polyamorphism in vapor-deposited 2-methyltetrahydrofuran: A broadband dielectric relaxation study

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Depositing a simple organic molecular glass-former 2-methyltetrahydrofuran (MTHF) onto an interdigitated electrode device via physical vapor deposition gives rise to an unexpected variety of states, as revealed by dielectric spectroscopy [1]. Different preparation parameters, such as deposition temperature, deposition rate, and annealing conditions, lead, on the one hand, to an ultrastable glass and, on the other hand, to a continuum of newfound further states. Deposition below the glass transition temperature of MTHF leads to loss profiles with shape parameters and peak frequencies that differ from those of the known bulk MTHF. These loss spectra also reveal an additional process with Arrhenius-like temperature dependence, which can be more than four decades slower than the main structural relaxation peak. At a given temperature, the time constants of MTHF deposited between 120 K and 127 K span a range of more than three decades and their temperature dependencies change from strong to fragile behavior. This polyamorphism involves at least three distinct states, each persisting for a duration many orders of magnitude above the dielectric relaxation time. These results represent a significant expansion of a previous dielectric study on vapor deposited MTHF [2]. Plastic crystal states and the effects of weak hydrogen bonding are discussed as structural features that could explain these unusual states.

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Dielectric relaxation and glassy dynamics in poly(diisopropyl fumarate) and its copolymers

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Poly(1,2-substituted ethylene) such as poly(diisopropyl fumarate)(PDiPF) has a structural character of the absence of a methylene spacer in the backbone chain contrary to the structure of viny polymers such as polyacrylate and polymethacrylate. Such geometrical character can be expected to affect the dynamics of the segmental motions and subchain motions. In this study, we investigated the relaxation behavior of PDiPF homopolymer and its copolymers with 1-adamantly acrylate (AdA) or n-butylacrylate (nBA) using dielectric spectroscopy (DS) and differential scanning calorimetry (DSC), and wide angle X-ray scattering (WAXS). We could observe the three different dynamical processes such as alpha-, beta-, and gamma-processes and measure the temperature dependence of the relaxation times of the three process for copolymers P(DiPF/AdA) and P(DiPF/nBA). We commonly found that the temperature dependence of the relaxation time of the beta-process can well be reproduced by the Vogel-Fulcher-Tammann (VFT) law, which suggests that there is a cooperative nature in a similar way to observed for the alpha-process. We could also evaluate the fragility index, Vogel temperature both for the alpha- and beta-processes. In this presentation, we will discuss the correlation between the alpha-process and beta-process in detail.

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Relaxation Behavior and Free Volume of Bio-based poly(trimethylene terephthalate)-block-poly(caprolactone) copolymers as revealed by Broadband Dielectric and Positron Annihilation Lifetime Spectroscopies

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Broadband Dielectric (BDS) and Positron Annihilation Lifetime Spectroscopies (PALS) have been used to investigate the relaxation behavior of novel bio-based aliphatic-aromatic block copolymers based on poly(trimethylene terephthalate) (PTT) and poly(caprolactone) (PCL). The dielectric relaxation of the PTT-block-PCL block copolymers is characterized by a a relaxation process above T_g and a bimodal b relaxation below T_g. The faster mode of the b relaxation has been assigned to the bond between the ester oxygen and the aliphatic carbon of the PTT block and the slower b mode has been attributed to the bond between the aromatic ring carbon to the ester carbon also in the PTT block. Both modes for the copolymers appear to be faster than those of PTT at comparable temperatures while a for the copolymer series a nearly similar subglass dynamics is observed. Since free volume values for PTT and PTT-block-PCL (75/25) as measured by PALS are very similar and those for the copolymers increase with PCL content this effect is likely to be attributed to change in the flexibility of the polymeric chain upon going from PTT to the copolymers rather than to a free volume dependence confirming the local nature, i.e. non cooperative, of the b relaxation. The weak dependence of the b relaxation dynamics with PCL content for the copolymers suggests that this relaxation is mainly related to the PTT block. The a relaxation becomes faster the higher the PCL content following the decrease of the T_g with increasing PCL content. This effect is supported by the free volume and o-Ps annihilation life time for the block copolymers measured by PALS. By scaling free volume and o-Ps annihilation life time with $T-T_g$, being T_g the corresponding glass transition temperature for every copolymer, a characteristic sigmoidal variation with temperature is observed.

Calculating the calorimetric glass transition trace of simplified industrial polymer mixtures from the neat components and the modeling of dielectric relaxation.

