8th International Conference on

BROADBAND DIELECTRIC SPECTROSCOPY AND ITS APPLICATIONS

Organized by
Institute of Physics,
University of Silesia in Katowice

September 14–19, 2014
Wisła, Poland

BDS 2014

PROGRAMME
& BOOK OF ABSTRACTS

8th International Conference
on BROADBAND DIELECTRIC SPECTROSCOPY
AND ITS APPLICATIONS

Joint Meeting of
The 8th Conference
of The International Dielectric Society
&
The 14th Conference
on Dielectric And Related Phenomena

September 14 – 19, 2014
Wisła (Poland)

Programme
& Book of Abstracts

Edited by Z. Wojnarowska

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The conference is organized by the **Institute of Physics at the University of Silesia** in Katowice (Poland) and supported by the Silesian Center for Education and Interdyscyplinary Research.

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SMCEBI

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PREFACE

The broadband dielectric spectroscopy (BDS) is a powerful method for investigations of molecular dynamics of various materials. It enables to monitor molecular mobility reflected in the relaxation processes over a wide frequency range up to 16 decades, at different temperatures and pressures. BDS finds application in many fields of science and technology. It is successfully employed in studies on (i) the molecular dynamics of liquids, liquid crystals, glasses, disordered crystals, (ii) charge transport in ionic liquids, semiconductors, organic crystals, ceramics, etc., (iii) structural material properties like phase compositions, (iv) non-linear electrical and optical effects. The BDS is also a very useful tool to monitor chemical reactions (including polymerization, tautomerization of drugs, mutarotation of sugars) and phase transitions, e.g. crystallization or vitrification. Consequently, numerous basic and applied topics are studied by dielectric techniques.

The conference provides a platform to discuss these exciting developments.

In detail, the following topics will be addressed:

S1 BDS in relation to other spectroscopic or scattering techniques (Neutron, X-ray, and Light scattering, NMR, IR-spectroscopy, DSC and AC-calorimetry, mechanical and ultrasound spectroscopy)
S2 Terahertz spectroscopy
S3 High pressure BDS
S4 Theory of dielectrics
S5 Glassy dynamics and its scaling
S6 Rotational and translational diffusion in conducting glasses and ionic liquids
S7 Electrode and Maxwell-Wagner polarization
S8 Charge transport and glassy dynamics in confined systems
S9 Dielectric properties of biological systems
S10 Dielectric properties of pharmaceutical systems
S11 Monitoring of chemical reactions and crystallization process
S12 BDS study of ferroelectrics, ceramics, and liquid crystals
S13 Non-linear electrical effects

Programme of the 8th International Conference on Broadband Dielectric Spectroscopy and its Applications, Wisła, Poland, September 14-19, 2014

Sunday 14th September	Monday 15th September		Tuesday 16th September		Wednesday 17th September		Thursday 18th September		Friday 19th September	
Welcome Day	O-1 ↓ O-4	S5 Chairman: Juan Colmenero	O-14 ↓ O-17	Friedrich Kremer Session Chairman: Marian Paluch	O-33 ↓ O-37	S5 Chairman: C. Michael Roland	O-52 ↓ O-56	S6 Chairman: Jeppe C. Dyre	O-72 ↓ O-76	S11 & S7 Chairman: George Floudas
	8:30	Welcome (10)	8:30	Friedrich Kremer (30)	8:30	Juan Colmenero (30)	8:30	Bernhard Roling (30)	8:30	Tiberio Ezquerra (30)
	8:40	Kia L. Ngai (30)	9:00	Tobias Wassermann (Springer) (20)	9:00	Angel Alegria (30)	9:00	James Runt (30)	9:00	Karolina Adrjanowicz (20)
	9:10	Alexei Sokolov (30)	9:20	Michael Wübbenhorst (30)	9:30	Fabienne Barroso-Bujans (20)	9:30	Stella Hensel-Bielowka (20)	9:20	Yasuhito Suzuki (20)
	9:40	Ernst Rössler (30)	9:50	Wilhelm Kossack (20)	9:50	R. J. Sengwa (20)	9:50	Max Fraenkl (20)	9:40	Anatoli Serghei (30)
	10:10	Daniel Fragiadakis (20)	10:10	Kamil Kaminski (20)	10:10	Allisson Saiter (20)	10:10	Shobhna Choudhary (20)	10:10	Avanish Bharati (20)
	10:30	**Coffee break**	10:30	**Coffee break**	10:30	**Coffee break**	10:30	**Coffee break**	10:30	**Coffee break**
	O-5 ↓ O-9	S2 Chairman: Yuri Feldman	O-18 ↓ O-21	Friedrich Kremer Session Chairman: Ernst Rössler	O-38 ↓ O-42	S5 Chairman: Alexei Sokolov	O-57 ↓ O-61	S13 & S4 Chairman: Anatoli Serghei	O-77 ↓ O-82	S12 Chairman: Friedrich Kremer
	11:00	Ryusuke Nozaki (30)	11:00	George Floudas (30)	11:00	C. Michael Roland (30)	11:00	Ranko Richert (30)	11:00	Reimund Gerhard (20)
	11:30	Hiromasa Ito (30)	11:30	Andreas Schönhals (30)	11:30	Jeppe C. Dyre (30)	11:30	Sylwester J. Rzoska (30)	11:20	Aurora Nogales (20)
									11:40	Valerică Raicu (20)
	12:00	Paul Ben Ishai (20)	12:00	Joshua Sangoro (30)	12:00	Andrzej Grzybowski (20)	12:00	Talam Satyanarayana (20)	12:00	Antoni Kocot (20)
	12:20	Kaori Fukunaga (20)	12:30	Martin Treß (30)	12:20	Zaneta Wojnarowska (20)	12:20	Masahiro Nakanishi (20)	12:20	Tristan Putzeys (20)
	12:40	Hiromichi Hoshina (20)			12:40	Kajetan Koperwas (20)	12:40	Shimon E. Lerner (20)	12:40	Bram Vanroy (20)

		13:00	**Lunch**	13:00	**Lunch**	13:00	**Lunch**	13:00	**Lunch**	13:00	**Ending Lunch**
		O-10 ↓ O-13	**S8** **Chairman: Michael Wübbenhorst**	**O-22 ↓ O-25**	**S9** **Chairman: Simone Capaccioli**	**O-43 ↓ O-45**	**Debye Process Session** **Chairman: Ranko Richert**	**O-62 ↓ O-67**	**S10** **Chairman: Kia L. Ngai**		**End of the conference**
		14:30	Simone Napolitano (30)	14:30	Yuri Feldman (30)	14:30	Roland Böhmer (30)	14:30	Simone Capaccioli (30)		
15:00 -...	**Registration**	15:00	Koji Fukao (20)	15:00	Anna Panagopoulou (20)	15:00	Limin Wang (20)	15:00	Katarzyna Grzybowska (20)		
		15:20	Wycliffe Kiprop Kipnusu (20)	15:20	Wojciech Skierucha (20)	15:20	Sebastian Pawlus (20)	15:20	Mohamed Shahin Thayyil (20)		
		15:40	Emmanuel Urandu Mapesa (20)	15:40	Sebastian Emmert (20)	15:40	**Debye Prize (20)**	15:40	Juraj Sibik (20)		
		16:00 ↓ 17:00	**Poster Session (P-1 → P-27) & Coffee break**	16:00 ↓ 17:00	**Poster Session (P-28 → P-51) & Coffee break**	16:00 ↓ 17:00	**Poster Session (P-52 → P-76) & Coffee break**	16:00	W. H. Hunter Woodward (20)		
								16:20	Justyna Knapik (20)		
								16:40	**Coffee break**		
		17:30 -...	**Event for Key Speakers**	**O-26 ↓ O-32**	**S8** **Chairman: Bernhard Roling**	**O-46 ↓ O-51**	**S1** **Chairman: Andreas Schönhals**	**O-67 ↓ O-71**	**S8** **Chairman: Jacek Ulanski**		
				17:00	Apostolos Kyritsis (20)	17:00	Gisèle Boiteux (30)	17:00	Yoshihito Hayashi (30)		
				17:20	Pit Sippel (20)	17:30	Jacek Ulanski (30)	17:30	Keisuke Tominaga (20)		
				17:40	Emmanuel Logakis (20)			17:50	Silviu-Sorin Tuca (20)		
18:00 - ...	**Welcome Party**			18:00	Roberto Macovez (20)	18:00	Cong Yu Bao (20)				
				18:20	Gerardo Martinez (20)	18:20	Josef Bartos (20)	18:10	Prabhakar Undre (20)		
				18:40	G. Govindaraj (20)	18:40	Helena Švajdlenková (20)				
		19:00 - ...	**Dinner**	19:00	Yuichi Anada (20)	19:00	Gamal Turky (20)	19:00	**Piano Concerto**		
				19:30	**Dinner**						
				21:00 - ...	**IDS Board Meeting**	20:00	**Bonfire**	20:00	**Conference Dinner**		

MONDAY

8:30 **Welcome**

Session S5: Glassy dynamics and its scaling, 8:40 – 10.30

Chairman: Juan Colmenero

8:40
O-1
An Alernative Explanation of of the Change in T-dependence of the Effective Debye-Waller Factor at Tc or TB
K.L. Ngai and J. Habasaki

9:10
O-2
Quantum Effects in the Glass Transition and the „Superstrong“ Behavior of Deeply Supercooled Water
A.P. Sokolov, V.N. Novikov, A.L. Agapov, R. Richert

9:40
O-3
From boiling point down to Tg – Evolution of the dynamic susceptibility of molecular and ionic liquids
B. Schmidtke, N. Petzold, R. Kahlau, B. Pötzschner, E.A. Rössler

10:10
O-4
Molecular dynamics simulations of the β relaxation in simple rigid molecules
D. Fragiadakis and C.M. Roland

Cofee break, 10:30 – 11.00

Session S2: Terahertz spectroscopy, 11:00 – 13.00

Chairman: Yuri Feldman

11:00
O-5
Temporal and spatial structures of molecular dynamics in glass forming alcohols
Ryusuke Nozaki

11:30
O-6
Overview of Nonlinear optics based efficient monochromatic THz-wave generation and detection
Hiromasa Ito, Hiroaki Minamide, Shin'ichiro Hayashi, and Kouji Nawata

12:00 **A Proton Cascade as the Origin of Water's Dielectric Relaxation**
O-7 Paul Ben Ishai, A. Puzenko and Yu. Feldman

12:20 **Dielectric measurement in the terahertz gap**
0-8 K. Fukunaga, M. Mizuno, T. Tosaka, K. Fujii, K. Sasaki, S. Watanabe

12.40 **Higher Order Structure of Polymers Studied by Terahertz Spectroscopy**
0-9 Hiromichi Hoshina

Lunch, 13:00 – 14:30

Session S8: Charge transport and glassy dynamics in confined systems, 14:30 – 16.00

Chairman: Michael Wübbenhorst

14:30 **Interparticle correlation and irreversible adsorption improve glass stability under confinement**
0-10 Bram Vanroy, Xiaoming Jiang, Michael Wübbenhorst, Wenbing Hu, Simone Napolitano

15:00 **Molecular dynamics of single and stacked thin polymer films**
0-11 Koji Fukao, Natsumi Taniguchi, Tatsuhiko Hayashi, Paul Sotta, Didier Long

15:20 **Molecular Order and Dynamics of Nanometric Thin Layers of Poly(styrene-b-1,4-isoprene) Diblock Copolymers**
0-12 Wycliffe Kiprop Kipnusu

15.40 **Molecular dynamics of itraconazole confined in thin supported layers**
0-13 Emmanuel Urandu Mapesa, M. Tarnacka, E. Kamińska, K. Adrjanowicz, M. Dulski, W. Kossack, M. Tress, W. K.Kipnusu, K.Kamiński, and F.Kremer

Cofee break & Poster session (P-1 to P-27), 16:00 – 17.00

Event for Key Speakers, 17.30 - ….

Dinner, 19:00

TUESDAY

Session: Friedrich Kremer Session, 8:30 – 10.30
Chairman: Marian Paluch

8:30 0-14	**The interplay between intra- and inter-molecular dynamics as studied by Broadband Dielectric – and Fourier-Transform Infrared – Spectroscopy** <u>F. Kremer</u>, W. Kossack, W.K. Kipnusu, E.U.Mapesa and M. Tress
9:00	<u>Tobias Wassermann - Springer</u>
9:20 0-15	**Low temperature deposited glycerol - some new insights from BDS and specific heat spectroscopy** <u>Michael Wübbenhorst</u>, Angeline Kasina
9:50 0-16	**Mutarotation of L-fucose as monitored by Dielectric and Infrared spectroscopy** <u>Wilhelm Kossack</u>, Wycliffe Kiprop Kipnusu, Kamil Kaminski, Friedrich Kremer
10:10 0-17	**High pressure studies on polymerization of epoxy amine systems** <u>K. Kaminski,</u> M. Tarnacka, O. Madejczyk, M. Dulski, M. Wikarek, S. Pawlus, K. Adrjanowicz, and M. Paluch

Cofee break, 10:30 – 11.00

Session: Friedrich Kremer Session, 11:00 – 13.00
Chairman: Ernst Rössler

11:00 **Local Composition and Dynamic Heterogeneity in Polymer Blends**
0-18 George Floudas

11:30 **Molecular dynamics of discotic liquid crystals in the bulk and embedded in nanochannels**
0-19 Andreas Schönhals

12:00 **Structural dynamics and charge transport in deep eutectic mixtures**
0-20 Tyler Cosby, Phillip Griffin, Roberto Benson, Joshua R. Sangoro

12:30 **Glassy Dynamics of Condensed Isolated Polymer Chains**
0-21 Martin Tress, Emmanuel U. Mapesa, Manfred Reiche and Friedrich Kremer

Lunch, 13:00 – 14:30

Session S9: Dielectric properties of biological systems, 14:30 – 16.00
Chairman: Simone Capaccioli

14:30 **The dielectric response of interfacial water – from the ordered structures to the single hydrated shell**
0-22 Yuri Feldman, Alexander Puzenko, Paul Ben Ishai, and Anna Gutina (Greenbaum)

15:00 **Dynamics of protein hydration water over wide ranges of hydration level. Globular versus fibrous proteins**
0-23 A. Panagopoulou, D. Aravopoulou, O. Vassiliadi, A. Kyritsis, P. Pissis

15:20 **Soil bound water/free water temperature effect determined by time domain reflectometry**
0-24 Wojciech Skierucha, Andrzej Wilczek, Agnieszka Szypłowska, Anna Nakonieczna, Marcin Kafarski

15.40 **Terahertz spectroscopy on amino acids**
0-25 Sebastian Emmert, Martin Wolf, Peter Lunkenheimer, Alois Loidl

Cofee break & Poster session (P-28 to P-51), 16:00 – 17.00

Session S8: Charge transport and glassy dynamics in confined systems, 17:00 – 19.20

Chairman: Bernhard Roling

17:00 **Interfacial effects in polydimethylsiloxane (PDMS) based nanocomposites: dielectric and calorimetric studies**
O-26 Apostolos Kyritsis, Panagiotis Klonos, Polycarpos Pissis

17:20 **Broadband dielectric spectroscopy of ionic liquids**
O-27 P. Sippel, M. Aumüller, S. Krohns, P. Lunkenheimer, A. Loidl

17:40 **X-ray induced TSC experiments on LDPE films: determination of trapping parameters and influence of antioxidants addition**
O-28 Emmanuel Logakis, Lorenz Herrmann, Thomas Christen

18:00 **Intrinsic and water-induced relaxation dynamics and conductivity of organic nanoporous materials and thin films**
O-29 Roberto Macovez, Manesh Zachariah, Efstratia Mitsari, Pragya Tripathi, Michela Romanini, Panagiota Zygouri, Dimitrios Gournis, Maria Del Barrio, and Josep Lluís Tamarit

18:20 O-30
Dielectric Relaxation of PU/acrylic waterborne hybrid adhesives
Gerardo Martinez Rugerio, Arantxa Arbe, Juan Colmenero, Angel Alegría

18:40 O-31
Novel non-Debye relaxation dynamics and analysis of dielectric loss of glycerol and ac conductivity of β-AgI
G. Govindaraj

19:00 O-32
Diversity of Microstructure of Polymer Solid Investigated by Motion of Impurity Ions
Yuichi Anada

Dinner, 19:00

IDS Board Meeting, 21:00

WEDNESDAY

Session S5: Glassy dynamics and its scaling, 8:30 – 10.30
Chairman: C. Michael Roland

8:30 O-33
Thermo Stimulated Depolarization Current Techniques applied to the study of chain dynamics: Evidence of non-exponential modes relaxation
Juan Colmenero, Silvia Arrese-Igor and Angel Alegria

9:00 O-34
Non-equilibrium effects on the normal mode relaxation: Chain dynamics below Tg
Angel Alegria, Silvia Arrese-Igor and Juan Colmenero

9:30 O-35
Novel cyclic polyethers with rich dynamics
Fabienne Barroso-Bujans, Angel Alegría and Juan Colmenero

9:50 O-36
Effects of solution processing techniques on dielectric properties and structures of PEO–PMMA blend films

R.J. Sengwa, Shobhna Choudhary

10:10 O-37 **Cooperativity and Dynamic Heterogeneity in polymer glasses : Comparison of temperature fluctuation approaches**
Bidur RIJAL, Laurent DELBREILH, Andreas SCHÖNHALS, Allisson Saiter

Cofee break, 10:30 – 11.00

Session S5: Glassy dynamics and its scaling, 11:00 – 13.00
Chairman: Alexei Sokolov

11:00 O-38 **Dynamic correlations and heterogeneity in the primary and secondary relaxations of molecular liquids**
C.M. Roland, D. Fragiadakis, and R. Casalini

11:30 O-39 **Why does entropy appear to control the relaxation time?**
Jeppe C. Dyre

12:00 O-40 **From the density scaling law to proper interrelations between time and length scales of molecular dynamics and entropy near the glass transition**
Andrzej Grzybowski, K. Grzybowska, K. Koperwas, M. Paluch

12:20 O-41 **Scaling behavior of the conductivity relaxation in supercooled ionic liquids**
Z. Wojnarowska, A. Grzybowski, M. Paluch

12:40 O-42 **Does the thremodynamic scaling idea and the concept of the dynamic heterogeneity can improve the Prigogine-Defay ratio?**
K.Koperwas, A. Grzybowski, and M. Paluch

Lunch, 13:00 – 14:30

Session: Debye process session, 14:30 – 16.00
Chairman: Ranko Richert

14:30 O-43 **Oligomeric shear modes, mixing enhanced susceptibility, low-frequency cut-off, and other surprises in Debye-type liquids**
Gainaru, S. P. Bierwirth, J. Lueg, K. Moch, P. Münzner, R. Böhmer

15:00 O-44 **Unusual dynamics in glass forming mixtures of water with a Debye liquid**
Li-Min Wang, Xin Li, Zeming Chen, Wenkang Tu and Yanqin Gao

15:20 O-45 **Mixtures of 2-Ethyl-1-hexanol with 2-Ethylhexyl bromide under pressure. Does compression influence the dynamics of supramolecular structures?**
Sebastian Pawlus, Michał Wikarek, Marian Paluch, Catalin Gainaru and Roland Böhmer

Debye Prize, 15:40

Cofee break & Poster session (P-52 to P-76), 16:00 – 17.00

Session S1: BDS in relation to other spectroscopic or scattering techniques (Neutron, X-ray, and Light scattering, NMR, IR-spectroscopy, DSC and AC-calorimetry, mechanical and ultrasound spectroscopy), 17:00 – 19.20

Chairman: Andreas Schönhals

17:00 O-46 **Relationship between Morphology, Mechanical and Electrical Properties in Structured Elastomers**
Boiteux G., Salaeh S., Nakason C., Gain O., Cassagnau P.