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Broadband dielectric spectroscopy (BDS) is an extendedly used technique that allows characterizing the relaxation behavior of a given material over an extremely broad frequency range in a single experiment. Differential scanning calorimetry (DSC) is commonly applied to determine the glass-transition temperature of diverse systems. These techniques provide very valuable information, but in complex systems as polymer blends the interpretation of the results and how to relate the magnitudes observed by the two methods is not straightforward. In this contribution we present a combined study by dielectric relaxation and calorimetric experiments on a simplified industrial system based on mixtures of styrene butadiene rubber (SBR) with a polystyrene oligomer (PS). Blends of different compositions were prepared (40, 50, 70% in weight of PS, w_{PS}) and exhaustively investigated by both methods. As a starting point, we have first done a full characterization of the homopolymers' dielectric response and calorimetric traces, to obtain all the parameters and information that we need to describe the experimental data on the mixtures. The description of the DSC curves for the neat polymers was based on three parameters characteristic for each component: the inflection point of the DSC trace (T_g), the width of the glass transition range and heat capacity (ΔC_p). The comparison with BDS results allowed connecting for each component the parameters describing the dielectric relaxation time and T_g. The next step consisted of modeling the a-relaxation in the blends. This was based on thermally driven concentration fluctuations and the self-concentration concept, the basic ingredients identified in academic polymer blend samples [1]. In a previous study [2] the same framework was used to describe the dielectric and mechanical relaxation processes for a similar simplified industrial system. Applying this model now to the dielectric results on our system, the values of the parameters involved –the width of the concentration fluctuations and the self-concentration of the components– were deduced. Last, by assuming that the connection found for the dielectric and DSC parameters of the homopolymers remains valid in the blends, the DSC modeling of the mixtures was obtained. For the blends investigated we found an overall good agreement between calculated and experimental DSC results.

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Molecular dynamics of Janus polynorbornenes: Glass transitions and nanophase separation

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We report the dielectric and calorimetric investigations of an homologous series of Janus polynorbornenes with rigid main backbone and flexible -$Si(OR)_3$ side groups, of differing length alkyl chains (R = Propyl, Butyl, Hexyl, Octyl, Decyl). Dielectric dispersion reveals two active processes at low temperatures, denoted as β- and α- relaxation. The former can be assigned to localized fluctuations, whilst the latter relates to the glassy dynamics of the flexible -$Si(OR)_3$ side groups, that creates a nanophase separation in both the alkyl chain rich and backbone rich domains. Temperature modulated DSC measurements and X-ray scattering experiment confirm the nanophase separation. Fast Scanning Calorimetry employing both fast heating and cooling rates detects the glass transition temperatures of the backbone rich domains, which are beyond or near to their degradation temperatures in terms of conventional DSC. The cooperative length scale of glass transition and the size of the alkyl chain rich domains increases with chain length. Alongside these results, a significant conductivity contribution was observed for all Poly(tricyclononenes) with $Si(OR)_3$ side groups, which is interpreted in terms of a percolation model.

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Layers of Distinct Mobility in Densely Grafted Dendrimer Arborescent Polymer Hybrids

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Using dielectric spectroscopy, differential scanning calorimetry and rheology we studied melts of multi-arm stars of 1,4-polybutadiene (dendrimer arborescent hybrids) with very high branching functionality (*f*) and small arm molar mass. In particular, a series of stars with 929, 1110 and 2830 side chains, with arm length of 1.5 kg·mol^{-1} and 5 kg·mol^{-1} behave as jammed colloids and show *distinct* layers of segmental mobility [1]. Three mobility layers were identified, comprising outer, intermediate and core segments all with Vogel-Fulcher-Tammann temperature dependence. Functionality affected even the dynamics of those segments located in the outer layer that showed slower dynamics and higher fragility as compared to linear chains. We show that intermediate and core segments have different power law dependencies on functionality (as $f^{1.3}$ and $f^{2.0}$, respectively). The corresponding glass temperatures increase as $f^{1/2}$, in qualitative agreement with the results from a recent simulation [2]. Our findings pave the way for further progress in this field by reconsidering previous theoretical treatments based on a single friction coefficient in hybrid nanoparticles such as densely grafted stars.

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Molecular Dynamics of Poly(dimethylsiloxane) Coordinated by Metal-Ligand Complexes

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Nowadays, development of flexible printed electronics and miniaturization of electronic devices determine the synthesis of new dielectrics with elevated dielectric permittivity and very good mechanical properties. Polymers cross-linked by metal-ligand coordination are good candidates for serving as fully stretchable dielectrics.

The main scope of this work is synthesis of dielectric poly(dimethylosiloxane) cross-linked by metal-ligand coordination (bpyPDMS-MeX_2) and investigation of their electrical properties and molecular dynamics with the reference to various metal-ligand cross-linkers (MeX_2). Chemical introducing of metal-bipyridine coordination bonds into the PDMS matrix enhanced the dielectric properties of the material because of the dipolar nature of the coordination bonds. The highest value of dielectric permittivity (ε') (4.3 at 1 MHz) was observed for bpyPDMS-$ZnCl_2$, which is almost twice as high as neat PDMS [1]. Moreover, a direct dependence between the ε' and dipole moments of metal-ligand bonds was calculated by the density functional theory. Performed study of molecular motions were done in a broad range of temperatures (143–373 K) as well as frequencies (10^{-1} to 10^6 Hz). It was noticed that the chemical incorporation of bpy moieties into long polymer chain suppress PDMS crystallization. Two relaxations called α and α_{ac} were found and described as segmental one. The α_{ac} relaxation in studied materials originates from the lower mobility of PDMS chains, as they are immobilized by metal-bpy coordination centers. Segmental motions for all synthesized materials were interpreted in terms of VFTH approach.

The research strategy done in this research allows well understanding of structure-dynamic relationship of novel polymers cross-linked by metal-ligand coordination. Presented methodology might be extended in the future to similar organometallics for evaluating their usability in flexible electronic devices.

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POSTERS ABSTRACTS

The Influence of surface polarity on the segmental dynamics of poly(phenyl methyl siloxane) confined in alumina nanopores

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Size and surface effects play an important role in the confined polymer dynamics. In this work, we have investigated the influence of surface modification on the segmental dynamics of poly(phenylmethyl siloxane) confined in alumina (AAO) nanoporous membranes by employing dielectric spectroscopy (BDS) and differential scanning calorimetry (DSC) techniques. Functionalization of the pore walls using highly polar phosphoric units separated by controlled number N of nonpolar triethoxysilane spacers (from N=1 to N=24) allowed us to precisely control the surface polarity. Analysis of the BDS and DSC data has revealed that the surface polarity affects the equilibration kinetics and can be used to control the time of the structural recovery to the equilibrium state. Furthermore, for the native nanopores, the DSC measurements exhibit the presence of three glass-transition events. Interestingly, our data indicate that chemical modification prevents the formation of the interlayer between the adsorbed layer and core volume observed in native membranes. Resulting in the appearance of only two endothermic processes.

How AC Electric Field Frequency Influences the Crystallization of a Molecular Liquid

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Controlling crystallization using electric field reveals a strong potential for material engineering. However, this ability is not completely explored neither understood. In this work, using dielectric spectroscopy, we study that the properties of alternating (AC) electric field can affect the crystallization behavior of vinylethylene carbonate, a high polar molecular system with field-induced polymorphism. We discover that adjusting the frequency and the amplitude of the electric field: the crystallization time can be changed; the dimensionality of crystal growth can be altered; and the crystallization outcome can be controlled to form one or another polymorph. We discuss that the field effects only are pronounced at below certain frequencies threshold, which orders of magnitude below the characteristic molecular orientation but consistent with the reorientation of polar crystal nuclei.

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Predicting molecular dynamics of amorphous drugs by combining artificial neural networks and theory

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Understanding molecular dynamics of drugs is important for pharmaceutical developments. The dynamics, characterized by structural relaxation time, is temperature dependent and can be experimentally determined using broadband dielectric spectroscopy. However, when designing new drugs, the synthesis procedure and subsequent characterization are very expensive and time- consuming processes, which delay and increase the costs of the drugs development. It is therefore necessary to propose new, cheaper but reliable tools to accelerate the process. In this work we combine the Elastically Collective Nonlinear Langevin Equation (ECNLE) theory and a neural network approach to predict the glass transition temperature and the temperature dependence of the structural relaxation time for amorphous drugs and other glass formers. Only chemical structure codified into a Simplified Molecular Input Line Entry System (SMILES) representation is required to enter our approach. To validate the method, we compare numerical results with experimentally derived quantities and find a good agreement without any fitting parameter.