17:30 O-47 **Raman and dielectric spectroscopic studies of molecular interactions in poly(vinyl methyl ether) hydrogels at low temperatures**
Marcin Pastorczak, Gustavo Dominguez-Espinosa, Lidia Okrasa, Marek Pyda, Marcin Kozandeecki, Slawomir Kadlubowski, Janusz M. Rosiak and Jacek Ulanski

18:00 O-48 **Cellulose Acetate/Plasticizer Systems: Structure, Morphology and Dynamics**
Cong Yu BAO, Koji FUKAO, Paul SOTTA, Caroll VERGELATI and Didier R. LONG

18:20 O-49 **Resolving the segmental dynamics in oligomeric 1,4-poly(isoprene)s by selective effect of polar small molecule organic compound**
J. Bartoš, H. Švajdlenková, S.Arrese-Igor, A.Alegría

18:40 O-50 **Relaxation data on m-Toluidine in relation to free volume and rotation dynamics from external probing PALS and ESR techniques**
H. Švajdlenková, O. Šauša, A. Ruff, P. Lunkenheimer, A. Loidl and J. Bartoš

19:00 O-51 **Dielectric behavior of hyperbranched polyamide-amine/kaolinite nanocomposites**
Sh. Said, A. Ghoneim, M. Abdel Rehim H. Osman, G. Turky, A. Schoenhals

Bonfire, 20:00

THURSDAY

Session S6: Rotational and translational diffusion in conducting glasses and ionic liquids, 8:30 – 10.30

Chairman: Jeppe C. Dyre

8:30 **$Li_{10}SnP_2S_{12}$: An Affordable Lithium Superionic Conductor**
O-52
Philipp Bron, Sebastian Johansson, Jörn Schmedt auf der Günne, Klaus Zick, Stefanie Dehnen, Bernhard Roling

9:00 **Dynamics of Precise Ethylene Acid Copolymers and Ionomers**
O-53
J. Runt, U.H. Choi, M. Soccio, H.Q. Masser, L.R. Middleton, F. Buitrago, K.I. Winey, J. Cordaro and K. Wagener

9:30 **Peculiarities in dynamics of supercooled ionic liquids studied by broadband dielectric spectroscopy**
O-54
Stella Hensel-Bielowka, Zaneta Wojnarowska, Katarzyna Grzybowska, Marian Paluch, Marzena Dzida, Andreas Heintz, Tim Peppel, Martin Köckerling

9:50 **Direct approach for impedance analysis of ion conducting glasses**
O-55
Max Fraenkl

10:10 **Dielectric and structural properties of ultrasonic and microwave irradiated plasticized polymer nanocomposite electrolyte**
O-56
Shobhna Choudhary, R.J. Sengwa

Cofee break, 10:30 – 11.00

Sessions S13 & S4: Non-linear electrical effects & Theory of dielectrics 11:00 – 13.00

Chairman: Anatoli Serghei

11:00 **Liquid and Glassy Dynamics by Non-Linear Dielectric Experiments**

O-57 Subarna Samanta and Ranko Richert

11:30 **Nonlinear Dielectric Spectroscopy in Critical Liquids**
O-58 Sylwester J. Rzoska and Aleksandra Drozd-Rzoska

12:00 **Dielectric Investigations on Manganese Ions Doped Tellurite Antimony Borate Glasses**
O-59 Talam Satyanarayana, G.S. Ajay Kumar Reddy, Gunnam Nagarjuna

12:20 **Temperature Dependences of Dielectric Intensities of Bound Systems**
O-60 Masahiro Nakanishi

12:40 **Meyer-Neldel Compensation as a feature of the Johari-Goldstein β-relaxation**
O-61 Shimon E. Lerner, Paul Ben Ishai, Yuri Feldman

Lunch, 13:00 – 14:30

Session S10: Dielectric properties of pharmaceutical systems, 14:30 – 16.40

Chairman: Kia L. Ngai

14:30 **Cooperative and local dynamics of amorphous pharmaceuticals under cooling, compression, ageing**
O-62 S. Capaccioli, D. Prevosto, K.L. Ngai, Wenkang Tu and Li-Min Wang

15:00 **Dynamic heterogeneity of ionic and non-ionic drugs near the glass transition**
O-63 Katarzyna Grzybowska, A. Grzybowski, Z. Wojnarowska, K. Kolodziejczyk, and M. Paluch

15:20 **Relaxation Processes in Glass Forming Pharmaceuticals and its Role on Amorphous Stability**
O-64 M. Shahin Thayyil, S. Capaccioli, U. Sailaja, M. Sahra, K.L. Ngai

15.40 **Terahertz spectroscopy of H-bonded glass-forming liquids and drugs**
O-65 Juraj Sibik and J. Axel Zeitler

16:00 **Determination of the Glass Transition Temperature of Drug Dispersions via Dielectric Spectroscopy**
O-66 W. H. Hunter Woodward & Kevin P. O'Donnell

16:20 **On the physical stability of amorphous pharmaceuticals: dielectric and calorimetric studies of EZB drug**
O-67 J. Knapik Z. Wojnarowska, K. Grzybowska, W. Sawicki, K. Wlodarski, M. Paluch

Cofee break, 16:40 – 17.00

Session S8: Charge transport and glassy dynamics in confined systems 17:00 – 18.30

Chairman: Jacek Ulanski

17:00 **Principles of Dielectric Blood Coagulometry**
O-68 Yoshihito Hayashi

17:30 **Temperature and Hydration Dependence of Complex Dielectric Spectra of Lysozyme from GHz to THz Frequency Region**
O-69 Naoki Yamamoto, Atuso Tamura Keisuke Tominaga

17:50 **A Microwave Microscope for Complex Impedance and Permittivity Operating From 1-20 GHz in Liquid for Life Science Investigations**
O-70 Silviu-Sorin Tuca, Georg Gramse, Manuel Kasper, Peter Hinterdorfer, Giorgio Badino, Ferry Kienberger

18:10 **Evaluation of Salivary Dielectric Properties in Oral Cancer (OSCC) Through Time Domain Reflectometry at Microwave Region: The Future Alternative for Diagnosis and Treatment**
O-71

A. Ranade, P. B. Undre, S. R. Barpande, J. V. Tupkari and S.C. Mehrotra

Piano Concerto, 19:00 – 20.00

Conference dinner, 20:00 - …

FRIDAY

Sessions S11 & S7: Monitoring of chemical reactions and crystallization process & Electrode and Maxwell-Wagner polarization 8:30 – 10.30

Chairman: George Floudas

8:30
O-72
Crystallization of aromatic polyesters by monitoring the dielectric β-relaxation: a quasi real time full dielectric method
M. Soccio, N. Lotti, A. Munari, A. Nogales, T.A. Ezquerra

9:00
O-77
Efect of High Pressure on the Crystallization Behaviour of Supercooled Liquids
Karolina Adrjanowicz, Andrzej Grzybowski, Kamil Kaminski, Jürgen Pionteck, Stefan Jurga and Marian Paluch

9:20
O-74
Effect of Confinement on Polymer Crystallization and on the Local Polymer Dynamics
Yasuhito Suzuki, Hatice Duran, Martin Steinhart, Hans-Jürgen Butt and George Floudas

9:40
O-75
Electrical and dielectric properties of composite materials: characteristic frequencies and scaling laws
M. Samet, A. Houachtia, A. Kallel, G. Boiteux, G. Seytre, A. Serghei

10:10
O-76
Tailoring dielectric properties of bi-phasic polymeric materials by tuning their morphology
Avanish Bharati, Ruth Cardinaels, Michael Wübbenhorst, Paula Moldenaers

Cofee break, 10:30 – 11.00

Session S12: BDS study of ferroelectrics, ceramics, and liquid crystals 11:00 – 13.00

Chairman: Friedrich Kremer

11:00 **Dielectric Spectroscopy of macrocopic sample resonances for all-electrical measurements of electro-mechanical, electrical and mechanical properties in polymeric ferro- or piezoelectrets**
O-77 Reimund Gerhard, Xunlin Qiu and Werner Wirges

11:20 **Nanostructured Ferroelectric Polymers. Implications on ferroelectricity and relaxation**
O-78 D.E. Martinez-Tong M Soccio, MC García-Gutiérrez, D Rueda, A. Sanz, A. Nogales, T.A. Ezquerra

11:40 **Dielectric properties of biological cells and macromolecules: an overview with some new insights**
O-79 Valerică Raicu

12:00 **Polar order and collective relaxation mode in biaxial nematic phase of bend core molecules**
O-80 Antonii Kocot and K Merkel

12:20 **Adsorption of Poly(ethylene terephthalate)-chains to an aluminium substrate studied via pyroelectric depth profiling and dielectric spectroscopy**
O-81 T. Putzeys, B. Vanroy, M. Wübbenhorst

12:40 **Molecular dynamics of confined poly(ethyl methacrylate) investigated by Broadband Dielectric Spectroscopy**
O-82 Bram Vanroy, Simone Napolitano, Michael Wübbenhorst

Ending lunch, 13:00 – 14.30

POSTER PRESENTATIONS

MONDAY: 16:00 – 17:00

Session S1: BDS in relation to other spectroscopic or scattering techniques (Neutron, X-ray, and Light scattering, NMR, IR-spectroscopy, DSC and AC-calorimetry, mechanical and ultrasound spectroscopy)

P-1 **Novel themoresponsive systems based on poly(methoxy diethylene glycol acrylate) copolymers**
D. Aravopoulou, K. Bika, K.Kyriakos, L. Augsbach, Z. Di, A. Miasnikova, A. Laschewsky, C.M. Papadakis and A. Kyritsis

P-2 **Role of H-bonds in the dynamics of concentrated solution of PDMAEMA**
Guido GORACCI, Angel ALEGRIA, Juan COLMENERO, Arantxa ARBE

P-3 **Adhesion analysis of Alfa fibres reinforced unsaturated polyester hybrid composites using the dielectric analyzer and the tensile testing**
A. Triki, Med .A. Omri, M. Guicha, Med Ben Hassen, M. Arous And A. Kallel

P-4 **Conductivity, dielectric relaxation, and nanoscale organization in binary mixtures of amphiphylic molecules**
Andrea Mandanici, Vincenzo Turco Liveri and Pietro Calandra

P-5 **Molecular dynamics of gradient poly(n-butyl acrylate-co-methyl methacrylate)**
Lidia OKRASA, Krzysztof MATYJASZEWSKI

P-6 **Study of molecular mobility in poly(lactic acid) / silica hybrids**
Christos Pandis, Sotiria Kripotou, Ioannis Katagas, José Luis Gómez Ribelles and Apostolos Kyritsis

P-7 **Dielectric relaxation in supramolecular polymeric systems**
N. Lou, A. P. Sokolov and H. M. Xiong

P-8 **Broadband dynamics in mixtures of 2-ethyl-1-hexanol and 2-ethyl-1-hexyl bromide**
M. Wikarek, S.Pawlus, M.Paluch

P-9 **Molecular Dynamics of Linear Poly(N-isopropylacrylamide) in Water Below and Above the Phase Transition: A Broadband Dielectric Relaxation Spectroscopy Study**
Marieke Füllbrandt, Elena Ermilova, Asad Asadujjaman, Ralph Hölzel, Frank F. Bier, Regine von Klitzing, and Andreas Schönhals

P-10 **Dielectric properties of organic photovoltaics based on polymer:perylene diimide blends**
A. Iosifidis, P. Keivanidis, G. Floudas

P-11 **Calorimetric glass transition of ultrathin poly-2-vinyl pyridine films**
Sherif Madkour, Huajie Yin, Andreas Schönhals

P-12 **Physical insight into kinetics of tautomerization of Etoricoxib drug**
M. Rams-Baron, Z. Wojnarowska, M. Dulski, P. Włodarczyk, A. Ratuszna, M. Paluch

P-13 **Dielectric Relaxation in Pure Amines through Time Domain Reflectometry Technique**
P. B. Undre, P. W. Khirade and S.C. Mehrotra

Sessions S2 & S13: Theory of dielectrics & Non-linear electrical effects

P-14 **Theoretical investigation of dielectric relaxation in ice H20 Ih**
Ivan Popov, Alexander Puzenko, Airat Khamzin and Yuri Feldman

P-15 **Linear and nonlinear impedance in BiV ceramics and BiV-SBO glass-ceramics**
Szreder N.A., Barczyński R.J.

Session S5: Glassy dynamics and its scaling

P-16 **Structure and Dynamics of Poly(styrene-b-1,4-isoprene) Diblock Copolymers under 1- and 2-D Confinement**

Mahdy M. Elmahdy, Wycliffe K. Kipnusu, Detlef-M. Smilgies, Jianqi Zhang, Christine Papadakis and Friedrich Kremer

P-17 **Water-rich glycerol mixtures; The origin of the liquid-liquid transformation**
Anna Greenbaum (Gutina), Ivan Popov, Alexander Puzenko and Yuri Feldman

P-18 **Segmental and local dynamics of stacked thin films of poly(methyl methacrylate)**
Tatsuhiko Hayashi and Koji Fukao

P-19 **Ultra-stable glass properties studied by simultaneous dielectric and ac-calorimetric measurements**
Angeline Kasina, Michael Wübbenhorst

P-20 **Kinetics of cold crystallization of 4-cyano-3-fluorophenyl 4-butylbenzoate (4CFPB) glass forming liquid crystal in microscopic, DSC and dielectric studies**
Tomasz Rozwadowski, Maria Massalska-Arodź, Katarzyna Grzybowska, Łukasz Kolek, Andrzej Bąk, Krystyna Chłędowska

P-21 **Fragile-to-strong transition of water and glass transition temperature in aqueous mixtures**
Kaito Sasaki, Masahiko Miyara, Rio Kita, Naoki Shinyashiki and Shin Yagihara

P-22 **Temperature-Volume Entropic Model for Structural Relaxation Times and Viscosities of Glass Formers**
Elzbieta Masiewicz, A. Grzybowski, A. P. Sokolov, and M. Paluch

Session S7: Electrode and Maxwell-Wagner polarization

P-23 **Electrode polarization vs. Maxwell-Wagner-Sillars interfacial polarization: scaling laws, similarities and differences**
M. Samet, A. Kallel, G. Boiteux, G. Seytre, A. Serghei

P-24 **Polymeric materials with giant permittivity**
V. Levchenko, G. Boiteux, E. Beyou, P. Alcouffe, G. Seytre, A. Serghei

P-25 **Influence of DC bias electric field on a low frequency dielectric relaxation in a transformer oil based ferrofluid**
M. Rajnak, J. Kurimsky, B. Dolnik, P. Kopcansky, M. Timko

P-26 **Method for Estimating Oil Viscosity via Dielectric Spectroscopy**
W.H. Hunter Woodward, Hagar Zohar, Robbyn Prange, Rakesh Srivastava, David Brennan, Suraj Deshmukh, & Jeff Mitchell

P-27 **Electrical and dielectric properties of composite materials: the role of interfaces and interphases**
M. Samet, A. Kallel, G. Boiteux, G. Seytre, A. Serghei

TUESDAY: 16:00 – 17:00

Session S9: Dielectric properties of biological systems

P-28 **A Dielectric Spectroscopy Study of Quenched Milk**
Daniel Agranovich, Paul Ben Ishai, Gil Katz, Dror Bezman and Yuri Feldman

P-29 **Effect of fish skin collagen on selected electric parameters of human skin in vivo**
Gauza M., Kubisz L., Dańczak-Pazdrowska A., Polańska A., Hojan-Jezierska D., Adamski Z., Osmola-Mańkowska A., Pankowski E.

P-30 **Dielectric Spectroscopic Study on Hydrated Stratum Corneum**
Masahiro Nakanishi, Anna Greenbaum (Gutina), Yegor Domanov, Florian Formanek, Bernard Querleux and Yuri Feldman

P-31 **Dielectric properties of juices and their variation over time during storage**
Anna Nakonieczna, Agnieszka Szypłowska, Andrzej Wilczek, Marcin Kafarski, Wojciech Skierucha

P-32 **Specific electric conductivity dispersion of vena saphena magna**
E. Pankowski, M. Pankowska, A. Gierszewska, L. Kubisz, M. Gauza

P-33 **Hydration of complexes between sodium copper chlorophyllin and serum albumines**
D. A. Pesina, O. V. Khorunzhaya, V. A. Kashpur, A. V. Shestopalova

P-34 **The dynamics and kinetics of water in a protein hydration shell**
Yael Kurzweil Segev, Anna (Gutina) Greenbaum, Masahiro Nakanishi, Alexei Sokolov and Yuri Feldman

Session S8: Charge transport and glassy dynamics in confined systems

P-35 **Dynamics of cis-1,4 Polyisoprene and 1,4 Polybutadiene confined to Nanoporous Alumina**
S. Alexandris, G. Sakellariou, M. Steinhart , G. Floudas

P-36 **Dynamics and phase transitions of zeptograms of matter**
Afef Houachtia, Gisèle Boiteux, Jean-François Gerard, Anatoli Serghei

P-37 **Relaxation phenomena and electrophysical properties vs. structural organization of the electroactive hybrid polymers containing ionic liquids**
Iurzhenko M., Boiteux G., Mamunya Ye., Serghei A., Lebedev E., Sverdliakovs'ka O., Shtompel V., Chervakov O.

P-38 **Structure-Property relationships of Nanocomposites Based on Epoxy and Layered Double Hydroxides**
Jing Leng, Franziska Emmerling, De-Yi Wang, and Andreas Schönhals

P-39 **Structure-Property relationships of Nanocomposites Based on Polylactide and Layered Double Hydroxides**
Jing Leng, Purv Purohit, De-Yi Wang, and Andreas Schönhals

P-40 **Orientational degrees of freedom of pure and water-containing fullerene derivatives**
Efstratia Mitsari, Manesh Zachariah, Michela Romanini, Panagiota Zygouri, Dimitrios Gournis, Josep Lluis Tamarit, María Del Barrio, Roberto Macovez

P-41 **Molecular Dynamics of nanometric Poly(2-Vinyl-Pyridine) brushes with varying grafting density**
N. Neubauer, M. Treß, R. Winkler, P. Uhlmann, M. Reiche and F. Kremer

P-42 **Dielectric behaviour study of silica-containing polyimide and poly(amide imide) hybrid films**
Corneliu Hamciuc, Marius Olariu, Elena Hamciuc, Valentina-Elena Musteata

P-43 **Dielectric Relaxation Behavior of Thin Films of Polyamide Random Copolymers**
Natsumi TANIGUCHI, Koji FUKAO, Paul Sotta, Didier Long

P-44 **Water–Triggered Conduction and Polarization Effects in a Hygroscopic Fullerene Salt**
Manesh Zachariah, Efstratia Mitsari, Michela Romanini, Panagiota Zygouri, Dimitrios Gournis, Maria Del Barrio, Josep Lluís Tamarit, and Roberto Macovez

P-45 **The role of size and charge delocalization in dissociation and charge transport in solvents of low polarity**
Ralph Moritz, George Zardalidis, Hans-Jurgen Butt, Manfred Wagner, Klaus Müllen, and George Floudas

Sessions S10 & S11 : Dielectric properties of pharmaceutical systems & Monitoring of chemical reactions and crystallization process

P-46 **Octaacetylmaltose - a very effective agent to improve physical stability of amorphous indomethacin**
E. Kaminska, K. Adrjanowicz, D. Zakowiecki, M. Tarnacka, L. Hawelek, M. Dulski, I. Kaczmarczyk- Sedlak, K. Kaminski

P-47 **Dielectric and thermal study of the interfacial dynamics and crystallization in polymer nanocomposites**
Panagiotis Klonos, Apostolos Kyritsis, Polycarpos Pissis

P-48 **Dielectric properties and conductivity of the crosslinked elastomeric polyurethane containing the small additions of the single-wall carbon nanotubes**
Novikov G.F., Rabenok E.V., Estrin Ya.I., Badamshina E.R.

P-49 **Impact factors on the mutarotation process in supercooled monosugars**
A. Cecotka, M. Paluch, K. Kamiński, and K. Grzybowska

P-50 **Molecular dynamics of itraconazole at different thermodynamic conditions**
M. Tarnacka, K. Kołodziejczyk, K. Grzybowska, K. Adrjanowicz, J.Piontek, K. Kamiński, A. Kocot, and M.Paluch

P-51 **Isothermal cold crystallization kinetics study of sildenafil**
K. Kolodziejczyk, K. Grzybowska, Z. Wojnarowska, M. Dulski, L. Hawelek, M. Paluch

WEDNESDAY, 16:00 – 17:00

Session S12: BDS study of ferroelectrics, ceramics, and liquid crystals

P-52 **Photodielectric Properties of the Poly[NiSalen] Metallopolymer Structures**
V.T. Avanesyan, M.U. Puchkov

P-53 **Dielectric spectroscopy of bismuth niobate powders prepared by solid state reaction**
L. C. Costa, M. P. F. Graça, C. S. Ferreira

P-54 **Impedance and modulus studies of ceramic oxide $Ba_2Co_2Fe_{12}O_{22}$(Co2Y) doped with V_20_5**
M.M. Costa, J.R. S. Miranda, P. M. V. Almeida, C. B. Gozzo, G. F. M. Pires, Jr., A.J.M Sales and A. S. B. Sombra

P-55 **Study impedance spectroscopy of MgO addition on the ceramic matrix BBT**
M.M. Costa, C. B. Gozzo, P. M. V. Almeida,M.A.S. Silva, A.J.M Sales,P.M.O Silva, A.S.B. Sombra

P-56 **Dielectric properties of (Bi1-xFex)NbO4 ceramics prepared by Sol-Gel method**
S. Devesa, M. P. F. Graça, L. C. Costa

P-57 **Dielectric measurements on Er3+/Yb3+ co-doped tungsten-Yttrium tellurite glasses**
M.P.F. Graça, P.R. Prezas, M.J. Soares, L. C. Costa

P-58 **Magneto-Dielectricity and Quantum fluctuations in $Ca_{0.90}Li_{0.10}Cu_3Ti_4O_{12}$**
Jitender Kumar and A.M.Awasthi

P-59 **Linear Dielectric Dispersion as a General Phenomenon in Solid Dielectrics**
Gavrilova N.D., Lotonov A.M., Novik V.K., Vorobiev A.V., Malyshkina I.A.

P-60 **Effect of electrode material on space charge relaxation in ferroelectric Vinylidene Fluoride – Tetrafluoroethylene copolymer**
V.V. Kochervinskii, I.A. Malyshkina, E.V. Chubunova, Yu.Yu. Lebedinskii, A.S. Pavlov

P-61 **Dielectric properties of thermosensitive polyelectrolyte hydrogels**
I.A. Malyshkina, E.E. Makhaeva, A.V. Yuganova

P-62 **Broadband Dielectric Relaxation of P(VDF-TrFE) Ferroelectric Nanoparticles**
D. E. Martinez-Tong, M Soccio, A. Sanz, A. Nogales, T.A. Ezquerra

P-63 **Water dynamics in phosphoric acid-based geopolymers**
H. Douiri, S. Baklouti, M. Arous, Z.Fakhfakh

P-64 **Dielectric properties of nanocomposites based on acrylic copolymer and cellulose whiskers**
I. Kaddoussi, A. Ladhar, M. Arous, S. Boufi, A. Kallel

P-65 **The influence of cellulose nanowhiskers on the thermal and dielectric properties of natural rubber based nanocomposite films**
A. Ladhar, M. Arous, H. Kaddami, M. P. F. Graçac, M. Raihane, L. C. Costa, A. Kallel

P-66 **Effect of coupling agent on the dielectric properties of low density polyethylene / short palm lignocellulosic fibers composites**
S. Hrichi, A. Ladhar, M. Arous, H. Kaddami, M. Raihane, A. Kallel

P-67 **Effect of magnetic field and lysozyme concentration on the dielectric properties of magnetic lyotropic liquid crystal**
P. Kopcansky, J.Jadzyn, J. Swiergel, J. Majorosova, Z. Gazova, K. Siposova, M. Timko, M. Rajnak, O.V. Kovalchuk, T.M. Kovalchuk

P-68 **Dielectric spectroscopy of Sodium Ferrite prepared by Sol-Gel method**
S. Soreto Teixeira, M. P. F. Graça, L. C. Costa

P-69 **Dielectric spectroscopy of the lacunar Ca_2MnO_{4}-δ system**
M. A. Valente,N. Chihaoui, M. Bejar, E. Dhahri, L. C. Costa, M. P. F. Graça

P-70 **Temperature dependent dielectric anomalies in Te(IV) doped Calcium Copper Titanate ($CaCu_3Ti_{3.8}Te_{0.2}O_{12}$)**
Nabadyuti Barman, K.B.R Varma

Session S6: Rotational and translational diffusion in conducting glasses and ionic liquids

P-71 **Electrophysical properties of ionic-conductive polymer systems on the base of an aliphatic epoxy oligomer and $LiClO_4$**
Boiteux G., Matkovska L.K., Iurzhenko M.V., Matkovska O.K., Mamunya Ye.P., Lebedev E.V., Serghei A

P-72 **Application of imidazolium ionic liquids as conductivity and processing enhancers in the nitrile rubber composites**
Gisele Boiteux, Anna Marzec, Anna Laskowska, Marian Zaborski, Olivier Gain, Anatoli Serghei

P-73 **Analysis of the conductivity of conjugated polymer/fullerene based blends by dielectric spectroscopy**
Jing Cui, Daniel E Martínez-Tong, Alejandro Sanz, Tiberio A Ezquerra, Aurora Nogales

P-74 **The role of size and charge delocalization in dissociation and charge transport in solvents of low polarity**
Ralph Moritz, George Zardalidis, Hans-Jurgen Butt, Manfred Wagner, Klaus Müllen, and George Floudas

P-75 **Electrophysical properties of solid polymer electrolytes based on epoxy oligomer and lithium perchlorate salt**
L.K. Matkovska, M.V.Iurzhenko, O.K Matkovska, Ye.P.Mamunya, E.V.Lebedev, G.Boiteux, A.Serghei

P-76 **Dielectric relaxation in (acetamide+ lithium bromide/ nitrate) melts**
Satya N. Tripathy, M. Paluch

Oral
contributions

An Alernative Explanation of of the Change in *T*-dependence of the Effective Debye-Waller Factor at T_c or T_B

K.L. Ngai[1] and J. Habasaki[2]

[1]*CNR-IPCF, Largo B. Pontecorvo 3, I-56127, Pisa, Italy*
[2]*Tokyo Institute of Technology, Yokohama, 226-8502, Japan*

The cusp-like temperature dependence of the Debye-Waller factor $f_Q(T)$ at T_c found by experiments in several fragile glassformers has been considered as critical evidence for validity of the ideal Mode Coupling Theory (MCT). A comprehensive review of experimental data of $f_Q(T)$ and beyond brings out other changes of dynamic and thermodynamic parameters taking place at or near T_c. Based on these experimental facts, we show there is an alternative explanation of the transitions of $f_Q(T)$ at T_c related to dissipation of the molecules while caged by the anharmonic intermolecular potential, and the change of *T*-dependence of the α-relaxation time τ_α at $T_B \approx T_c$ and at T_g. Experiments as well as molecular dynamics simulations found $f_Q(T)$ changes *T*-dependence not only at T_c but also at T_g. The latter is not addressed by the ideal MCT but is a natural consequence in the alternative explanation. It also explains the experimentally observed fact that the sharpness of the two changes at T_c and T_g are correlated. The changes of *T*-dependence of $f_Q(T)$ at T_c and T_g as well as τ_α at $T_B \approx T_c$ and T_g are accompanied by changes of free volume deduced from positron annihilation spectroscopy and also the size of cooperative rearranging region obtained from adiabatic calorimetry measurements, indicating the connection to thermodynamic properties. The molten salt, $0.4Ca(NO_3)_2$-$0.6KNO_3$ (CKN), was the first glassformer measured by neutron scattering to verify the cusp-like behavior of $f_Q(T)$ at T_c predicted by ideal MCT. While the fits of the other scaling laws of MCT to viscosity, light scattering, and dielectric relaxation data all give T_c in the range from 368 to 375 K, there is no evidence of cusp-like behavior of $f_Q(T)$ at T_c from more accurate neutron scattering data obtained later on by Mezei and Russina at temperatures below 400 K. Our alternative explanation is able to resolve this conundrum because T_B is $\geq$ 400 K, and hence the change of *T*-dependence of $f_Q(T)$ at T_c was not observed in data taken at temperatures lower than 400 K. The alternative explanation also can rationalize the difference between fragile and non-fragile glassformers in the strength of the observed changes of $f_Q(T)$ at T_c and T_g as well as τ_α at $T_B \approx T_c$ and T_g.

Quantum Effects in the Glass Transition and the „Superstrong“ Behavior of Deeply Supercooled Water

A.P. Sokolov[1,2], V.N. Novikov[1], A.L. Agapov[1], R. Richert[3]

[1]*Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA*
[2]*Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA*
[3]*Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA*

Studies of the glass transition usually neglect any quantum effects in structural relaxation of glass forming systems. However, low Tg liquids of light molecules might have significant contribution of quantum effects. Our analysis shows [1] that quantum effects should lead to a significant decrease of the glass transition temperature T_g with respect to the melting temperature T_m, so that the ratio T_g/T_m can be much lower than the typical value of 2/3. Indeed this is observed for many materials where T_g is near or below ~ 60 K [1]. Furthermore, it is demonstrated [1] that the viscosity or structural relaxation time in such low temperature glass-formers should exhibit highly unusual temperature dependence, namely a decrease of the apparent activation energy upon approaching T_g, instead of traditional increase (i.e. sub-Arrhenius dependence instead of the usual super-Arrhenius). Combining neutron scattering and dielectric relaxation spectroscopy we show that quantum fluctuations are not negligible in deeply supercooled water. Our dielectric measurements of the vapor deposited water revealed the anomalously weak temperature dependence of structural relaxation at T close to T_g~136K. The fragility appears unusually low, m~14, in agreement with the recent studies of LDA water [2]. We demonstrate that this anomalous behavior can be explained well by quantum effects in structural relaxation. We specualte that the apprent fragile-to-strong crossover in water, and its low value of T_g/T_m~0.5 are caused by quantum effects in deeply supercooled water. At the end, we present dielectric spectroscopy data on several low-Tg liquids and discuss criteria that defines the importance of quantum effects in the glass transition.

1. Novikov, V. N. & Sokolov, A. P. Role of quantum effects in the glass transition. **Phys. Rev. Lett. 110**, 065701, (2013).
2. Amann-Winkel, K. *et al.* Water's second glass transition. **Proc. Natl. Acad. Sci. 110**, 17720, (2013).

From boiling point down to T_g – Evolution of the dynamic susceptibility of molecular and ionic liquids

B. Schmidtke, N. Petzold, R. Kahlau, B. Pötzschner, E.A. Rössler
Experimentalphysik II, Universität Bayreuth, D-95444 Bayreuth, Germany

Depolarized light scattering (DLS) spectra of molecular and ionic liquids are studied by applying Fabry-Pérot interferometry, double monochromator and photon correlation spectroscopy. Temperatures between the boiling point T_b and the glass transition temperature T_g are covered and the crossover from simple liquid to glassy dynamics is monitored. It is characterized by merging of primary (α-) relaxation and vibrational excitations, and an Arrhenius temperature dependence of $\tau_\alpha(T)$ at temperatures approaching T_b. The spectra and likewise the corresponding reorientational correlation functions are characterized by stretching parameter β_{CD} for the long-time decay (α-process), strength of fast dynamics $1 - f$, and time scale at shortest times expressed by $k_B T/I^*$. An additional (intermediate) power-law regime (or excess wing in the frequency domain) between fast dynamics and α–process has to be taken into account; it affects the susceptibility minimum at low temperatures. For a given liquid the spectral parameters are virtually temperature independent up to T_b, i.e., frequency-temperature-superposition applies for α-process. The quantity I^* reflecting inertia effects correlates with molecular mass, and the larger $1 - f$, the smaller is I^*. Concerning $\tau_\alpha(T)$, by decomposing the apparent activation energy $E(T)$ in a constant high-temperature value E_∞ and a ”cooperative part” $E_{coop}(T)$ depending exponentially on temperature, a generalized fragility is introduced via a plot $E_{coop}(T)/E_\infty$ vs. T/E_∞, and it is suggested that E_∞ instead of the conventionally defined T_g controls the energy scale of the glass transition phenomenon. In contrast to other claims no correlation of the stretching parameter β_{CD} and fragility m is found. Regarding molecular vs. ionic liquids, no relevant difference in their DLS spectra is observed. The orientational dynamics of ionic organic liquids is fundamentally the same as that of van der Waals liquids.

Molecular dynamics simulations of the β relaxation in simple rigid molecules

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In addition to the structural or α relaxation, glass-forming materials commonly show faster molecular motions. Of particular interest among these is the Johari-Goldstein (JG) β relaxation. It is intermolecular in nature, being present even in systems with completely rigid molecular structures, seems universally present in glass-forming materials, and unlike other types of secondary relaxations is closely correlated with the α process. Several decades after its discovery, the origin of this JG process remains unclear.

We perform molecular dynamics simulations on liquids and glasses of simple molecules, composed of two rigidly attached particles of different sizes. In addition to the α relaxation these systems show a faster1 β process, which cannot be intramolecular in nature. This process is well described by a Cole-Cole function in the glass, and the temperature dependence of its timescale, strength and shape mirror those of experimentally observed secondary relaxations. Varying the molecular asymmetry and bond length produces a rich variety of behaviors of the α and β relaxations, ranging from a separate α-onset, to α-β merging, to an excess-wing like scenario.

We find that this β process shows the unique characteristics of the JG relaxation experimentally observed in glass-forming materials: merging with the α relaxation at high temperatures, correlation of its timescale with the breadth of the α relaxation, and sensitivity to pressure and physical aging. This gives us some confidence that the motions underlying the β process in this very simple system are similar to those underlying the experimental JG relaxation.

Using this model system we can investigate several open questions about the JG relaxation. Both an “islands of mobility” and a uniform scenario have some validity, and apply more accurately at lower and higher temperatures respectively. We find pronounced heterogeneity of both its relaxation time and strength; the former is, surprisingly, unrelated and the latter related to the more well-studied heterogeneity of the α process. Examining the angular distributions of motions on the β timescale allows us to shed some light on the origin of different responses in the α-β regime obtained by different experimental probes of rotational dynamics (dielectric spectroctopy vs. NMR and light scattering techniques).

Temporal and spatial structures of molecular dynamics in glass forming alcohols

Ryusuke Nozaki

Department of Physics, Faculty of Science, Hokkaido University

Broadband dielectric response of glass forming materials shows several common dispersions corresponding to different temporal and spatial structures such as the β relaxation process, the JG-β relaxation process and the boson peak. Molecular dynamics of liquid alcohols consisting of hydroxyl group (OH) attached to the hydrocarbon parts can be well investigated by means of broadband dielectric spectroscopy (BDS) because OHs will be suitable probes to study details of the dynamic processes connected to the liquid-glass transition through the dispersions. We have demonstrated that polyhydric alcohols such as glycerol and sorbitol show typical features of the dynamic processes from the BDS measurements [1-3]. In this case, breaking and reconstructing of hydrogen bonds between molecules composing hydrogen-bonding networks are attributed to the origin of the alpha process [4]. On the other hand, it is being considered that monohydric alcohols don't always compose the hydrogen-bonding networks, unlike polyhydric alcohols [5]. We have reported that molecular dynamics associated with the local structure of OHs strongly depends on the chemical structure of alcohols, from the THz dielectric studies on pentanol isomers [6-9]. In this work, we will discuss about the dielectric dispersions of liquid alcohols not only in the supercooled state but also at temperatures above melting point, and suggest that the multiple dielectric processes being spread in an extremely wide time range have cross-terms.

1. A. Minoguchi. K. Kitai, R. Nozaki, Phys. Rev. E., 68 (3), 031501 1-7 (2003).
2. R. Nozaki, A. Minoguchi, AIP CP 1027, 1285 (2002).
3. M. Nakanishi, R. Nozaki, Phys. Rev. E, 83, 051503 1-5 (2011).
4. M. Nakanishi, R. Nozaki, Phys. Rev. E 84, 011503 (2011).
5. Matija Tomšič et.al., J. Phys. Chem. B, 2007, 111 (7), 1738 (2007).
6. Y. Yomogida et.al., J. Mol. Struct. 970, 171 (2010).
7. Y. Yomogida et.al., Physica B 405, 2208 (2010).
8. Y. Yomogida et.al., in Recent Advances in Broadband Dielectric Spectroscopy, edited by Y. P. Kalmykov, Berlin: Springer-Verlag, (2012).
9. R. Nozaki, "THz dielectric dispersions in pentanol isomers and origin of boson peak in polyhydric alcohols", AIP CP 1518, 276 (2013).

Overview of Nonlinear optics based efficient monochromatic THz-wave generation and detection

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The development of nonlinear optical techniques has been extended into the terahertz (THz)-wave region, while THz-waves have proved over the past 20 years[1] to be very attractive to both fundamental sciences and advanced industrial applications. THz-wave generation works in early days are also reviewed.

Recently, a remarkable breakthrough related to radiation peak power in an injection-seeded THz-wave parametric generator using $LiNbO_3$ crystal was achieved using microchip Nd:YAG laser pumping with injection seeding. The THz-wave peak power is almost 100 kW level with the spectral bandwidth of less than 10 GHz. This talk describes advanced studies of intense monochromatic THz-wave generation, as well as highly sensitive THz-wave detection with frequency agility both based on nonlinear optics.

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A Proton Cascade as the Origin of Water's Dielectric Relaxation

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The H-bonded cluster structure of water still stands as a major point of debate in liquid science today. Much of this discussion is devoted to the understanding of its dynamic nature. This has a direct impact on deciphering anomalies of water, such as its exceptional heat capacity and others. Of these properties its dielectric permittivity and relaxation stand out. The argument rages as to whether the almost Debye like character of the dispersion is the result of the reorientation of an apparent dipole moment of the water cluster, or simply the cumulative effect of single water molecule reorientation. Furthermore, like many glass formers, it has a high frequency excess wing, that does not fit into the model of a single relaxation time of the main peak. We present evidence that the microscopic origin of both the excess wing and the main relaxation process of pure water is the same. The origin of these two features is explored and we suggest a new paradigm for water relaxation based on the concept of a proton cascade leading to a cluster reorientation. If so then this mechanism will have further implications for how the H-bonded cluster is maintained inside a spanned percolated network.

Dielectric measurement in the terahertz gap

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Since 1990s, technologies in the terahertz (THz) range of which frequency is approximately from 0.1 to 10 THz, has become emerging topics in telecommunication, and in optics for material analyses as well as non-destructive testing. For example, the wireless communication at 120 GHz is planned to be in service in 2014, and the 300 GHz system is under development. For designing suitable telecommunication equipments and to establish propagation models, it is essential to have dielectric characteristics of materials used in the system as well as in the environment such as wall materials. However, the applicable frequency is limited to 110 GHz, in the case of a commercial free-space system with a vector network analyser (VNA). Thus, we have developed a system which can measure complex permittivity up to 300 GHz. As a tool for spectroscopy, on the other hand, the spectra in the mid-infrared region (approximately from 12 to 120 THz) can be obtained by a common Fourier transform infrared (FTIR) spectroscopy and absorption peaks are theoretically assigned. In the THz frequency range, it is expected that molecular and inter-molecular behaviour, such as phonon absorption in crystals and weak hydrogen bonds appears.

To fill the "THz gap" of dielectric spectroscopy, various systems have been developed by using either interferometer (FT-THz) or on time domain (TDS). In general, FT-THz system covers from 2 to 20 THz, and recent TDS systems including the attenuated total reflectance (ATR)-TDS system cover from 0.03 to 7 THz. However, the methodology of THz spectroscopy has not been fully established.

We have examined the dielectric spectroscopy systems with different principles (VNA, TDS, ATR-TDS, FTIR) –by measuring the same sample. The complex permittivity values of deionised water from 3 GHz to 3 THz measured by five different systems were fitted to the single Debye relaxation equation (Fig. 1), and absorption peaks of a mineral pigment observed in the frequency range from 0.3 to 20 THz by three systems are in good agreement. We will continue methodological investigation to reduce uncertainty of dielectric measurement in the THz frequency band.

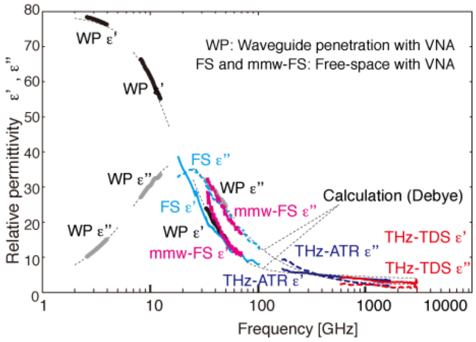

Fig. 1 Complex permittivity of deionised water from 3 GHz to 3 THz.

Higher Order Structure of Polymers Studied by Terahertz Spectroscopy

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Spectroscopy in the terahertz (THz) frequency region has become easier with the recent development of the terahertz time-domain spectroscopy (THz-TDS) technique. Low frequency vibrational peaks observed in THz spectra show information about intermolecular structure rather than intramolecular structure. THz spectroscopy will become a powerful tool for monitoring higher order conformations of large molecules.

Recently, we have measured the THz spectra of poly(3-hydroxybutyrate) (PHB) and found clear differences between the spectrum of amorphous PHB and that of crystalline PHB. The THz polarization spectra are measured for a stretched PHB sample and the directions of the vibrational transition moments are determined. To investigate low frequency vibrational modes more thoroughly, low-frequency Raman spectra are also measured for crystalline PHB. The observed vibrational modes in both THz and Raman spectra were successfully assigned by a quantum mechanical simulation of spectra with the Cartesian coordinate tensor transfer method, which can provide realistic spectra of the PHB by considering the intermolecular interactions among polymer chains.

On the basis of these results, the structural change in PHB has been studied. The isothermal crystallization of PHB was monitored with the help of THz absorption spectra. The observed spectra clearly show the crystal growth, and the crystallization rate by Avrami's model. The isothermal crystallization spectra are analyzed using two-dimensional correlation spectroscopy. By using the synchronous and asynchronous data plots, the correlation between the absorption peaks and the temporal order of the changes in spectral intensity is determined.

We have also observed the THz absorption spectra of polyamides. Spectra of Nylon6, Nylon6/6, Nylon12, Nylon11 were measured and compared with the X-ray diffraction patterns. A peak at 3 THz was commonly observed in the spectra of all nylons and assigned as the characteristic vibrational mode of NH...OC hydrogen bonds. The other peak at 6.6 THz was observed only in the spectra of nylons in α crystal form. Using this peak, Brill transition of Nylon-6, in which α form changes into other crystal structure, was monitored in the temperature dependent spectra. The drastic change of the absorption intensity was observed at the Brill transition temperature.