Effects of Polymer Tacticity on the Segmental Dynamics of Poly(methyl methacrylate) (PMMA) under Elevated Pressure and Geometrical Nanoconfinement

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The properties of polymers are influenced by many different factors, including molecular weight, tacticity, geometrical nanoconfinement, and so on. For this reason, the study of spatial configuration in confined geometry is extremely useful to understand how to produce materials with desired behavior and functions. In this work, our main aim was to investigate the glass transition dynamics of isotactic and syndiotactic PMMA under high-pressure and geometrical nanoconfinement. Our results show that for both stereoisomers, the relaxation processes are observed in different temperature ranges. Tacticity also affects the behavior of PMMA under high-pressure conditions. The segmental relaxation of the isotactic PMMA is strongly modified by compression compared to syndiotactic stereoisomers. Base on that, we have predicted that the isotactic PMMA is more sensitive to density fluctuations induced by the geometrical nanoconfinement. Then, we have also demonstrated that in the case of i-PMMA thin films, segmental dynamics slightly accelerates with decreasing film thickness. However, for s-PMMA, the temperature dependence of the α-relaxation time resembles the behavior of the bulk sample. Apart from the differences in sensitivity to density/pressure changes, tacticity also affects the interactions of the polymer with the substrate seen in the amount of irreversibly absorbed chains. Stronger interactions are observed for syndiotactic stereoisomer. This fact leads to a slowdown in the segmental dynamics. Our study shows that tacticity is an essential aspect of polymer science, as it affects not only the glass transition dynamics but also the interactions with the substrate but also the sensitivity to the density variations.

The nature of low-temperature relaxation crossover of water in confinement

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The mechanisms of low-temperature crossover of water in different types of confinements – hard confinements, solutions and hydrated biopolymers is still an open question [1, 2]. In this paper the interplay between adsorbed water at hard hydrophilic centers and hydration water near soft hydration centers is studied. Porous borosilicate glasses with cylindrical pore channels of 10 nm filled with silica-gel balls of 5nm were specially fabricated to produce a confinement free space of 2.5 nm. Samples with different humidity levels (5.4-23.8%) were characterized by Novocontrol, Alpha Impedance Analyzer in a wide frequency range (0.01Hz-1MHz) at low temperatures (133K – 210K). Two relaxation Cole-Cole processes have been discovered for all the humid samples. A clear ice-like water relaxation process with a crossover around 180K has been observed for all the samples (Fig.1 - filled symbols). In addition, low humidity sample demonstrate an Arrhenius process at more high frequencies, which is completely screened for heavy humidified samples (Fig.1 - crosses). In contrary, additional low frequency process for heavy humidified samples is observed at frequencies lower than the main relaxation peak (Fig.1 - empty symbols). Based on a difference in hydrophilic properties of silica-gel and silicate matrix, we propose a qualified model reviewing the nature of the dynamic crossover of humid materials.

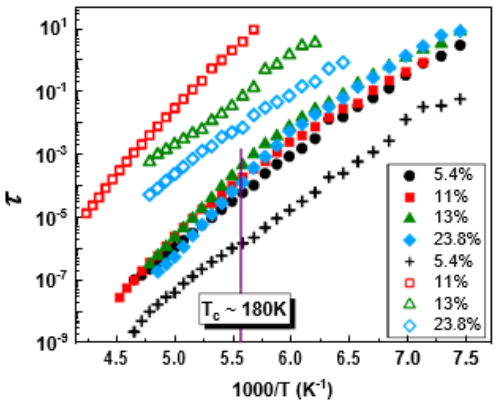

Figure 1 – Temperature dependences of the relaxation times for humidified samples.

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The role of entropy in the description of the relaxation dynamics of ionic liquids

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In the past few decades, ionic liquids (ILs) have attracted enormous attention from both the scientific community and industry. Due to high thermal stability, non-flammability, and high ionic conductivity, they are promising materials for developing advanced electrolytes in high-energy storage devices. Understanding the relationship between transport properties (*i.e.*, conductivity and viscosity) and the thermodynamics (*i.e.*, temperature, volume, and entropy) in ILs is critical for their optimized design in these devices.