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Interparticle correlation and irreversible adsorption improve glass stability under confinement

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Polymers do not crystallize easily. Similarly as smaller molecules, crystallization of polymers get even more sluggish upon confinement at the nanoscale level where the conversion rate strongly decreases, and below a system-dependent critical size, the formation of ordered structures is not observed within experimental time scales exceeding several months. This evidence implies that at the nanoscale glasses are more stable against devitrification. The molecular origin of this nanoconfinement effect is, however, not completely clear. The tremendous in crystallization rate could be, in fact, associated to various mechanisms involving, for example, a reduction of nuclei number, larger entropic penalties upon ordering of interfacial chains, a suppression of mass transport diffusivity or slower interfacial dynamics. Recently, we have demostrated that finite size effects and interfacial energy are not sufficient to univocally determine the crystallization kinetics of thin polymer films. It is obvious that one or more key parameters are still missing.

To unveil the mechanisms yielding to the suppression in devitrifrication rate, we performed a new series of experiments where we elucidated the role of interfacial dispersive forces on the crystallization under 1D confinement and considered the role of interparicle correlations on the stabilization of glassy layers in polymers under 1D confinement. In particular, we monitored the crystallization kinetics of ultrathin films of poly(ethylene terephthalate) embedded, in parallel with noncrystallizable polystyrene layers, into metallic slabs. Upon reduction of the thickness of the noncrystallizable layer, we observed smaller crystallization rates and a reduction in the melting point, not explainable in terms of finite size effects. We attributed the slower crystallization kinetics to an increase in interfacial dispersive forces acting on the crystallizable layer, which, enhancing physisorption of segments at the interfaces, reduce the amount of crystallizable chains. The universality of our results was validated via dynamic Monte Carlo simulations of thin film crystallization of a lattice polymer model. Finally we will discuss on the. Analysis of the thickness dependence of the dielectric strength permitted to verify that an increase in interparticle correlations provides larger reductions in crystallization rate upon confinement.

Molecular dynamics of single and stacked thin polymer films

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Glass transition and the dynamics of the alpha-process in thin polymer films have been widely investigated over recent years using dielectric relaxation spectroscopy. In our group, several properties of single and stacked thin polymer films have been elucidated in recent years [1,2]. In this presentation, the results of two related topics will be given.

As the first topics, the dielectric relaxation of amorphous polyamide thin films has been investigated [3]. In this polymeric system, 4 different relaxation signals such as gamma, beta, alpha and electrode polarization (EP), can be observed over a wide temperature and frequency range. The thickness and temperature dependence of the relaxation times and dielectric relaxation strength of the EP and alpha-processes have been evaluated. The temperature dependences of the relaxation times of both the processes have stronger temperature dependence than that of the Arrhenius type. The temperature dependence of the relaxation time of EP process can well be reproduced by the VFT law, which is usually observed for that of the alpha-process. This suggests that there is a strong correlation between the EP and alpha-processes. Because the molecular origin of EP process is related to mobility of charge carrier between the electrodes and that of the alpha-process is due to the segmental motion, there is a possibility of the coupling and decoupling between the segmental motion and the mobility of charge carrier, which can be discussed through the present measurements.

As the second topics, the dynamics of the alpha- and beta-processes in stacked thin films of poly(methyl methacrylate) (PMMA) have been investigated using dielectric relaxation and differential scanning calorimetry. The glass transition temperature Tg of as-stacked thin films show a thin-film-like one, and the Tg increases with increasing annealing time for isothermal annealing. At the same time, the dynamics of the alpha-process changes from faster one to slower one with annealing, while the dynamics of the beta-process remains almost unchanged. These results can well be explained if the interfacial interaction between thin polymer layers changes with annealing. The time evolution of density profile of the stacked PMMA thin films has been measured very recently using neutron reflectivity measurements in order to elucidate the change in the interface between thin layers. Such measurements will reveal the nature of the dynamics in thin polymer films, together with those of dielectric relaxation spectroscopy.

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Molecular Order and Dynamics of Nanometric Thin Layers of Poly(styrene-*b*-1,4-isoprene Diblock Copolymers

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Order and dynamics of poly(styrene-*block*-1,4-isoprene), P(S-*b*-I) diblock copolymers in nanometer thin layers with different isoprene volume fraction (f_{PI}) and identical molecular weight of the styrene blocks are studied by a combination of Grazing-Incidence Small-Angle X-ray Scattering (GISAXS), Atomic Force Microscopy (AFM) and Broadband Dielectric Spectroscopy (BDS). GISAXS and AFM reveal randomly oriented lamellar structures in the films and a parallel orientation at the top surface, respectively. Long range ordered samples consisting of predominant perpendicular lamellae were obtained by solvent annealing and monitored in-situ by GISAXS. Using BDS, three well separated relaxation processes are detected, (i) and (ii) the dynamic glass transitions (segmental mode) in the styrene and isoprene blocks respectively and (iii) the normal mode relaxation representing fluctuations of the isoprene chain as a whole or parts of it. While the two former do not show any thickness dependence in their spectral positions, the latter becomes faster with decreasing sample thickness.(*1*) This reflects the difference in the length-scale on which the molecular fluctuations take place. Evolution of the normal mode of isoprene blocks during solvent annealing and overall dielectric relaxation of oriented samples will also be presented.

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Molecular dynamics of itraconazole confined in thin supported layers

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Broadband Dielectric Spectroscopy (BDS) is used to study the molecular dynamics of thin layers of itraconazole – an active pharmaceutics ingredient with rod-like structure and whose Differential Scanning Calorimetry (DSC) scans reveal liquid crystalline-like phase transitions. It is found that (i) the structural relaxation process remains bulk like, within the limits of experimental accuracy, in its mean relaxation rate, while (ii) its shape is governed by two competing events: interfacial interactions, and crystalline ordering. Additionally, (iii) the dynamics of the δ-relaxation – assigned to the flip-flop rotation of the molecule about its short axis – deviates from bulk behaviour as the glass transition is approached for the confined material. These observations are rationalized within the framework of molecular dynamics as currently understood.

The interplay between intra- and inter-molecular dynamics as studied by Broadband Dielectric – and Fourier-Transform Infrared – Spectroscopy

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The inter- and intra-molecular interactions of low molecular weight and polymeric glass-forming model systems are studied by Broadband Dielectric (BDS) - and Fourier-Transform Infrared (FTIR) - Spectroscopy. Analyzing the temperature dependencies of specific IR absorption bands, reflecting the intramolecular potentials of dedicated molecular moieties, enables one to unravel on a submolecular scale the process of glass formation and to compare it with the dielectrically determined primarily intermolecular dynamics. By that a wealth of novel information is obtained proving that the different units of a glass former show specifically different temperature dependencies. This demonstrates the fundamental importance of intra-molecular mobility giving refined insights into the underlying interactions beyond coarse-grained models treating the glassformer as rigid body.

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Low temperature deposited glycerol - some new insights from BDS and specific heat spectroscopy

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Physical vapour deposition (PVD) of supercooled liquids into the glassy state yields occasionally glasses with extraordinary high packing density resulting in an extremely low fictive temperature and high kinetic stability [1]. While a couple of organic molecules have be proven to be (ultra)stable glass formers, we have recently shown that PVD might also induce enhanced molecular order in H-bonded liquids like glycerol that even persist after recovery the liquid state on time scale up to 10^{10} times the structural relaxation time τ_α [2].

This paper focuses on the dynamics of glycerol and related compounds, particularly in the glassy state, as studied by dielectric spectroscopy and chip-based ac-calorimetry in an OMBD setup. The combination of specific heat and dielectric relaxation measurements revealed a couple of interesting results that will be discussed in detail:

1. Glassy films of glycerol, threitol and xylitol show two distinct relaxation processes, which were attributed to surface mobility and a residual bulk mobility.
2. The relaxation pattern, particularly the surface dynamics depends strongly on the deposition rate.
3. Heating of the glassy film to temperatures above T_g-15K results in structural reorganisations including partial crystallization of glycerol as manifested in changes in the specific heat.
4. Finally, experimental indications for a distinct β-relaxation in glycerol will be discussed and compared with previous findings from aging and hyperquenching experiments.

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Mutarotation of L-fucose as monitored by Dielectric and Infrared spectroscopy

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Fourier Transform Infrared Spectroscopy (FTIR) and Broadband Dielectric Spectroscopy (BDS) are combined to study the temperature dependent kinetics of mutarotation in L-fucose. By monitoring the growth of anomerically specific bands in the FTIR spectra after the sample has been quenched from T = 418 K down to temperatures between T = 313 K and 328 K, changes in concentration of two out of four proposed anomeric species are shown to follow a simple exponential time dependence. On the other hand, the structural (α) relaxation process, as observed by BDS after similar thermal treatment, shifts to lower frequencies according to a stretched exponential time dependence (stretching exponent of 1.5). The corresponding constant rates as deduced from vibrational absorptions of α- or β-fucopyranose differ slightly in value, increase with temperature and are at T = 313 K nearly one decade faster than the one obtained from the shift of the α-relaxation. From the Arrhenius-like T-dependencies of all the aforementioned rates, activation energies, E_a, are extracted, being largest (139 kJ/mol) for the case of BDS and smallest for α-fucopyranose (102 kJ/mol), whereas for β-fucopyranose E_a is intermediate (111 kJ/mol). These facts prove that BDS can be utilized to follow the equilibration of the macroscopic structure upon mutarotation originating from changes of the chemical composition as monitored by FTIR.

High pressure studies on polymerization of epoxy amine systems

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Broadband Dielectric and Fourier Transform Infrared spectroscopies were applied to study dynamics and kinetics upon polymerization of bisphenol-A diglycidyl ether (DGEBA) and three different amines i.e. 2-ethylhexylamine, cyclohexylamine and aniline at different thermodynamic conditions. We found out that polymerization constant rates as well as activation barriers determined from both methods are almost the same (within the experimental uncertainty). High pressure studies have enabled to calculate the activation volume which varies significantly dependently on the system we measured. One can add that activation volume was lying within the range -18-36 cm3-mol for T=293 K and p=0.1 MPa. These results have questioned common practice to describe given kind of polymerization with the use of very narrow range (or even single constant) value of activation volume. Finally, we have also verified the validity of the time-temperature-pressure superposition (TTP) rule with respect to the structural relaxation process that seems to be crucial point in the context of the proposed protocol of the data analysis.

Local Composition and Dynamic Heterogeneity in Polymer Blends

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We discuss the issues of miscibility, local composition and dynamic heterogeneity [1,2] in partially miscible and in perfectly miscible blends. The first system based on polystyrene/poly(methyl phenyl siloxane) (PS/PMPS), is partially miscible (UCST) [3]. The phase separation was studied in situ by laser scanning confocal microscopy (LSCM) and by fluorescence correlation spectroscopy (FCS) at macroscopic and microscopic length scales, respectively. FCS when combined with LSCM can provide independent information on the local concentration within the phase-separated domains as well as the interfacial width [4]. The second system based on poly(vinyl acetate)/poly(ethylene oxide) (PVAc/PEO) has a miscibility window in composition [5]. Local dielectric spectroscopy (LDS) was employed which is a sensitive probe of the presence of dynamic heterogeneity in polymer films [6]. Second, we were able to deduce the local blend composition at the nanoscale. Third, the local blend composition was used to quantitatively account for the kinetics of phase demixing in the thin films. Overall, LDS can be employed in studying thermodynamically miscible blends where the relevant length scale controlling the segmental dynamics is of the order of the Kuhn length. The last system based on binary blends of polystyrene with oligostyrene, is perfectly miscible (χ=0) yet still dynamically heterogeneous [7]. The self-concentration model with a single intramolecular length scale qualitatively describes the slower segmental dynamics. A quantitative comparison based on MD, however, requires a composition-dependent length scale. The pertinent dynamic length scale that best describes the slow segmental dynamics in miscible blends relates to both intra- and intermolecular contributions.

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Molecular dynamics of discotic liquid crystals in the bulk and embedded in nanochannels

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Discotic liquid crystals (DLCs) are self-assembled materials where self-assembly is driven by noncovalent intermolecular interactions. The coresponding molecules consist of a flat and rigid aromatic core substituted by flexible aliphatic side chains. While the former is responsible for the π-stacking, the latter gives rise to an increased solubility, processability, and rich thermotropic behavior. The disc-shaped molecules form columns that further assemble into two-dimensional arrays with a hexagonal mesophase. The alkyl chains fill the intracolumnar space giving rise to a nanophase separated state. Two different homologous systems based on triphenylene derivatives were investigated as model systems for DCLs where the length of the aliphaitic side chains is widely varied. Measurements were carried out in the bulk state and confined to the nanometre wide channels of anodic aluminum membranes (Pore diameter 25 nm, 40nm, 80 nm and 180 nm) by means of calorimetry, dielectric relaxation spectroscopy and inelastic / quasielastic neutron scattering. For the latter experiments both the vibrational density of states (Boson Peak) from neutron time-of-flight spectroscopy as well as the molecular dynamics on a time scale of ca. 1 ns (elastic scans from neutron backscattering spectrometers) were considered. Structural information is retriefed by X-ray diffraction carried out on a synchrotron.

The dynamics of these unique soft matter materials are discussed in detail considering their structure (lenghts of the aliphatic side chains) and the effects of self-confinement (of the aliphatic chains in the intracolumnar space) and outer confinement (influence of the pore size) [1,2]. Comparison is further made to pyrene based system [3-5].

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Structural dynamics and charge transport in deep eutectic mixtures

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Deep eutectic mixtures are a new class of materials with exceptional properties for applications in solar cells, thermoelectric energy conversion, supercapacitors, chemical sensors, SO_2 and CO_2 solubility, chemical separation processes, drug solubility and environmentally benign solvents for chemical synthesis. These mixtures offer several advantages including simple preparation procedure, cheap approach to chemical synthesis of versatile materials as well as the possibility for design of task-specific materials for different applications. However, the physicochemical properties of deep eutectic mixtures such as melting and glass transition temperatures, electrical conductivities, proton dissociation constants, viscosities as well as structural dynamics cannot be described by simply considering the weighted contributions of the constituent pure compounds as would be expected from the current theories of mixtures. In this talk, studies of charge transport and structural dynamics in selected series of deep eutectic mixtures characterized using broadband dielectric spectroscopy, depolarized dynamic light scattering, calorimetry, and Fourier transform infrared spectroscopy, will be presented. Additionally, complementary results from molecular dynamics simulations performed to assess the degree of proton transfer between the neutral parent molecules will also be discussed. The emerging picture of the interplay between hydrogen bonding and proton transfer in deep eutectic mixtures will be presented.

Glassy Dynamics of Condensed Isolated Polymer Chains

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While structure and conformation of condensed, isolated low molecular weight and polymeric molecules are well explored, knowledge concerning their dynamics, as measured in a broad spectral range and at widely varying temperatures is sparse. To overcome this, Broadband Dielectric Spectroscopy is combined with nano-structured electrodes [1] having 35 nm separation and the dynamics of condensed isolated poly(2-vinylpyridine) (P2VP) coils is measured. The condensed coil conformation is revealed by Atomic Force Microscopy scans of the identical samples with an average coil volume corresponding to the estimate for a single chain (using the molecular weight and bulk density). Hence, for the first time the dynamic glass transition of condensed isolated polymer chains is directly measured and found to be bulk-like; only segments close (< 0.5 nm) to the substrate are weakly slowed down [2]. The observation of bulk-like dynamics is in full accord with the length scale on which the dynamic glass transition is to be expected. In contrast, the emersion of new, slower relaxation modes is attributed to attractive interactions of the P2VP segments with the supporting silica surface, a finding which is corroborated by complementary infrared experiments. Our approach paves the way for numerous experiments on the dynamics of isolated molecules.

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The dielectric response of interfacial water – from the ordered structures to the single hydrated shell

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Water is the universal solvent in nature. Does this imply, however, that its interaction with its environment is also a universal feature? While this question maybe too fundamental to be answered by one method only, we present evidence that the broadening of the dielectric spectra of water presents universal features of dipolar interactions with different types of matrixes. If in aqueous solutions the starting point of waters state can be considered as bulk, with only partial interactions with the solute, then the state of water adsorbed in heterogeneous materials is determined by various hydration centers of the inhomogeneous material (the matrix) and it is significantly different from the bulk. In both cases, the dielectric spectrum of water is symmetrical and can be described by the Cole-Cole (CC) function. The phenomenological model that describes a physical mechanism of the dipole-matrix interaction in complex systems underlying the CC behavior has been applied to water adsorbed in porous glasses. It was then extended to analyses of the dynamic and structural behavior of water in nonionic and ionic aqueous solutions. The same model is then used to analyses the CC relaxation processes observed in clays, aqueous solutions of nucleotides and amino acids.

Dynamics of protein hydration water over wide ranges of hydration level. Globular versus fibrous proteins

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Studies on the dynamics of protein hydration water and its coupling to protein dynamics are crucial to understanding the molecular basis of biological function and may contribute to several applications such as disease detection or food preservation.

Here we present a comparative study of globular and fibrous hydrated proteins, namely, bovine serum albumin (BSA), lysozyme, elastin and collagen. In addition, measurements on hydrated casein peptone, a digest derivative of the globular protein casein, are presented for comparison. A main parameter incorporated is the hydration level which is varied over wide ranges, starting from dry protein samples to dilute solutions (globular) or swollen samples hydrated through immersion (fibrous). The dynamical characteristics of the underlying molecular processes are recorded by Dielectric Relaxation Spectroscopy (DRS). Complementary experimental techniques such as Differential Scanning Calorimetry, to study thermal properties, Water Equilibrium Sorption Isotherms, to study hydration properties and Attenuated Total Reflectance (ATR) spectroscopy are also employed.

The main dielectric relaxation associated with the dynamics of uncrystallized water molecules which trigger the motion of polar groups on the protein surface (ν relaxation [1]) shows similar hydration dependence and dynamical characteristics for globular and fibrous proteins hydrated at relatively low hydration levels [1,2]. Low levels of hydration facilitate the study of uncrystallized water dynamics because the contribution of ice is either absent or negligible in the particular hydration range, according to DSC. By increasing the hydration level several additional processes are recorded which are attributed to different forms of crystallized or uncrystallized water molecules [1]. In the high hydration level region, the contributions of both, crystallized and uncrystallized water populations, are differentiated among different systems depending on the structure.

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Soil bound water/free water temperature effect determined by time domain reflectometry

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The purpose of this study is to determine the temperature influence on the soil bulk dielectric permittivity, ε_b, calculated from the measurement of the electromagnetic wave velocity of propagation along the parallel waveguide in a TDR probe, i.e. a probe working in time domain reflectometry technique. The experimental evidence shows that the existing models do not completely describe the temperature effect. However it has been confirmed that the observed temperature effect is the result of two competing phenomena; ε_b increases with temperature following the release of bound water from soil solid particles and ε_b decreases with temperature increase following the temperature effect of free water molecules. It has been found that there is a soil type characteristic moisture value, θ_{eq}, named the equilibrium water content, having the specific temperature property. The temperature effect for this moisture is not present, which means that for soils with the moisture value equal to θ_{eq} the both competing phenomena mentioned earlier compensate each other (fig. 1).

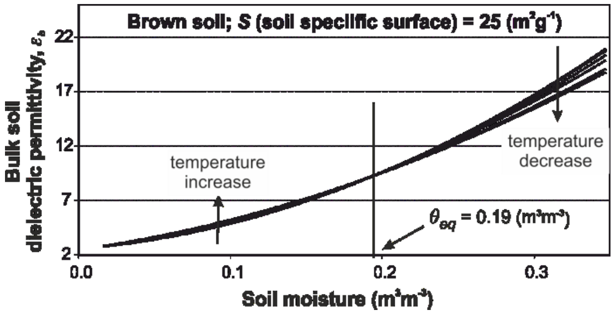

Fig. 1. TDR calibration curves for the sample of brown soil at various temperatures changing from 5°C to 55°C in 10°C steps, showing the localization of the water content equilibrium point, θ_{eq}.

The equilibrium water content, θ_{eq}, is correlated with the soil specific surface area. The temperature correction formula adjusting the soil moisture determined by TDR, θ_{TDR}, at various temperature to the corresponding value at 25°C, based on knowledge of θ_{eq} decreases the standard deviation of the absolute measurement error of soil moisture θ_{TDR} by the factor of two as compared to the uncorrected values.

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Terahertz spectroscopy on amino acids

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Using submillimeter and terahertz spectroscopy, it is possible to close the gap between microwave and far infrared frequencies, which was extremely difficult to access in the past. We employ terahertz time-domain spectroscopy (THz-TDS), which allows simultaneously monitoring real and imaginary part of the complex dielectric function in the frequency range 0.1 – 4 THz.

We performed THz-TDS transmission experiments on some of the 23 standard amino acids that are the basic building blocks of all known proteins. For amino-acids crystals, due to hydrogen bonding and Van-der-Waals interactions, low lying excitations are expected in the THz frequency range. Indeed all samples investigated exhibit numerous resonances in their complex permittivity spectra. The evolution of all modes was studied as function of temperature from 4 – 300 K and analyzed by fits using Lorentzian line shapes. From these fits eigenfrequencies, oscillator strengths, and damping constants of the modes were determined. The temperature dependence of resonance frequencies and mode strengths reveals the nature of these modes and allows discriminating between intra- and intermolecular excitations. Further characterization of the modes is possible by comparing the results with existing quantum chemical simulations providing a complete assignment of the observed excitations.

These experiments document that amino acids can serve as a model system for the analysis of terahertz spectra of molecular crystals and are touchstones for solid-state simulations. In addition, one could draw conclusions concerning the intermolecular binding abilities of this fundamental class of molecules.

The results from the terahertz measurements are complemented by broadband dielectric spectra, which shed further light on the characteristic relaxation dynamics of some of the bonds.

Interfacial effects in polydimethylsiloxane (PDMS) based nanocomposites: dielectric and calorimetric studies

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There is increasing evidence in literature that the significant improvement of properties in polymer nanocomposites is related to interfacial effects resulting in modification of glass transition and polymer dynamics in the vicinity of the dispersed nanoparticles. In this work we are presenting, in a comparative way, results obtained on PDMS/silica and PDMS/titania nanocomposites that are prepared in two different ways: fisrtly, silica or titania particles (5 – 20 nm), generated by sol-gel techniques in the presence of the polymer matrix, are dispersed in PDMS matrix (0 – 36 wt% inclusion) and secondly, silica/PDMS and titania/PDMS core-shell nanocomposites were prepared by sorption of linear PDMS on silica or titania pre-prepared particles (0 – 60 wt% oxide particles, 100 nm up to 100 μm aggergates)[1]. The effects of interfaces and interphases in the molecular dynamics of PDMS chains were investigated by employing differential scanning calorimetry (DSC) and dielectric techniques (broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC) methods). Our study focuses on the segmental dynamics (α relaxation), associated with the PDMS glass transition, and on a slower relaxation process (α′ relaxation) attributed to a polymer fraction with reduced mobility due to interactions with the particle surface [2].

The use of oxide particles with strong PDMS/particle interactions (silica) or weaker interactions (titania) in both types of nanocomposites, along with the use of different types of silica particles in core-shell nanocomposites allow us to study the dependence of interfacial dynamics on the strength of interactions and/or on the surface morphology of the oxide particles. The overall behaviour is similar in the two types of nanocomposites, however distinct differences have also been observed and are under further investigation. Our results indicate that tuning the textural porosity of the silica particles, both, the time scale and the dielectric strength of the interfacial α′ relaxation process shifts towards the (lower) values obtained for the PDMS/titania nanocomposites (attributed to weaker polymer/surface interactions[2]). The question whether the strength of interactions or the interfacial chain configurations adopted by the polymer and dictated by the surface morphology is the crusial factor for the slow α′ interfacial relaxation is the central subject matter of the present work.

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Broadband dielectric spectroscopy of ionic liquids

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Due to their high potential for applications, e.g. in energy-storage devices such as supercapacitors or batteries, during recent years ionic liquids have come into the focus of research [1]. Ionic liquids are composed of large non-symmetrical organic cations and weakly coordinating anions. Finding the anion/cation composition, best suited for application, is a challenging task and requires a thorough understanding of the charge-transport mechanism in this class of electrolytes [2]. An essential method for the study of ionic transport is the analysis of the temperature- and frequency-dependent dielectric properties as permittivity, conductivity, and dielectric modulus.

In the present talk, I will show dielectric results on a large variety of ionic liquids, covering a broad frequency range from the mHz to the GHz regime and temperatures starting from the glass transition and extending deep into the liquid regime. This allows obtaining valuable information on phenomena like dc charge transport, the glass transition, electrode polarization, and relaxation processes arising from the reorientational motions of the asymmetric cations. We analyze the dielectric spectra using an equivalent-circuit approach [3], combining contributions from ionic charge transport, reorientational motions and a distributed RC-circuit, accounting for the electrode polarization. Amongst others, this enables the deduction of the relaxation times of the involved dynamic processes. We conclude that the main reorientational relaxation process of these ionic liquids, the α relaxation, is closely linked to the temperature-dependent behaviour of the dc-conductivity. This provides insight into the underlying conductivity mechanisms and, thus, the mobility of the ionic charge carriers. Moreover, a number of secondary relaxation processes is found, including hints on the presence of a Johari-Goldstein relaxation process [4].

Systematic detailed analyses of ionic liquids by dielectric spectroscopy as presented here can pave the way to find new ionic liquids that exhibit useful electrical properties for applications, e.g., in supercapacitors or batteries.

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X-ray induced TSC experiments on LDPE films: determination of trapping parameters and influence of antioxidants addition

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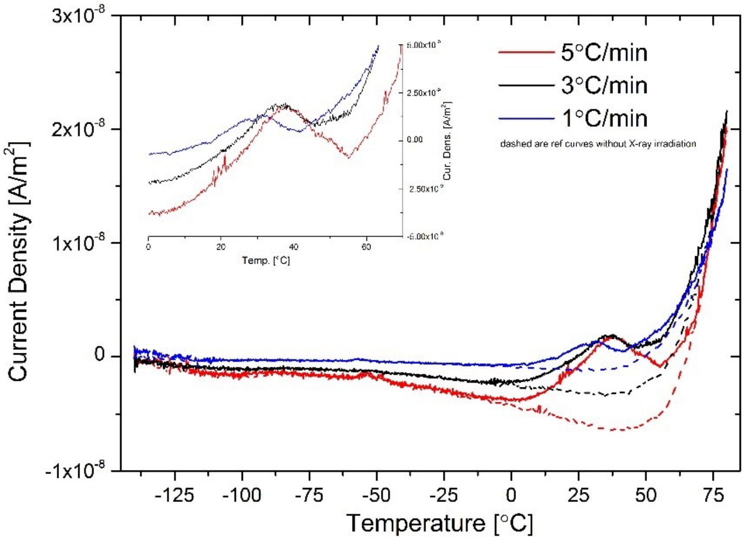
To understand the underlying physics of electric transport in dielectrics subjected to DC voltage is essential in order to further develop insulation materials for high voltage DC applications towards higher ratings. For this purpose, X-ray induced thermally stimulated current (TSC) measurements can serve as a very useful tool for the determination of trapping parameters (trap depths, densities of trapped carriers, kinetic coefficients). Irradiation with X-rays at low temperature results in a population of traps with carriers that are released during subsequent heating. Broadband dielectric spectroscopy (BDS) measurements in a wide temperature range can additionally be employed to separate thermally induced capacitive currents from conduction currents.

In this contribution, charging (or polarization) TSC results on low density polyethylene (LDPE) thin films without and with additives (antioxidants) are discussed and compared to established knowledge [1,2]. Parameters such as the strength of the DC electric field applied during heating, the heating rate, and the dose of the radiation are varied to derive relevant trapping parameters (see as an example the figure below).



X-ray induced TSC measurements on pure LDPE films at various heating rates (dashed lines correspond to the reference curves without X-ray irradiation).

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Intrinsic and water-induced relaxation dynamics and conductivity of organic nanoporous materials and thin films

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We employ dielectric spectroscopy to investigate the effect of water on the conductivity and dielectric properties of two hygroscopic polycrystalline molecular salts: the $C_{60}O_{24}Na_{24}$ fulleride[1,2] and rhodamine 6G chloride[3,4] ($C_{28}H_{31}N_2O_3Cl$). $C_{60}O_{24}Na_{24}$ was studied both in its bulk-hydrate form, stable below 370 K, and in its pure form. Charge transport in the hydrate is dominated between 320 and 380 K by a structural-water-induced contribution, which leads to a conductivity higher than that of the pure material by almost two decades at 360 K. Exposure of the pure material to air results in the condensation of a hydration layer on the crystallites' surface, with an increase of the room-temperature conductivity by four orders of magnitude. Both conductivity enhancements are likely due to a proton shuttling mechanism.[2] All dielectric spectra exhibit a single loss feature in the radiofrequency range, which is related to charge conduction and whose intensity is affected by the presence of hydration water. No ionic contribution to the conductivity is observed up to the highest temperature probed (550 K).[1] In hydrated rhodamine 6G, two types of water-related dynamic processes are observed in the temperature range from 200 to 450 K. The slower process stems from the reorientation of bound H_2O molecules attached directly onto organic molecules and counter-ions, while the faster one is the dynamic signature of water in higher hydration layers. Both processes are observed near room temperature and exhibit non-monotonic temperature dependence and decreasing spectral strength upon heating.[3] In addition, the rhodamine molecule is polar and displays two relaxations of its own in bulk form.[3,4] By performing silicon-chip-based dielectric measurement on thin rhodamine films, we were able to identify a slow, collective relaxation of the rhodamine dipoles, and a much faster relaxation which is related to the motion of an intramolecular dipole associated with the chlorine counter-ions.[4]

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Dielectric Relaxation of PU/acrylic waterborne hybrid adhesives

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Hybrid miniemulsion polymerisation is commonly used to produce various industrially important chemically active materials. Among these, polyurethane (PU) dispersions are widely used in different applications such as coatings and adhesives due to their superior properties. In this work we present a study of the structural and dynamical features of PU/acrylic hybrids obtained by diferentes synthesis conditions. In order to understand fundamental structure-adhesive properties of these systems we have made use of thermal, structural and dynamic characterization techniques to stablish a quantitative structure-property relationships.

Thermodynamic characterization results evidence very similar characteristics among the investigated materials. In agreement with this, the structures as determined by means of wide angle X-ray scattering (WAXS) measurements are also quite similar. However, larger scale structural differences are revealed by small angle X-ray scattering (SAXS) experiments. To get insight on the dynamics of these materials we carried out broadband dielectric spectroscopy (BDS) measurements of the complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\,\varepsilon''$) as a function of frequency. Experiments were performed isothermally from 120 to 410 K in sets of 10K using a frequency range between 0.01 Hz and 10 MHz. These BDS experiments allow us identifying three different relaxation processes: one relatad to the segmental dynamics (alpha relaxation), the second (slower) one associated to the presence of urethane side chains and the third and slowest one linked to the presence of a three dimensional polymer network. As would be expected this slowest relaxation present the major differences among the adhesive materials investigated.

Novel non-Debye relaxation dynamics and analysis of dielectric loss of glycerol and ac conductivity of β-AgI

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The physical basis of non-Debye relaxation (NDR) is shown to be the evolution of ensemble of Debye dipole ($\rho^{-}\rightarrow\rho^{+}$) of charge ρ, into ensemble of non-Debye g-g dipoles: ($g\rho^{-}\rightarrow g\rho^{+}$), [$(1-g)\rho^{-}\rightarrow(1-g)\rho^{+}$], -[$(1-g)\rho^{-}\rightarrow(1-g)\rho^{+}$], ($(2-g)\rho^{-}\rightarrow(2-g)\rho^{+}$), referred as g, [1-g], -[1-g], 2-g dipoles, g=1 is the Debye dipole. The g lying between 0<g<1 is emerged as unique power law *exponent*. The g-g dipoles evolution and their coupled polarization processes lead to coexistence of slow [1] and fast rates of relaxation times $\tau^{g}=\tau/\tau^{1-g}$ and $\tau^{2-g}=\tau/\tau^{-(1-g)}$ of g and 2-g dipoles, where τ^{1-g} and $\tau^{-(1-g)}$ is the consequence of transient [1-g] and -[1-g] dipoles due to the molecular interactions and defect disorder, τ is thermally activated Debye relaxation time. Dielectric loss of glycerol [2] and ac conductivity of β-AgI [3] data are shown in Fig.1 with non-Debye $(g\text{-}g)_{str}$ and $(g\text{-}g)_{tra}$ dipoles of structural and translational relaxation. The existing NDR are variants of proposed NDR under different circumstances. These novel results will be presented and discussed.

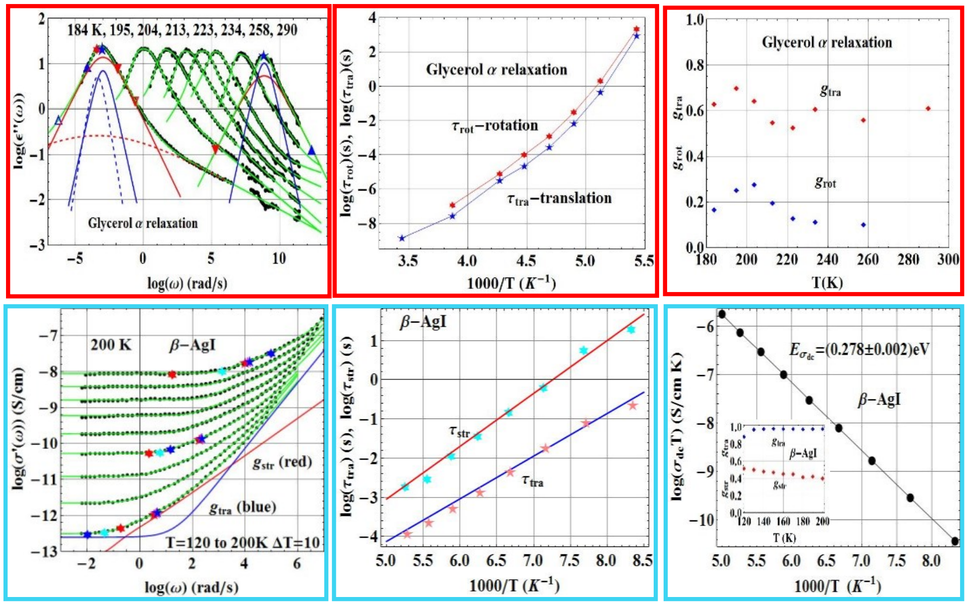

Fig. 1: The red and cyan panels show fit results with present model for the 17 decades of dielectric loss in glycerol and 9 decades of ac conductivity of β-AgI for temperature range of 184-290K and 120-200K, Debye relaxation times, g_{rot}/g_{str} and g_{tra} and dc conductivity of β-AgI obatined form the measured spectra.

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Diversity of Microstructure of Polymer Solid Investigated by Motion of Impurity Ions

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In polymers crystallized from melting state, impurity ions move through free spaces in non-crysatalline part. The free spaces are considered to have various size in correspondance with inhomogenity of inter-lamellae microstructure. According to these free spaces, impurity ions in the melt-crystallized polymers have inhomogeneous paths to move depending on microstructure of the non-crystalline part. The ionic motion in such inhomogeneous free spaces affects the electrical properties of polymer solids. In fact, an existence of plural kinds of motion of impurity ions is recognized from the electric modulus as a function of frequency in low frequency region below 10 Hz for several polymers; polyvinyl chloride-polybutadiene blends (PVC-PBD) [1], low density polyethylene (LDPE) [2] and isotactic polypropylene (iPP) [3]. In previous study of this laboratory[4], the conductiviry relaxation time of the ion motion[5] was analized for some polymers such as poly(vinyl chloride) plasticized with dioctyl phthalate, iPP and LDPE. As a results, it was found that the conductivity relaxation time reflect the diffrence of the micro-structure of non-crystalline part between these polymers. In this study, poly(chlorotrifluoro ethylene)(PCTFE) is investigated as continuation of this study.

Electrical measurement was made by the apparatus of Schlumberger SI1260 Impedance/Gain-Phase Analyzer with an amplifier of Keithley428. At the frequencies lower than 10Hz, the amplifier of Keithley428 was used with the impedance analyzer. On the other hand, the amplifier was not used at frequencies higher than 10 Hz. The three-Terminal-Configuration Electrodes were used. The thickness of the film of PCTFE is 0.1mm.

Frequency dependence of the loss permittivity of PCTFE shows the characteristic of dc conduction below about 1Hz in frequency. The electric modulus-frequency curve shows the characteristic of single conductivity relaxation. Namely, it is the Debye type dispersion. The cunductivity conductivity relaxation time analyzed from this curve is 0.63 at 130℃This value is near that of iPP but larger than those of LDPE and plasticized poly(vinyl chloride). This result suggests that the inhomogeneity of PCTFE is similar to that of isotactic poly(propylene).

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Thermo Stimulated Depolarization Current Techniques applied to the study of chain dynamics: Evidence of non-exponential modes relaxation

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Fluctuations of the end-to-end vector of a polymer chain governing the global chain dynamics are at the basis of viscoelastic properties. The most basic model for chain dynamics, the Rouse model, pictures a linear polymer chain as a series of beads and springs subjected to random forces in a medium with constant friction representing the intermolecular interactions exerted by the surrounding chains. The correlation function for the end-to-end vector is given in terms of the so called Rouse-modes correlators $C_p(t)$, where p (from p=1 to p=N-1, being N the number of chain segments) is the mode number. In the Rouse model only the odd Rouse modes contribute to the end-to-end vector correlation function. Besides, the contribution from the high p modes is strongly suppressed due to the amplitude factor, which approximately behaves as $1/p^2$, and therefore, the end-to-end correlation function is dominated by the slow (low-p) Rouse modes. The Rouse expression for the correlation function of the end-to end vector would still remain formally valid in the case of non-exponential relaxation of the modes provided these were orthogonal. The orthogonal and exponential nature of modes arise as a consequence of neglecting, respectively, the spatial and time correlations of the random forces acting on a polymer segment. From an experimental point of view it is very difficult to access the response of a single mode, and generally exponential modes are assumed, i.e. time correlations between forces are neglected, particularly in the high temperature range where the relaxation functions decay relatively fast and are experimentally accessible. Here we present for the first time how the relaxation of the p = 1 mode can be isolated by means of thermostimulated depolarization current (TSDC) technique. Moreover, the very low frequency range naturally covered by TSDC allows to investigate chain dynamics at relatively low temperatures close to that of the glass transition -T_g- for various molecular weights, a range where end-to-end fluctuations were never explored in detail before. We show that in this range the p = 1 mode significantly deviates from the exponential behavior. This effect is found to be a consequence of the closeness of the structural α-relaxation. The scenario resembles that of polymer blends with high dynamic asymmetry where the chain dynamics of the fast component broadens when approaching the α-relaxation of the slow component and suggests a possible general interpretation in terms of the effect of density fluctuations on chain dynamics.

Non-equilibrium effects on the normal mode relaxation: Chain dynamics below Tg

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According to Rouse and reptation tube models for polymer chain dynamics, the characteristic time of the chain motion is defined in terms of the so-called friction coeficient and its temperature variation. Traditionally, the friction coeficient has been identified with that controlling the motions of the polymer segments forming the chain. This leads to the expectation that both chain dynamics and the structural α-relaxation should have equal temperature dependences. However, systematic experiments had proven that this is not the case and that the α-relaxation shows stronger temperature dependence than that of the chain modes, especially as temperature approaches the glass transition one, T_g.

Thermally stimulated depolarization current (TSDC) is a dielectric time-domain technique that results a very powerful tool to study chain dynamics in detail at ultra-low equivalent frequencies (down to μHz). Consequently, TSDC allows exploring relatively low temperatures, close to T_g in particular, a range where chain end-to-end fluctuations detected by dielectric experiments have scarcely been investigated. Thus, TSDC is a very suitable technique to study in detail the chain dynamics behavior on approaching and crossing T_g and also to explore the relationship between segmental and chain timescales in that range.

Here, we report TSDC results on the chain and segmental dynamics of several monodisperse polyisoprenes (PI) accessing both dynamical processes at ultra-low frequencies in order to explore the relationship between segmental and chain timescales around the glass transition. Non-equilibrium effects are very apparent for the segmental dynamics, but more interestingly also for the slowest chain mode. The latter is mainly detected for PI polymers with relatively low molecular weights (typically bellow the entanglement moleuclar weight). These non-equilibrium effects are undoubtedly evidenced when comparing the dielectric normal mode relaxation of PI annealed a few degrees below the glass transition with that of the non-annealed one. The quantitative analysis of these results strongly indicates that both dynamical processes (chain and segmental relaxation) become fully coupled once in the glassy state. The implications of this result in the current understanding of the polymer dynamics will be also discussed.

Novel cyclic polyethers with rich dynamics

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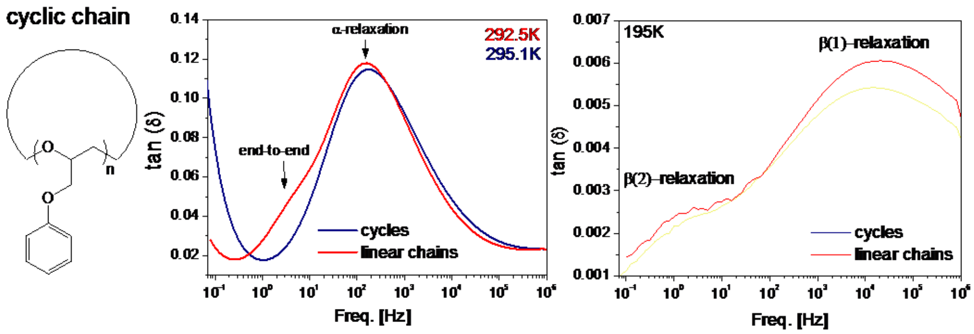
Cyclic polymers possess unique physico-chemical properties compared to their linear counterparts as a result of the absence of end-groups and the equivalence of all monomer units. These differences may be expressed in their hydrodynamic, rheological, optical and thermal properties. In particular, cyclic poly(oxyethylene)s have been the cyclic polyethers most studied in the literature. These polymers crystallize and therefore, much attention has been directed toward the crystallization behavior of cycles compared to linear chains.[1] In this contribution, we report our recents discoveries on the molecular dynamics of novel cyclic polyethers decorated with side groups.[2] These side groups prevent the crystallization of the polymers allowing a complete characterization of their dynamics by BDS. In particular, cyclic poly(glycidyl phenyl ether) exhibits three dielectric relaxations: the segmental α-relaxation and two local β-relaxations, assigned to twisting motions of the main chain and the libration of the side groups.[3] When compared to linear poly(glycidyl phenyl ether), the dielectric spectra of cyclic chains reveal the anticipated suppresion of the end-to-end relaxation for chains with no end-groups (see figure below). This result demonstrates the suitability of using BDS as a probe to certify the cyclic nature of polymers with an end-to-end mode. Concerning the β-relaxations of cyclic chains, they are nearly identical to those of their linear counterparts but exhibiting a reduced signal at the highest frequencies. This difference is interpreted as originated by the specific contributions of the chain-ends.