In this poster, we analyze the conductivity, viscosity, and entropy behavior of several typical room temperature ILs over a wide thermodynamic condition. The analysis of these data in the framework of the classical Adam-Gibbs entropic model and the newly established "thermodynamic scaling" enable us to probe the role of entropy in the description of the relaxation dynamics of ILs. We found that the Adam-Gibbs theory fails to interpret the relaxation dynamics of ILs, indicating that the configurational entropy is insufficient to govern the dynamic process in ILs. We also found that the entropy scaling exponent (*i.e.*, the Grüneisen parameter γ_G) is a linear function of the total entropy. This linear relation strongly correlates to the typical intermolecular interactions of ILs. At last, the thermodynamic scaling behavior of a polymerized ionic liquid is discussed to investigate the effect of macromolecular structure on the conductivity and entropy.

Dielectric α-relaxation of supercooled sugar alcohols near the glass transition temperature

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It is known that the broadband dielectric spectroscopy (BDS) on supercooled liquids shows some relaxation processes with different time scales, such as the α-process and JG-β process. The former is directly involved in the glass transition in the meaning of increase in relaxation time of the α-process with decreasing temperature with divergent behavior in the same manner of viscosity.
In this work, measurements were made under several conditions and the results imply the possibility of more precise measurements at slower cooling rates.

Effect of aromaticity on molecular dynamics of glass-forming liquids

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The effect of structure on molecular dynamics is still a topic of great interest to researchers. Herein, using an example of two compounds differing from each other only in the type of six-carbon ring, i.e., benzene vs. cyclohexane, we show how aromaticity affects the relaxation dynamics behavior of supercooled liquid and glass by performing the experiments at ambient and elevated pressure.

In Situ Monitoring the Imbibition and Adsorption Kinetics of *cis*-1,4-Polyisoprene in Nanopores by Nanodielectric Spectroscopy

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Elucidating the mechanism of how polymers penetrate into narrow pores is important across wide fields such as the inkjet printing for commercial xerography or identification of proteins through nanopores. In this study, using *in situ* nanodielectric spectroscopy, we investigated the imbibition and adsorption kinetics of *cis*-1,4-polyisoprene (**PI**) by following the evolution of the dielectrically active longest normal mode. With respect to homopolymer **PI 42k**, we found that two regimes of imbibition kinetics with effective viscosity are both higher than bulk viscosity. Moreover, the dielectric intensity of longest normal mode stops growing although the polymer continues entering into nanopores. A microscopic scenario considering the competition from an increasing number of chains entering the pores and a decreasing number of fluctuating chain-ends is proposed to interpret this phenomenon. To clarify the adsorption kinetics of **PI**, a systematic investigation on the pore size and molecular weight effects is further performed. We found that, for a given pore diameter, the adsorption times are nearly 8 orders of magnitude slower than the terminal relaxation times and more than 12 orders of magnitude slower than the segmental times. On the other hand, the molar mass dependence of the characteristic adsorption times ($\tau_{ads} \sim N^{2.6}$) is in good agreement with a scaling theory proposed by de Gennes and later refined by Semenov and Joanny. With respect to the **PI** blend, by taking advantage of the difference in imbibition speeds of the respective homopolymers, the shorter chains penetrate first the nanopores whereas the longer chains enter only at the late stages of the filling process.

Ionic Conductivity in Polyfluorene-Based Diblock Copolymers Comprising Nanodomains of a Polymerized Ionic Liquid and a Solid Polymer Electrolyte Doped with LiTFSI

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The environmental pollution increases the demand for reliable solid-state Li-ion batteries. Mixed ionic and electronic conductors are of great importance, as they can be employed as cathode binder materials in Li batteries.[1] In our earlier study[2], a simple ″stick and jump″ model was proposed to describe the ion transport in mixed conductors based on imidazolium Polymerized Ionic Liquids (PILs) bearing a π-conjugated Polythiophene backbone. In a subsequent effort, diblock copolymer electrolytes based on a π-conjugated polyfluorene (PF) backbone were synthesized comprising nanodomains of a polymerized ionic liquid (PIL) and of a solid polymer electrolyte (SPE).[3] The former consists of a single-ion conductor based on an imidazolium alkyl chain with a $[Br]^-$ counteranion grafted on the PF backbone. The latter consists of short ethylene oxide (EO) chains, grafted on the PF backbone and further doped with LiTFSI. The two nanophases support ionic conductivity, whereas the rigid PF backbone provides the required mechanical stability. In the absence of LiTFSI, ionic conductivity in the PIL nanophase is low and exhibits an Arrhenius temperature dependence. LiTFSI substitution enhances ionic conductivity by about 3 orders of magnitude and further changes to a Vogel−Fulcher−Tammann temperature dependence. However, at ambient temperature, ionic conductivity is lower than in the corresponding PEO/LiTFSI electrolytes. X-ray studies and thermal analysis revealed that the conjugated backbone imparts liquid-crystalline order that can be fine-tuned through the EO side group length. Ionic conductivity measurements performed as a function of pressure identified local jumps of $[Li]^+$ and $[Br]^-$ ions in the respective SPE/PIL nanophases as responsible for the ionic conductivity. Between the two ions, it is $[Li]^+$ that has the major contribution to the ionic conductivity. The current results provide designing rules for new copolymers that comprise two different ionic nanodomains (PIL and SPE) and a conjugated backbone that can further support electronic conduction.