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Effects of solution processing techniques on dielectric properties and structures of PEO–PMMA blend films

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In the advancement of high performance polymeric materials, the blending of poly(ethylene oxide) (PEO) with poly(methyl methacrylate) (PMMA) has become an effective and economic way for the creation of technological useful physico-chemical properties [1–5]. Such properties of the solution cast PEO–PMMA blend films are governed by the heterogeneous polymers interactions and their molecular dynamics.
In order to confirm the effects of polymer blend solution processing techniques on the structures, dielectric properties and molecular dynamics, the PEO–PMMA blend films were prepared by solution casting method using the magnetic stirred, ultrasonic assisted and microwave irradiated solutions. These solution cast films were melted and pressed to achieve the smooth surfaces. The complex dielectric function of these films was investigated in the frequency range 20 Hz–1 MHz at different temperatures. Results reveal that the dielectric/electrical behaviour and molecular dynamics of these films strongly depend on the solution processing techniques. Single relaxation is observed in the loss tangent spectra (Fig. 1) whereas double relaxations are found in loss modulus spectra of the magnetic stirred and ultrasonic processed solution cast films (Fig. 2). These relaxation times obey the Arrhenius behaviour (Fig. 3). The x-ray diffraction studies also confirm the variation in amorphous phase owing to the preparation methods.

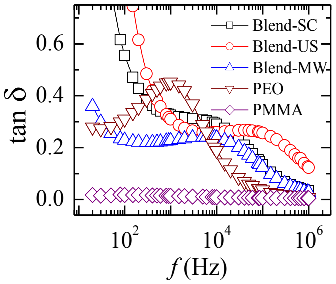

Fig. 1. tanδ vs *f* plots

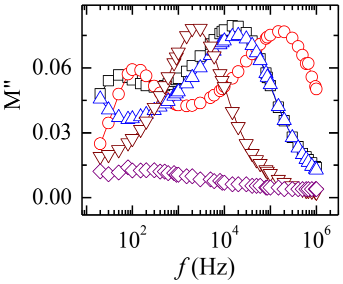

Fig. 2. *M″* vs *f* plots

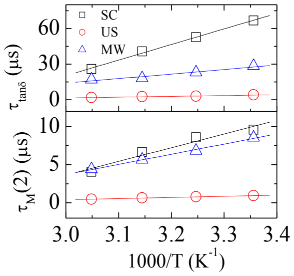

Fig. 3. Arrhenius plots

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Cooperativity and Dynamic Heterogeneity in polymer glasses : Comparison of temperature fluctuation approaches

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The time and temperature dependence of molecular mobility is a long standing problem for the glass-forming materials such as amorphous polymers. Recent works [1,2,3,4,5,6] concerning the change in the dynamics of liquids cooled towards glass transition prove that is still an unsolved issue in the condensed matter physics. In this work, we studied different fully amorphous glass-forming materials (PBAC, PETg, PVC, PLA, and PVAc) chosen to explore a large range of glass transition temperature. Broadband Dielectric Spectroscopy (BDS) and Temperature Modulated Differential Scanning Calorimertry (TMDSC) measurements have been performed in order to characterize the cooperative molecular motions as a function of temperature and relaxation time. Our goal is to determine the characteristic length of cooperativity according to the model proposed by Donth [7] and the dynamic heterogeneities from four point correlation (χ4)-model proposed by Berthier et al. [8,9]. The main idea is to put in evidence (or not) convergence between these two temperature fluctuation approaches.

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Dynamic correlations and heterogeneity in the primary and secondary relaxations of molecular liquids

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Molecules in a dense, viscous liquid exert reciprocal influences, and these many-body interactions are a distinguishing feature of the supercooled dynamics. Manifestations of these interactions include dynamic heterogeneity, dynamic correlations, and intermolecular cooperativity, phenomena that are not the same, although obviously related. We examine dynamic heterogeneity and dynamic correlations of both the primary α- and β-relaxations using dielectric measurements and molecular dynamics simulations. The latter facilitates interpretation of the former, because MD simulations enable single-molecule dynamics to be analyzed. Objectives of our experiments include assessment of (i) density scaling of the dynamic correlation length and (ii) the idea that intermolecular-correlated secondary relaxations function as the precursor to structural relaxation.

Why does entropy appear to control the relaxation time?

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This paper discusses the role of entropy for the relaxation time in, primarily, supercooled glass-forming liquids, but also in less-viscous „ordinary“ liquids. The talk is personal and subjective by starting from the fact that I for many years was unable to understand why entropy could possibly have any relation to dynamics. The paper summarizes early works by Chang & Bestul and by Adam & Gibbs, followed by Rosenfeld's entropy arguments from the 1970's and by Dzugutov's 1996 Nature paper [1]. If time permits the experimental situation will be summarized. We then jump to developments of the last five years that have taught at least me much about entropy's proposed role via the study of a large class of systems, the so-called „Roskilde (R) systems“ (comprising most or all van der Waals liquids and metallic liquids, as well as the weakly ionic and/or dipolar liquids). For this class of liquids one may argue that it is not quite correct to state that „entropy controls the relaxation time“ – if anything, it is more accurate to say that „the relaxation time controls the entropy“. In this connection we discuss the existence of isomorphs in the phase diagram of R systems and how they „explain“ the role of entropy [2].

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From the density scaling law to proper interrelations between time and length scales of molecular dynamics and entropy near the glass transition

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Our thorough analyses of high pressure experimental data of various glass formers that belong to different material groups (such as van der Waals supercooled liquids, polymer melts, and supercooled ionic liquids) clearly show that some previous suppositions concerning interrelations between time and length scales of molecular dynamics and entropy near the glass transition require revisiting. This is a straightforward consequence of two phenomena of isochronal decoupling, which have been recently observed by us (i) between time and dynamic length scales of molecular dynamics [1-3] as well as (ii) between the time scale of molecular dynamics and the total system entropy of real materials near the glass transition [4]. At first glance, these results seem to be disadvantageous to perspectives of finding a simple universal description of the glass transition and related phenomena. However, a very successful application of the density scaling law to both the decoupling phenomena yields a very positive outcome of our investigations. Based on the analyses of high pressure experimental data, we give evidence that the structural dielectric relaxation time, the characteristic length scale of molecular dynamics (evaluated from the height of the peak of the four-point dynamic susceptibility function using estimates suggested [5] for the novel four-point measure of the dynamic heterogeneity of systems approaching the glass transition) as well as the total system entropy obey the density scaling law relied on the scaling quantity defined as density$^{\gamma}$/temperature, where the scaling exponent γ is a material constant, but its value is in general different for different physical quantities. We prove that such different scaling behaviors straightforwardly imply the experimentally established decoupling phenomena. This promising conclusion sheds new light on fundamental problems of the glass transition physics, the successful solution of which can be sought after in terms of the density scaling law that allows different values of the scaling exponent for different physical quantities.

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Scaling behavior of the conductivity 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 as potential pharmaceutical ingredients, or green solvents as well as, promising electrolytes for fuel cells and batteries. The use of ionic liquids in electrochemical devices is driven by their unique physical properties, such as low melting points, low vapor pressure, non-flammability, thermal and chemical stability, or broad electrochemical window. However, 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 such as viscosity, conductivity relaxation or diffusion coefficient) 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 is frequently implied that the parameter γ, which is regarded as a characteristic material constant, is straightforwardly related to the one third of the exponent appearing in the repulsive part of the soft Lennard-Jones (LJ) potential. 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. Thus, the question about the validity of density scaling for ILs over a wide temperature range, *i.e.* from the deeply supercooled liquid (where $\eta \approx 10^{12}$ Pa·s) to normal liquid state (where $\eta \approx 10^{-2}$ Pa·s) is still open.

In this talk we examine the thermodynamic scaling concept in the vicinity of the glass transition region for various protic and aprotic ionic with different charge transport mechanisms (Grotthuss vs vehicle). To determine the value of scaling exponent γ, the electrical conductivity data were analyzed in the temperature-pressure-volume thermodynamic space in terms of the modified Avramov entropic model. Finally, we propose a new approach based on the thermodynamic scaling concept for analysis the correlation between electrical conductivity and structural relaxation time.

Does the thremodynamic scaling idea and the concept of the dynamic heterogeneity can improve the Prigogine-Defay ratio?

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One of the strong evidences that the glass transition cannot be treated as a pure second order thermodynamic transition is the difference between the prediction of well-known Ehrenfest's equations, which determine the pressure coefficient of the glass transition temperature dT_g/dP, and the value of dT_g/dP obtained from experimental measurements. Furthermore the Progogine-Defay ration, which is a combination of Ehrenfest's equations are not equal to unity for majority of glass formers, against expectations. A very hopeful alternative for estimating the pressure coefficient of the glass transition temperature and improving the Prigogine-Defay ratio are our new equations, which describe dT_g/dP. The first one [1] is developed in the thermodynamic scaling regime, i.e., if structural relaxation times can be plotted on one master curve (independently of thermodynamic conditions) as a function of TV^γ (γ is a material constant interpreted as m/3 where *m* is the exponent of the repulsive part of effective intermolecular potential). The second one employs the concept of the dynamic heterogeneity and their approximations according to which the degree of the dynamic heterogeneity triggered by enthalpy fluctuations is equal to a good approximation to the sum of the degrees of the dynamic heterogeneity triggered by temperature and volume fluctuations [2]. We show that the values of dT_g/dP from our new equations are consistent with those estimated from experimental $T_g(P)$ and the Prigogine-Defay ratio which results from our new equations is equal to unity to a very good approximation. It is worth noting that our relations, which link dT_g/dP with the exponentγ, reflect the relative role of thermal activation ($\gamma \rightarrow 0$) and free volume ($\gamma \rightarrow \infty$) in molecular dynamics near the glass transition, therefore it takes part in the discussion on a single- or two-order-parameter model of glass-forming liquids [4,5] and shows when single-order-parameter models can be used.

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Oligomeric shear modes, mixing enhanced susceptibility, low-frequency cut-off, and other surprises in Debye-type liquids

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Monohydroxy alcohols constitute a large class of liquids that feature a slow, often strictly exponential response, named after Debye [1], in their dielectric relaxation. As recently emphasized [2], a number of other than dielectric techniques such as high-resolution shear rheology [3], inelastic neutron scattering [4] etc. are useful to unravel the structure and dynamics of these supramolecular liquids. In this presentation we will mostly focus on *mixtures* involving monohydroxy alcohols. A surprizing phenomenon recently discovered by various experimental methods is the enhancement [5,6,7] of Debye-like relaxations as a consequence of, e.g., monohydroxy alcohol mixing. Furthermore, suitable alcohol mixtures were found to exhibit a low-frequency cut-off in their dielectric spectra that relates to a Debye process. For those mixtures it will be demonstrated that the common procedure of treating different contributions to dielectric relaxation spectra as additive fails badly to describe frequency domain data. Here, the Williams-Watts convolution approach [8] turns out useful. With reference to the experimental identification of Debye-type relaxations in other types of supramolecular liquids perspectives for future work in this field are discussed.

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Unusual dynamics in glass forming mixtures of water with a Debye liquid

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The dynamics of supercooled water can be explored by studying the dynamics of glass forming aqueous mixtures which can survive in deep supercooling down to the glass transition and, in the past decades, chemicals with multiple hydroxyls or amino such as polyalcohols, disaccharides and polysaccharides have been widely used to make glass forming mixtures [1]. Debye liquids are proven to be of special chain-like associations, and recent studies show that the dielectric relaxation of the mixtures constituted by two Debye-typed monoalcohols is still Debye typed, while when mixing with non-Debye liquids, the Debye relaxation of monoalcohols would disappear at a specific mole fraction [2,3]. It is therefore expected that the studies of the aqueous mixtures of Debye liquids would offer new knowledge of the dynamics of supercooled water. Unfortunately, the typical Debye liquids, long alkyl-chain monoalcohols, do not work well due to the limited miscibility.

Recent studies show that secondary amides which exhibit excellent miscibility with water featured by the large and negative mixing heat are also Debye liquids [4,5]. Here, the aqueous mixtures with the Debye liquid, N-ethylacetamide, are studied by dielectric and calorimetric measurements in the highly viscous regimes near the glass transition. Calorimetric measurements found that adding water to N-ethylacetamide remarkably enhances the glass transition temperature, in analog to the observation in the mixtures of N-ethylacetamide with a non-Debye, 1,2-propanediamine. However, strikingly, the dielectric measurements found that the main relaxation in the mixtures of water mole fraction up to 60% reproduces the typical dynamic characters observed in mixtures composed of two Debye liquids, N-ethylacetamide and 2-ethyl-1-butanol, prior to the characteristic phase transitions identified in aqueous solutions. The unique calorimetric and dielectric features in the N-ethylacetamide - water mixtures might imply the possibility of the presence of chain-like intermolecular associations.

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Mixtures of 2-Ethyl-1-hexanol with 2-Ethylhexyl bromide under pressure. Does compression influence the dynamics of supramolecular structures?

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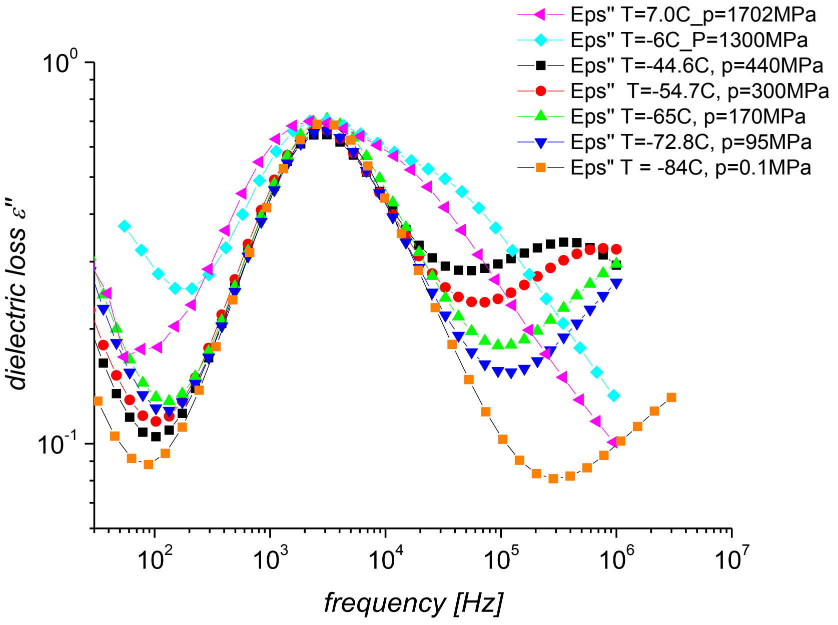
In type I monohydroxy alcohols the Debye process related to the supramolecular hydrogen bonded structures is dominating over the structural relaxation and time separation between these two processes is small. Consequently, to estimate e.g. influence of different thermodynamic conditions, especially at elevated pressure, on molecular dynamics of both relaxations, deconvolution procedure has to be apply. Fortunately, for moderately diluted alcohols e.g. 2-Ethyl-1-hexanol the slow Debye process separates significantly from the structural relaxation. This enable to follow temperature dynamics of both relaxations without any deconvolution procedures. However, there is still lack of investigations of the alcohol mixtures at high pressure conditons. We present for the first time, results of dielectric measurements of these mixtures at elevated pressure. Presented data clearly indicate that compression is condition strongly influencing dynamics not only structural but also the Debye relaxation (see figure below). Consequently, pressurization markedly modified H-bonded supramolecular structures.



Relationship between Morphology, Mechanical and Electrical Properties in Structured Elastomers

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Thermoplastic elastomers (TPEs) are attractive materials because they have easy processing characteristics like thermoplastics and behave like elastomeric materials at ambient temperature. There are obtained by two techniques. First, elastomer and thermoplastic are prepared by mixing through simple blend technique called thermoplastic polyolefin blends (TPOs), second, the blend preparation is the same that with TPO but the elastomer phase is vulcanized during its melt-mixing or during its dynamic vulcanization which is obtained by vulcanized elastomer particles dispersed in melt-processable matrix. These types of blends are called thermoplastic vulcanizates (TPVs). Thermoplastic elastomers (TPO and TPV) based poly(vinylidene fluoride) and epoxidized natural rubber having epoxide group 50 mol% [called ENR-50] blends have been prepared by melt mixing process at different blend ratio. The incorporation of barium titanate ($BaTiO_3$) or BT particles into polymer are widely studied to enhance, in particular, permittivity of materials due to their high permittivity and low dielectric loss factor.

The dynamic mechanical properties, dielectric analysis and morphological properties of TPEs were investigated. From temperature dependence, the both TPO and TPV showed two relaxations : α_a and α relaxations of PVDF and ENR-50, related to segmental motion in amorphous phase of PVDF and ENR-50, respectively. Their evolutions will be studied as function of the composition and morphology of the different materials.

In the case of TPO, the phase structure of 80/20 PVDF/ENR-50 exhibited dispersed phase of ENR-50 in PVDF continuous phase while 50/50 PVDF/ENR-50 showed co-continuous phase structure. The incorporation of barium titanate particles into PVDF/ENR-50 blends affected to physical properties and morphological properties. In 80/20 blends, the BT particles were localized at interface between PVDF and ENR-50 while in 50/50 PVDF/ENR-50 blend, BT particles move to ENR-50 phase leading to change the morphology from co-continuous morphology to dispersed phase/matrix morphology so changing also the properties. Barium titanate particles can be blocked by using dynamic vulcanization process and it will be located at interface of the two phases to act as filler for functionnality or compatibilizer. In general, the filled TPO and TPV at blend ratio 80/20 PVDF/ENR-50 blends showed higher storage modulus and permittivity than that of 50/50 blends due to higher content of polar PVDF.

Raman and dielectric spectroscopic studies of molecular interactions in poly(vinyl methyl ether) hydrogels at low temperatures

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In this work we studied states of water at temperatures below 0°C in poly(vinyl methyl ether) (PVME) hydrogels of various crosslinking degrees using Raman and dielectric spectroscopy (DS), supported by differential scanning calorimetry (DSC). Water interacting with a polymer reveals a number of properties very different to bulk water, since such interactions lead to redistribution of hydrogen bonds resulting in modification of thermodynamic properties and molecular dynamics of water. Such modified water is particularly well observable at temperatures below 0°C, when the bulk water crystallizes. Analysis of the dielectric spectra of the hydrogels allowed us to estimate fraction of water able to rotate at temperatures below 0°C, while from the DSC thermograms the amounts of both non-freezing and pre-melting water was determined. We found a good agreement between the DSC and the DS-based estimations of the hydration number of the PVME monomer unit. Thanks to high sensitivity of Raman spectroscopy to a local environment of molecules we perceived that between -163°C and -60°C the PVME chains are fully dehydrated. This analysis allows us to compare various physical properties of the bulk and the pre-melting water. It was found that the pre-melting process starts in significantly lower temperatures than it was observed by BDS and DSC, i.e. around -60°C, and proceeds with simultaneous reconstruction of hydrogen bonding between the polymer and water molecules. Based on obtained results we postulate also the molecular mechanism responsible for the pre-melting of part of water in the hydrogels.

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Cellulose Acetate/Plasticizer Systems: Structure, Morphology and Dynamics

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Due to its biodegradability and renewability, a great interest has been devoted to investigating cellulose acetate (CA) in order to expand its potential applications. In this context, the characterization of CA is one of the keys to promote further developments. Due to their high glass transition temperature, cellulose acetate based systems are processed when blended with plasticizers. It is thus of utmost importance to study the miscibility and plasticizing effects of various molecules. We prepared CA films via solvent casting method with diethyl phthalate and triacetin as plasticizers.

Miscibility and dynamical characterizations were mainly carried out by broadband dielectric spectroscopy (BDS). Secondary relaxations were first discussed. Complementary details were provided from calorimetry (MDSC), X-ray diffraction (XRD) and mechanical experiments (DMTA analysis). Phase diagrams were established by MDSC analysis and the results are consistent with BDS findings. Two glass transitions have been found both in BDS and MDSC characterizations when phase separation occurs between CA and plasticizers. These miscibility and dynamical results will be discussed in the light of structural studies performed by Small-Angle Neutron Scattering (SANS). By BDS, we could furthermore identify the α-relaxation of these CA-plasticizer systems in the frequency range from 0.06 Hz to 10^6 Hz, which allowed for describing for the first time the dynamics in the so-called Vogel-Fulcher-Tammann regime (VFT).