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Effects of nanometer confinement on the self-assembly and dynamics of Poly(*γ*-benzyl-L-glutamate) homopolymers and its copolymers with polyisobutelene

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Synthetic polypeptides play an important role in biomedical sciences because of their exceptional similarity to proteins. The control of their secondary structure and dynamics, especially under confinement, is a challenge for biological applications. Poly(*γ*-benzyl-L-glutamate), a model rigid-rod polymer,[1-3] was studied as a homopolypeptide and as a copolymer with the flexible polyisobutelene (PBLG-*b*-PIB), and investigated in the bulk and under nanometer confinement in aloumina pores with diameters from 400 nm to 40 nm. Confinement affects the persistence length of their secondary structure (α-helices), as well as the coherence length of the hexagonal packing of the helices. A comparison is made on the self-assembly and dynamics of PBLG polymerized directly from the aloumina pore walls[4] and of PBLG infiltrated from the solution state. A reduction in the glass temperature was found in both cases but the reduction was more severe in the former case. The infiltration method affects also the self-assembly and produces less ordered chain configurations. Infiltration from the solution forces the polypeptide to "break" the ideal helices as it enters the pores. In the copolymers PBLG-*b*-PIB, phase mixing of the two blocks reduces the persistence length of the polypeptide secondary structure, whereas nanometer confinement further destabilizes the α-helices and their hexagonal packing. Inevitably, phase mixing and confinement reduces PBLG order. Such effects should be considered when biomacromolecules are entering narrow pores.

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Effect of Confinement on the Dynamics of Monohydroxy Alcohols

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Hydrogen Bonds (HBs) are present in a variety of substances, such as in water, alcohols, and proteins playing a significant role in several physical, chemical, and biological processes. [1] Monohydroxy alcohols are among the simplest hydrogen-bonded systems that can easily be supercooled, allowing the study of HBs by changing their chemical structure. In dielectric loss curves of monohydroxy alcohols, beyond the secondary (Johari-Goldstein β-process) and the primary (α-process – related to the liquid-to-glass temperature) relaxations expected from glass-forming systems, there exists a process (known as the "Debye" process) with dielectric strength that depends strongly on the molecular architecture, temperature and pressure reflecting supramolecular HB assemblies. [2, 3] In this study, we investigate the effect of confinement on the dynamics of three monohydroxy alcohols (1-propanol, 2-ethyl-1-hexanol and 4-methyl-3-heptanol) differing in their chemical structure and, consequently, in the dielectric strength of the "Debye" process. [4] First we employ DFT calculations in bulk 1-propanol to obtain the energetics of linear and ring-like associations composed of up to 5 repeat units. The results show that the ring structures with a low dipole moment (~ 2 D) are energetically preferred. On the other hand, the long-lived *metastable* linear associations have a dipole moment of 2.18 D per repeat unit. The confining media were nanoporous alumina templates covering a broad range of pore diameters (from 400 nm to 20 nm). We find that, irrespective of the molecular architecture, all dynamic processes speed-up under confinement. The characteristic temperatures of freezing for the α and Debye-like processes follow the pore size dependence: $T_{a,D} = T_{a,D}^{bulk} - A/d^{1/2}$, where d is the pore diameter. The slow and α-processes decrease by 6.5 K and 13 K in confined 1-propanol, by 9.5 K and 17 K in confined 2-ethyl-1-hexanol and by 8 K and 21 K in confined 4-methyl-3-heptanol) within the same 25 nm pores. In addition, the slow Debye process in 1-propanol turns non-Debye in 2-ethyl-1-hexanol and 4-methyl-3-heptanol where the signal is dominated by the ring-like supramolecular assemblies. Lastly, we studied the effect of surface treatment of alumina nanopores. Silanization of alumina pore walls recovers the bulk-like dynamic behavior.

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