Resolving the segmental dynamics in oligomeric *1,4-poly(isoprene)s* by selective effect of polar small molecule organic compound

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A combined thermodynamic and dynamic study on several oligomeric samples of Type A + B chain systems exhibiting both the parallel and perpendicular electric dipole moment component, i.e., a series of *1,4-poly(isoprene)s* (*1,4-PIP*) of different molar masses in the pure state as well as in the doped one with a small amount of polar small molecular compound *2,2,6,6–tetramethyl-piperidine-1-oxyl (TEMPO)* was performed using differential scanning calorimetry (DSC) and broadband dielectric spectroscopy (BDS) techniques with the focus of resolving the complex overlapped BDS spectra from both the normal and segmental relaxation peaks.

DSC measurements on this series of the *1,4-PIP* samples indicated that a few wt. percent of the polar additive causes the small decrease in the glass transition temperature with respect to the pure *1,4-poly(isoprene)'s* matrices due to plasticization effect. Next, detailed BDS investigations over a wide frequency range 10^{-2} – 10^{9} Hz revealed a small influence of the dopant on the spectral features of the normal mode relaxation and a mild acceleration and very strong intensification effect on the primary α process. Subsequently, the complex overlapped BDS spectra for all the members of the investigated serie of *1,4-PIP* were analyzed in terms of the model consisting of the *Havriliak - Negami* (*HN*) relaxation function for the segmental relaxation process and the modified *Rouse* dynamic model for the global end-to-end vector chain relaxation one with the aim of the first complete description and interpretation using of this combined phenomenological-microscopic approach. We have found that whereas the slight shift in the normal mode relaxation times was removed by including the plasticization effect on T_g values, the times of the resolved α relaxation process are effected by specific contributions of the polar solute *TEMPO* to that of the *1,4-PIP* segmental relaxation process.

Relaxation data on *m-Toluidine* in relation to free volume and rotation dynamics from external probing PALS and ESR techniques

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m-Toluidine (m-TOL) is a very interesting model glass-former with the tendency to create the intermolecular H-bonds and the relatively high fragility m_g = 79 or 84 [1-3]. So far DS studies addressed predominantly the primary α relaxation and the β relaxation in the glassy state [2,3]. Our contribution is focused on an extension of the frequency range: $10^{-2} - 10^{+9}$ Hz as well as on obtaining the β-relaxation data above T_g^{DSC} = 187 K [1]. The BDS spectra over the whole T range from 186 K up to 295 K were fitted by using the HN and CC model. The novel feature of the α process is the presence of four different regions of the spectral shape of the α process giving three characteristic BDS temperatures $T_{B1}^{\beta HN}$=209 K, $T_{B2}^{\beta HN}$=237 K, $T_{B3}^{\beta HN}$=259 K. The newly revealed β-process above T_g exhibits the VFTH dependence with: $\tau_{0\beta}=1.65 \times 10^{-14}$ s, B_β=933 K, $T_{0\beta}$=160 K. The primary α-relaxation times over the entire T range can be described by using the two order parameter (TOP) model [4] in terms of the *solid*- and *liquid*-like domains with the characteristic temperatures: T_0 =152 K, T_m^C =202 K, T_A =269 K. From comparison of the afore-mentioned BDS data with these TOP parameters the following relations can be found: $T_0 \cong T_{0\beta}$, $T_m^c \cong T_{B1}^{\beta HN}$ and $T_A \cong T_{B3}^{\beta HN}$.

The existence numerous characteristic BDS temperatures is supported by empirical findings from external atomistic and molecular probing *m-TOL* by PALS or ESR techniques, respectively. The temperature dependence of *o-Ps* lifetime, τ_3, as a measure of free-volume, shows up five regions of distinct thermal behavior characterized by PALS temperatures: T_{b1}^G = 159 K, T_{b1}^L = 195 K and T_{b2}^L = 235 K. Similarly, spectral parameter of mobility of *TEMPO*, $2A_{zz'}$, and rotational correlation time, τ_c, being two measures of the molecular probe mobility, exhibit five regions with characteristic ESR temperatures: T_{X1}^{slow} = 157 K, T_{X2}^{slow} = 200 K and $T_{50G} = T_c$ = 240 K. All these characteristic BDS, PALS and ESR temperatures are in acceptable agreement suggesting the same origin of the underlying processes. According to the TOP model the changes at $T_{b1}^G \cong T_{X1}^{slow} \cong T_{0\beta} \cong T_0$ can be associated with the onset of the *liquid*-like domains in the glassy state and $T_{b1}^L \cong T_{X2}^{slow} \cong T_{B1}^{\beta HN} \cong T_m^c$ to the dominance of the *liquid*-like domains over the *solid*-like ones.

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Dielectric behavior of hyperbranched polyamide-amine/kaolinite nanocomposites

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Broadband Dielectric Spectrometer (BDS) is employed to investigate the dielectric properties of nanocomposites based on hyperbranched polyamide amine and modified Kaolinite. Synthesis of the nanocomposite samples of different ratios of modified kaolinite using two methods, namely, in situ and ex situ, is described in some details. The prepared samples are characterized using different techniques. It is found that the plasticizing effect of the inorganic nano filler which reduces the glass transition temperature enhances at the same time the electrical conductivity of the polymer. We address the question if the method of preparation affects the dielectric behavior of the sample.

$Li_{10}SnP_2S_{12}$: An Affordable Lithium Superionic Conductor

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Until now, the integration of solid electrolytes in batteries was strongly hindered by the poor ionic conductivity of most solid lithium ion conductors. In 2011, Kanno et al. reported the synthesis of $Li_{10}GeP_2S_{12}$.[1] With a conductivity of 12 mS/cm at 27 °C it exhibits the highest lithium ion conductivity known to date. But the major drawbacks for its application in batteries are the scarce deposits and high cost of germanium.

We synthesized and characterized the thiostannate analogue $Li_{10}SnP_2S_{12}$, which exhibits a very high grain conductivity of 7 $mS \cdot cm^{-1}$ at 27 °C.[2] The replacement of Ge by Sn should reduce the raw material cost by a factor of about 3, and the total conductivity of 4 mS/cm still exceeds the lithium ion conductivity of the carbonate-based liquid electrolytes, when the lithium transference numbers are taken into account.

The impedance spectra of $Li_{10}SnP_2S_{12}$ in contact to ion-blocking metal electrodes and in contact to reversible Li electrodes are discussed. It is shown that interfacial impedances play an important role for the application of $Li_{10}SnP_2S_{12}$ in solid-state batteries.

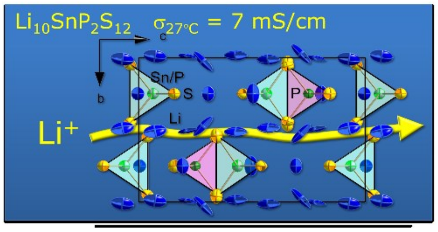

Fig. 1: Illustration of Li^+ ion transport in $Li_{10}SnP_2S_{12}$

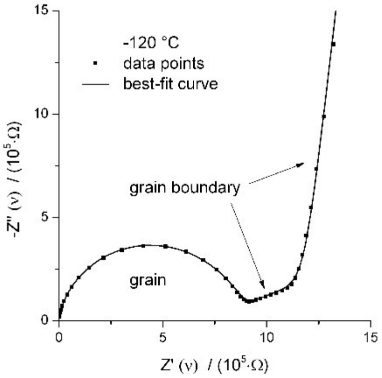

Fig. 2: Nyquist impedance plot of $Li_{10}SnP_2S_{12}$ in contact to ion-blocking electrodes

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Dynamics of Precise Ethylene Acid Copolymers and Ionomers

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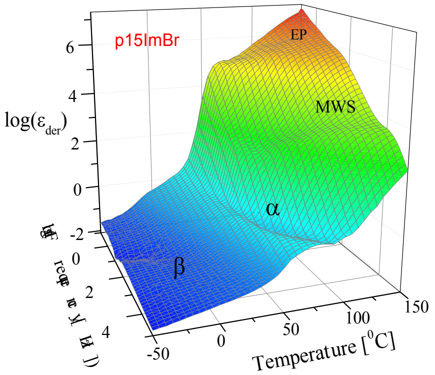
This presentation will focus on our recent research on the dynamics of novel linear polymers, consisting of monodisperse ethylene sequences between very precisely spaced acrylic acid or ionic functionality, using dielectric spectroscopy. The non-polar ethylene portions of the acid copolymers and ionomers exhibit very low dielectric loss, allowing one to focus on the molecular motions of the acid and/or ionic functionality. Companion X-ray scattering experiments were conducted in order to provide insight into the self-assembled microphase separated morphology of the polar species in the polyethylene matrix. Incorporating ions in precise acid copolymers (via neutralization of a portion of the acid functionality) results in significant changes in the association state of the acid and ionic groups, as well as polymer and ion dynamics. In addition, polymers with longer ethylene sequence lengths crystallize to some degree, which also has an important influence on the dynamics.

We focus on linear high molecular weight poly(ethylene-co-acrylic acid) copolymers with precisely spaced acid groups (exactly on every 9th, 15th and 21st backbone carbon) and their lithium-neutralized ionomers. In addition, the dynamics of linear PE with 1-methylimidazolium bromide (ImBr) units precisely substituted on every 9th, 15th, or 21st carbon will be discussed.

Supported by the National Science Foundation, Polymers Program.



Dielectric loss spectrum (with dc conductivity contribution removed) of the precise ethylene copolymer with ImBr units on every 15th main chain carbon atom.

Peculiarities in dynamics of supecooled ionic liquids studied by broadband dielectric spectroscopy

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A lot of ionic liquids in supercooled state behave similarly to molecular liquids. It means that their transport properties like viscosity, diffusivity and ionic conductivity are coupled with each other and with the relaxation of structure. Moreover, like molecular liquids, ionic ones reveal a change in the temperature dependence of structural relaxation times and conductivity slightly above the glass transition temperature (usually around $1.2T_g$). However, there are exceptions to these rules. The best described in literature are [BMIm][PF6], CKN and several protic ionic liquids with quite pronounced decoupling between ionic conductivity and structural relaxation or viscosity. Also the change from one VFT-dependence to another is not observed for all ionic materials.

Another key problem in dynamics of supercooled and glassy ionic materials is origin of their secondary relaxations. Although generally it is believed that these phenomena come from interconversion of dipolar units within ions lately some evidence has been given that some of them possibly originate from local movements of whole ions being some kind of ionic Johari-Goldstein relaxation.

Since all mentioned above issues are of the paramount importance in understanding the glass transition phenomenon it is absolutely necessary to find reasons for these peculiarities. However, to form any general conclusion experimental data are needed.

$[BMIm]_2[Co(NCS)_4]$ and $[EMIm]_2[Co(NCS)_4]$ are very interesting ionic liquids. They have rather simple chemical structures and very common cations. Despite that, their dynamics is very interesting and not similar to majority of well-known imidazolium-based ionic liquids. Results obtained from dielectric studies will be discussed and compared to that obtained from rheological and thermal analysis.

Direct approach for impedance analysis of ion conducting glasses

Max Fraenkl

Solid-state ion conductors are an important class of materials. These materials attract considerable interest due to their potential applications in the field of electrolytes in batteries and fuel cells, gas sensors, etc.[1,2]

Electrochemical impedance spectroscopy (EIS) is powerful method for understanding dynamics of ionic transport. Measured data are mainly analyzed by using equivalent electrical circuits (EEC) or Poisson-Nernst-Planck (PNP) equation [3]. The EEC method does not provide physical parameters such as the diffusion coefficient, the number of mobile ions, etc. The PNP approach (in principal macroscopic method) is not so popular, probably due to the high mathematical complexity.

Being unhappy with these drawbacks and limitations we propose our direct microscopic approach of analysis EIS [4-6]. Studied systems are chlacogenide glasses doped with Ag.

Our model based on Dyre's random walk theory [7]. Give us directly important physical parameters, such as

i, iffusion coefficient of ions and
ii, number of mobile ions

The study shows, how helpful this approach can be to understand the electrode polarization as well as ionic transport mechanism. Proposed approach can be used for description of the various ion conductive systems.

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Dielectric and structural properties of ultrasonic and microwave irradiated plasticized polymer nanocomposite electrolyte

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Solid polymer electrolytes (SPEs) have been recognized as novel materials for ion conducting devices particularly for rechargeable batteries [1]. Enormous work is in progress on the preparation and characterization of SPE materials based on various polymers, alkali salts, plasticizers and inorganic nanofillers [1–4].

In the progress on SPEs materials, the poly(ethylene oxide) as host matrix with lithium perchlorate salt, poly(ethylene glycol) as plasticizer and montmorillonite clay nanofiller based electrolyte film has been prepared by ultrasonic and microwave irradiated solution casting followed by melt-pressed method. The complex dielectric function, ac electrical conductivity, electric modulus and impedance spectra of the electrolyte film have been investigated in the frequency range 20 Hz–1 MHz at temperatures 25–55 ^{o}C. The complex permittivity shows a non-linear decrease with increase of frequency and its high values at low frequencies are due to contribution of electrode polarization effect (Fig. 1). Single relaxation peak is observed in dielectric loss and tanδ spectra corresponding to cations coordinated polymer chain segmental motion. The dc ionic conductivity of the electrolyte obeys the Arrhenius behaviour. The complex impedance plots have spike at low frequencies and an arc at high frequencies (Fig. 2). The amorphous phase and exfoliated/intercalated clay structures of the electrolyte film are investigated by x-ray diffraction and scanning electron microscopy (Fig. 3). The sufficiently high value of ionic conductivity of the film (> 10^{-5} S cm^{-1}) confirms its suitability as electrolyte material for lithium ion batteries.

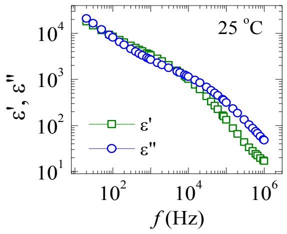

Fig. 1. ε′, ε″ vs *f* plots

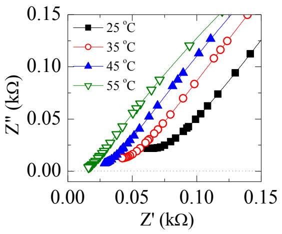

Fig. 2. *Z″* vs *Z′* plots

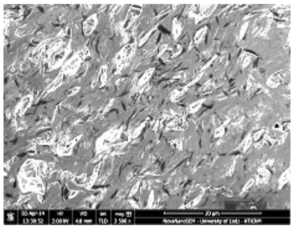

Fig. 3. SEM image

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Liquid and Glassy Dynamics by Non-Linear Dielectric Experiments

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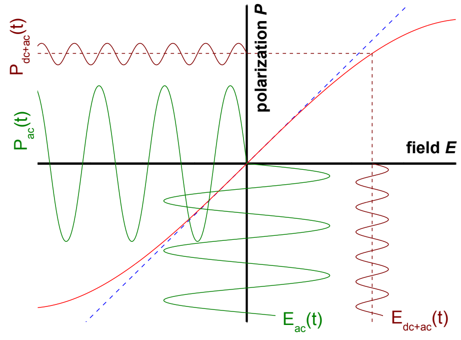
Most dielectric relaxation experiments are performed in the regime of linear responses, in which the magnitude of the field has no impact on the permittivity result, $\varepsilon^*(\omega)$. At higher field amplitudes, several additional effects can occur: electrostriction (only an apparent change in permittivity), dielectric saturation, chemical and similar effects, as well as the changes in behavior resulting from the energy that the sample absorbs from the electric field [1].



While the analysis of non-linear response data is far from straightforward, the reward is that more detailed information is obtained relative to the linear regime counterpart. Examples will be provided for different experimental approaches to non-linear dielectric behavior. One obvious alternative is the use of a large amplitude sine wave field versus a small sinusoidal field on top of a large bias field, as indicated in the figure. The various approaches to quantifying the field induced effects are also discussed, i.e., the difference between the third harmonic response, χ_3, and the field induced change of the permittivity at the fundamental frequency, $\varepsilon_{\mathrm{hi}} - \varepsilon_{\mathrm{lo}}$.

Among the results reported on the basis of non-linear dielectric work are the heterogeneous nature of dielectric polarization, the dependence of dielectric saturation on the relaxation details, the added insight into the role of hydrogen-bonded structures on the dielectric polarizability, understanding the effect of energy irreversibly transferred from the field to the sample, and the quantification of the number of dynamically correlated particles and nontrivial length scales. The examples clearly demonstrate that much is gained from going beyond the linear regime.

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Nonlinear Dielectric Spectroscopy in Critical Liquids

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In the year 1936 Arkadiusz Piekara noted an extraordinary increase of the strong electric field induced changes of dielectric permittivity (*nonlinear dielectric effect*: NDE) on approaching the critical consolute point in nitrobenzene-hexane critical solution of limited miscibility.[1] The quantative description of this phenomenon was given only in 1993, basing on the novel „mixed criticality (*classical/nonclassical*)" model.[2,3] In subsequent years NDE developed to the dual-field nonlinear spectrocopy (NDS). It enabled tests of the stationary NDE responses following DC and AC pulses of the strong electric field as well related relaxation/decay times. The AC case lead to the frequency-selecive excitation of multimolecular fluctuations/heterogeneties in tested liquid samples.[4,5] This contribution presents basic NDE/NDS results for critical mixtures, liquid crystals (LC) as well as mixtures of LC and a nonmesogenic compounds, including the case of limiting miscibility. New results related to the evolution of the „nonlinear" relaxation time for the DC and AC cases are also shown and explained via the developed „mixed criticality model". Finally, results associated with the NDE/NDS insight into the issue of supercriticality, including the challenging case of the gas – liquid critical point, are discussed.

Presented investigations cover both temperatures and pressure paths and show extraordinary possibilities of NDE/NDS technique for estimating locis of critical and other „characteristic" points in liquids, including the hardly available negative pressures domain.[6] NDS: the 21st century successor of BDS great success ?

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Dielectric Investigations on Manganese Ions Doped Tellurite Antimony Borate Glasses

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TeO_2-Sb_2O_3-B_2O_3 glasses mixed with different concentrations of MnO (ranging from 0 to 3.0 mol %) were prepared. These glass samples were characterized by X-ray diffraction and scanning electron microscopy. The dielectric constant (ε′), dielectric loss (tan δ) and a.c. conductivity σ_{ac} over a wide range of frequency and temperature have been investigated. The XRD studies and SEM pictures have clearly indicated that the samples prepared were of amorphous in nature. The variation of dielectric loss with temperature for these glasses exhibited dielectric relaxation effects. With the help of other auxiliary experimental results (viz., optical absorption and ESR) it has been identified that manganese ions co-exist in Mn^{3+} state in addition to Mn^{2+} state in these glass matrices. Tellurium ions and Mn^{2+} are assumed to be responsible for the relaxation character of dielectric loss. The dielectric parameters viz., ε′ & ε′′, and $\sigma_{a.c}$ are found to increase with the increase in the concentration of MnO up to 2.0 mol %, indicating an increase in the concentration of Mn^{3+} ions that take part as modifying position in this concentration range. The bonding defects generated by the modifying ions do create easy path ways for the migration of charge carriers that would build up space charge polarization and facilitate to increase in the dielectric parameters. These studies have indicated that as the concentration of MnO is increased up to 2.0 mol%, the insulating strength of the glasses decreases.

Temperature Dependences of Dielectric Intensities of Bound Systems

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Unlike with normal liquids, dielectric constant (or relaxation amplitude) of mixed systems exhibits anomalous temperature dependence. Relaxation amplitude of normal liquids are described essentially 1/*T* dependence, where dielectric constant increases with decreasing temperature [1]. On the other hand, relaxation amplitudes of mixed system, such as nano-confined solvent, protein with solvent, and binary aqueous mixtures, often exhibit opposite temperature dependence, namely relaxation amplitude decreases with decreasing temperature [2]. Irrespective of its ubiquity, physical mechanism of this anomalous temperature dependence has not been understood yet.

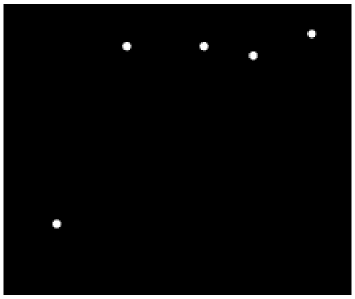

Fig. 1: Free energy diagram of the two states model assumed here.

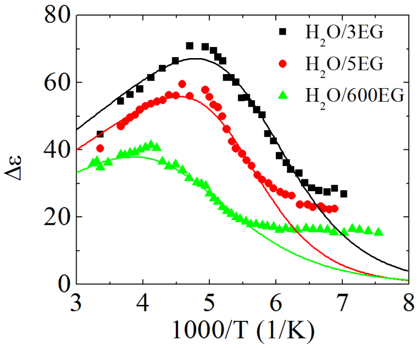

Fig. 2: Temperature dependence of the dielectric relaxation intensity of v-process of water/EG oligomer mixture. Points shows experimental data [2], and full lines represent the best fit by the present theory.

In this talk, we are going to propose a theoretical model to describe this anomalous temperature dependence. We assume two discreet states, bound and free (unbound) states of solvent molecules (Fig. 1). When a solvent molecule is free, it contributes to the fluctuation of electric moment, whereas when it is bound, it doesn't any more. Applying this model to the Frölich's general dielectric equation [1] yields orientational correlation factor *g*,

$$g = e^{-\beta F}\frac{2+e^{-\beta F}}{(1+e^{-\beta F})^2}\xrightarrow{\beta\to\infty}2e^{-\beta F},$$

where *β* is reciprocal temperature, *F* is free energy difference between free and bound states (Fig. 1). This equation successfully describes reported anomalous temperature dependences, such as water/ origomeric ethylene glycol (EG) mixture (Fig. 2), water/LiCl solution, hydration water on protein, and binary cluster of carboxylic acid.

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Meyer-Neldel Compensation as a feature of the Johari-Goldstein β-relaxation

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Despite its appearance in a large number of glass formers the full scope of the Johari-Goldstein β-relaxation is not yet completely understood. It is clear that it originates on the molecular level, often serving as a precursor to the α-relaxation. Relations between the Activation Energy and the Glass Transition Temperature (T_g) have been extensively studied and analyzed. We wish to introduce a new ubiquitous relation, one involving the Activation Energy on the one hand and the minimal relaxation time on the other.

Collected data from a wide array (>80) of glass formers show a common feature in the behavior of the prefactor of these relaxations. They all obey the Meyer-Neldel compensation law linking the relaxation behavior to the entropy of a multi-exitation process. The glass formers involved include; Hydrogen bonded networks (simple as well as poly alcohols), van der Walls liquids, hydrated proteins, polymer blends, small organic molecules, epoxy systems, saccarides and some others as well. This connection between the activation Energy and the relaxation precursor has been noted in isolated instances before, but never characterized as a universal feature.

It shall be demonstrated that this relation shows much promise towards improving our understanding of glass formers. The universal behavior must be intrinsically connected to the microscopic origins of the process and should help shed light on its nature. It may also help provide a definitive way of distinguishing between different types of β relaxation, as well as a clear indication when an excess wing actually emanates from such a process. A preliminary explanation for this universal feature is provided and its implications are discussed.

Cooperative and local dynamics of amorphous pharmaceuticals under cooling, compression, ageing

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Active pharmaceutical ingredients (API) are preferred in amorphous solid state for their improved bioavailability, but their safe long term storage could be limited for the enhanced tendency to crystallize. Indeed, the recently reported anomalous crystallization of molecular pharmaceutical near and below the glass transition temperature opens new perspectives of investigation [1]. Moreover, surface crystal growth much faster than in bulk have been reported in some molecular pharmaceuticals, reflecting fast surface mobility [2]. Some recent extensive experimental studies and new theories have been presented, but an explanation of the fast mode of crystal growth (FCG) is still missing [1,3]. Its presence was correlated to high fragility, strong translational/rotational decoupling and broad relaxation time distribution. Some studies report that also the local secondary β-relaxation may control the FCG and the surface diffusivity [4], so that the suppression of local mobility, due to some specific interaction, could stabilize amorphous drug against crystallization [5]. The effect of density over the thermal fluctuations in favoring FCG has been also theorized [3], but experiments give controversial results [6], since high pressure variations affect dynamic properties in manifold ways.

Here we will present a broadband dielectric spectroscopy study about API dynamics under temperature and pressure variations, with the aim to connect the role of cooperative and local molecular mobility in bulk and at nanoscale to the stability against crystallization. The effect of physical ageing will be also presented, paralleling recently reported effects on surface and bulk diffusivity [7].

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Dynamic heterogeneity of ionic and non-ionic drugs near the glass transition

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Molecular dynamics of the deeply supercooled liquids is highly heterogeneous. It means that molecules only a few nanometers away from each other may have relaxation rates that differ by several orders of magnitude. Near the glass transition, a significant increase in the length scale of molecular dynamics is observed, which suggests that the spatial heterogeneities can be responsible for the glass transition dynamics [1,2]. Therefore, in the last half-century, the dynamic heterogeneity of various glass-former liquids has been intensively studied to gain a better insight into our understanding of the glass transition and the related phenomena. The latest theoretical, simulation and experimental investigations suggest that there is a relationship between the glass formation, dynamic heterogeneity, and crystal nucleation, which can play an important role in recrystallization mechanism of amorphous materials [3-5].

One of the most important questions which arises in the heterogeneous picture of molecular dynamics is “how the different molecular interactions affect the degree of the dynamic heterogeneity?”.

In this work, we evaluate the length scale of heterogeneity for several drugs which are bases (i. e. non-ionic liquids) as well as their hydrochloride salts that belong to protic ionic liquids. Such studies are very interesting, because molecules of these pharmaceuticals have nearly the same chemical structure but their intermolecular interactions are completely different. In this way, we check how the different kinds of intermolecular interactions influence the dynamic heterogeneity of molecular dynamics near the glass transition.

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Relaxation Processes in Glass Forming Pharmaceuticals and its Role on Amorphous Stability

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Solubility and permeability are two decisive factors quantifying the bioavailability of an active pharmaceutical ingredient (API) administered via oral route. Amorphous pharmaceuticals are promising when API is poorly water soluble, while having good permeability. Amorphous pharmaceuticals have attracted keen interest from researchers [1-4], since most of the newly formulated life saving APIs are in solid form with low aqueous solubility at ambient conditions. Though glassification of API is possible, the stability of this phase during long period of storage is required at least 2 to 3 years shelf life demanded by the pharmaceutical industry. Many a times, the amorphous drug reverts to most stable crystalline state during storage, which posing serious problems in applying the APIs in the amorphous form. Crystallization is characterized by long range ordering of molecules and hence the molecular relaxation dynamics related with intermolecular degrees of freedom are relevant to finding ways to enhance stability of the glassy phase. The effort is facilitated by recent experimental studies and theoretical considerations on glass-forming systems in general have established the fact that intermolecular secondary relaxation called Johari-Goldstein β-relaxation [5] is supposedly a universal feature of amorphous dynamics by having strong correlation [6-8] to the structural relaxation and it is the only effective relaxation present below the glass transition temperature Tg

To understand the glass forming phenomena and factors governing the stability of amorphous phase we have chosen nine APIs having different physical and chemical properties and investigated by broadband dielectric spectroscopy ($10^{-2} – 10^{7}$ Hz) deep into glassy state and up to the molten state. Together with the data of other pharmaceutical samples and classic glass-formers from the literature we infer that the Johari-Goldstein β-relaxation is governing a decisive role in the crystallization dynamics of amorphous drugs and by suppressing the former can in effect enhance the stability of the amorphous phase to have longer shelf life.

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Terahertz spectroscopy of H-bonded glass-forming liquids and drugs

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While dielectric spectroscopy is one of the standard tools used to analyse disordered materials over a wide frequency range it remains difficult to access the dynamics at terahertz frequencies. Terahertz time-domain spectroscopy is a complementary technique that can access frequencies between 0.3-3.0 THz over a broad temperature range making it possible to measure samples in the glassy, supercooled liquid and liquid states. In a previous study we have investigated the terahertz response of a group of polyalcohols [1]. It was shown that while the main contribution to the terahertz absorption originates from the coupling of photons to the vibrational density of states (VDOS), dielectric relaxations also contribute to the observed losses. Upon lowering the temperature, we found that the primary and the Johari-Goldstein (JG) secondary relaxation decouple from the VDOS at T_g and 0.67 T_g, respectively, where T_g is the glass transition temperature. Such universality is rather striking and we believe it is linked to a change in the hydrogen bonding dynamics.

In this work, glycerol and sorbitol are studied at temperatures from 80 K up to 500 K, revealing further changes in the losses above T_g. The results are discussed in line with hydrogen bond breaking as proposed in the past by neutron scattering studies [2]. Further, on the sample of celecoxib we examine the effect of non-JG secondary relaxations on the terahertz spectra. Celecoxib has been reported to exhibit three secondary relaxations, two of which are non-JG type [3].

The JG relaxation is often linked to the crystallisation of amorphous drugs at temperatures below T_g [3] and hence any change in hydrogen bonding dynamics might affect the crystallisation from the amorphous phase. Naproxen has a very strong tendency to crystallise below T_g and we found that its crystallisation ability is significantly enhanced at temperatures above 0.67 T_g. The absorption levels of amorphous drugs were found to increase linearly with temperature between 0.67 – 1.00 T_g which we believe can be linked to the contribution from the JG relaxation. For amorphous paracetamol, simvastatin and naproxen:indomethacin mixtures we show that the increase in terahertz absorption between 0.67 – 1.00 T_g strongly correlates with the stability of the amorphous drugs.

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Determination of the Glass Transition Temperature of Drug Dispersions via Dielectric Spectroscopy

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Knowledge of the glass transition temperature of drug dispersions is important if the dispersion is to be processed via hot melt extrusion. The purpose of this study was to evaluate analytical techniques for the measurement of the glass transition temperature of hydroxypropyl methylcellulose (HPMC) and formulated solid dispersions thereof. Unmodified samples of various grades of HPMC and solid dispersions of HPMC and the drug itraconazole produced by hot melt extrusion were analyzed by thermomechanical analysis, differential scanning calorimetry, thermally stimulated depolarization current, and dielectric spectroscopy. It was found that dielectric spectroscopy offers the best accuracy and reproducibility for analysis of the base HPMC powders regardless of the substitution type or viscosity grade and that the obtained results were not frequency dependent. The results of dielectric measurements of solid dispersions prepared by hot melt extrusion were compared with predicted values of the Gordon-Taylor equation. It is concluded that time-temperature superposition effects make broadly applying the determination of the glass transition temperature in drug dispersions by dielectric spectroscopy prohibitively difficult.

On the physical stability of amorphous pharmeceuticals: dielectric and calorimetric studies of EZB drug

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Ezetimibe (EZB) is a novel cholesterol-lowering drug, which acts at the small intestinal brush border membrane, where it selectively inhibits the absorption of dietary and biliary cholesterol. That is the reason why the EZB drug is extremely useful for the treatment or prevention hypercholesterolemia. It should be pointed out that the commercial form of this API available on the market exhibits low oral bioavailability (35%), which is attributed to its poor water solubility (8.4 mg/l). In order to increase the solubility and consequently bioavailability of EZB we have converted the crystalline drug to its amorphous counterpart. It should be stressed that the amorphous materials are usually unstable systems and may easily return to the crystalline form during the storage [1,2]. Therefore, in this presentation we will thoroughly investigate the physical stability of amorphous EZB drug. As reported by many authors, the most important factor affecting recrystallization from the disordered state is the molecular mobility of the system [3]. That is why, herein using the broadband dielectric spectroscopy (BDS) we described the molecular dynamics of EZB in a wide temperatures (153.15 K – 385.15 K) and pressure (0.1 MPa – 140 MPa) range. The dielectric as well as calorimetric data collected above the glass transition temperature (Tg = 334 K) have indicated that the tested drug easily undergoes cold crystallization. In order to characterize this process we have studied the kinetics of isothermal recrystallization in terms of the Avramov model [4]. Additionally, the Adam and Gibbs (AG) entropic model have been used to predict the physical stability of examined material at room temperature conditions i.e. below Tg of EZB [5]. As a final point, we have tried to stabilize the amorphous EZB by preparing the binary amorphous mixture ezetimibe + 20% wt. soluplus.

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Principles of Dielectric Blood Coagulometry

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Dielectric blood coagulometry (DBCM) is a novel method invented by us to test blood coagulability through dielectric spectroscopy (DS) measurements of a whole blood sample [1]. The blood coagulability is related to both thrombosis and bleeding risks. For example, a hypercoagulable state of blood increases the risks of cardiovascular diseases, brain infarction, and venous thromboembolism. Therefore, patients having those diseases frequently receive anticoagulant therapy to avoid lethal events. However, excess dose of the anticoagulant conversely induces a hypocoagulable state and increases a risk of bleeding in the brain that is also fatal. Sometimes, controlling the blood coagulability is also a problem in major surgeries (including trauma surgeries), and clinical discretion for blood transfusion and choice of blood products (platelet, fresh frozen plasma, and so on) is difficult without appropriate coagulation tests. In general, a plasma sample is used for standard blood coagulation tests such as prothrombin time international normalized ratio (PT-INR) and activated partial thromboplastin time (APTT). Therefore, they do not evaluate contributions from platelets and erythrocytes, though these cell components are known to be important for clot formation. Other existing methods also have certain limitations in sensitivity, specificity, ease of use, or cost. In this sense, a comprehensive blood coagulation test for a whole blood sample with an automated system is required.

In this work, fresh human whole blood samples were used for DS measurements at 37^{o}C over a frequency range from 1 kHz to 40 MHz by using a prototypical dielectric coagulation analyzer developed by us. The main dielectric relaxation process of whole blood is the interfacial polarization of erythrocytes in the β-dispersion frequency region [1]. In lower frequencies, electrode polarization is dominant; it is also sensitive to the conductance changes of the sample through the blood coagulation process. Figure 1 shows a typical three-dimensional pattern of the normalized permittivity changes along with blood coagulation. Following blood coagulation, the permittivity at around 10 MHz increases significantly, and there are non-monotonic changes at lower frequencies. These responses are informative to evaluate the coagulation time, clot strength, platelet function, aggregation of erythrocytes, erythrocyte sedimentation rate (ESR), and hematocrit level. The detailed mechanisms of the DBCM response will be discussed.

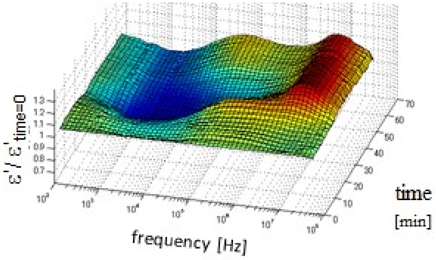

Fig.1 Typical DBCM signal

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Temperature and Hydration Dependence of Complex Dielectric Spectra of Lysozyme from GHz to THz Frequency Region

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Understanding of structures and dynamics of proteins is a fundamental problem for studies on protein function. When protein expresses the function, large structural changes often occur. These changes are induced by the collective motions of many atoms in protein, corresponding to the low-frequency motion below a few tens of wavenumbers. Therefore, the low-frequency spectra of protein contain information on the motions relevant to the function of protein. In this study we obtained and analyzed complex dielectric spectra in the THz region. We studied temperature and hydration dependence on the dielectric spectra of lysozyme from GHz to terahertz (THz) frequency regions.

In both dehydrated and hydrated states the complex dielectric spectra linearly increase as temperature rise below 180 K as shown in Figure 1. However, at higher temperatures the spectral components of the dielectric spectra increase more in the hydrated state than the dehydrated state. We performed spectral analysis of the complex dielectric spectra, $\varepsilon^*(\nu)$, using some model functinos such as a sum of an underdamped mode and a Cole-Cole function. We discuss temperature dependencies of these parameters obtained from the analysis.

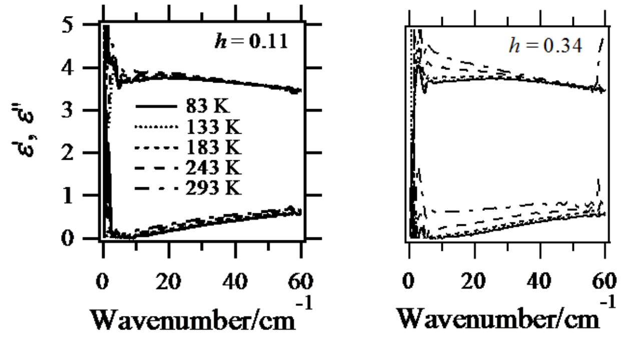

Figure 1. Temperature dependence of complex dielectric spectra of the dehydrated state (left) and a hydrated state (right), respectively. In each panel the upper and the lower groups correspond to the real parts and the imaginary parts, respectively. The hydration degree, which is defined by the value of *h* (weight of water divided by weight of protein) is shown in each figure.

A Microwave Microscope for Complex Impedance and Permittivity Operating From 1-20 GHz in Liquid for Life Science Investigations

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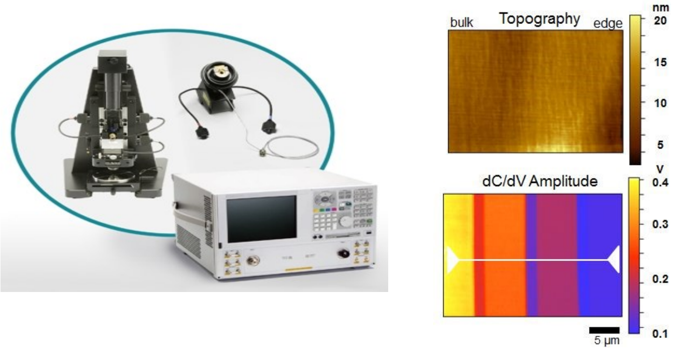
Here we present the nanoscale measurement of bio-samples in liquid up to 20 GHz using scanning microwave microscopy (SMM). SMM is a recent development in nanoscale imaging technique that combines the lateral resolution of atomic force microscopy (AFM) with the high measurement precision of microwave analysis at GHz frequencies. It consists of an AFM interfaced with a vector network analyzer (VNA). SMM allows measuring complex materials properties for nanoelectronics, materials science, and life science applications with operating frequencies ranging between 1 MHz and 20 GHz. Here we present the basic working principles of SMM and advanced applications. In particular, calibrated capacitance and resistance measurements are shown with a noise level of 1 aF [1, 6]. Calibrated dopant profiles are measured from 10E14 to 10E20 atoms/cm3 for nanoelectronics characterization [2, 3]. Experimental investigations are complemented by finite element radio frequency modeling using the 3D architecture of the probe and the sample, done with the Agilent software EMPro [4, 5]. We will present first GHz measurements of cells with nanoscale resolution in liquid environment.



Left panel: SMM setup. The AFM is interfaced with a Vector Network Analyzer measuring the electromagnetic properties of the sample. Right panel: Topography and dopant density (dC/dV) image of a semiconductor dopant sample with different dopant concentrations for quantitative and calibrated measurements.

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Evaluation of Salivary Dielectric Properties in Oral Cancer (OSCC) Through Time Domain Reflectometry at Microwave Region: The Future Alternative for Diagnosis and Treatment

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Oral Squamous Cell Carcinoma (OSCC) is the eleventh most common malignancy worldwide. Dielectric relaxation studies have been carried out for saliva of patients having tobacco habit but no squamous cell carcinoma (SCC) and those having tobacco habit with SCC using picoseconds time domain reflectometry over the frequency range of 10 MHz to 20 GHz at room temperature. The above two groups were compared with the control group. Dielectric parameters have been obtained by fitting complex permittivity spectra to Debye equation. In the present study, a total of 88 (48 oral cancer and 40 healthy) subjects were assessed and compared for the salivary dielectric properties (Parameters) viz. permittivity (ε), relaxation time (τ) and conductivity (σ). The values of dielectric parameters were compared with the histopathological grades and clinical stages of malignancy. Statistical analysis was done by applying '*t*' test. The results also show change in dielectric parameters with change in histopathological grades and clinical stage of the oral SCC biopsy sample.

Crystallization of aromatic polyesters by monitoring the dielectric β-relaxation: a quasi real time full dielectric method

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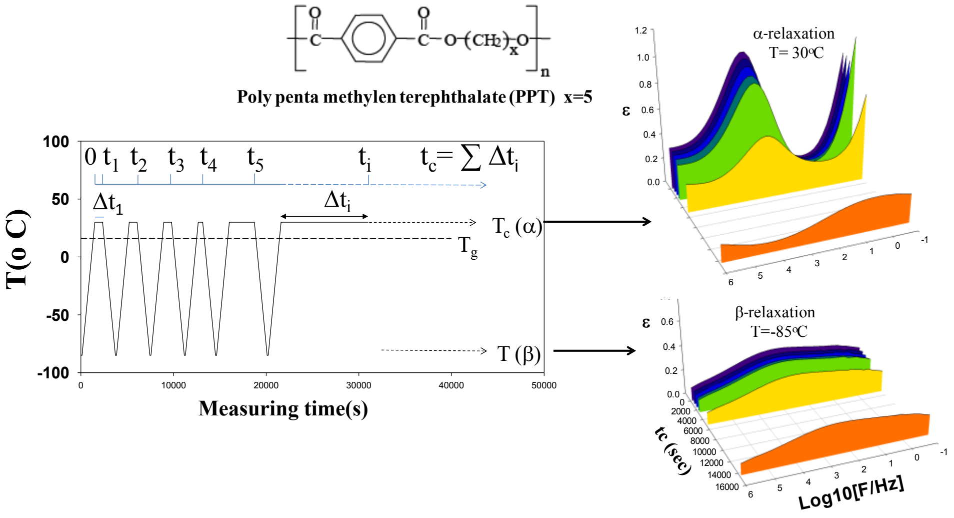
Aromatic Polyesters are semicrystalline polymers of relevance as engineering thermoplastic materials. Crystallinity is one of the key factors affecting most of their physical properties. Dielectric Spectrosocpy (DS) can be used to characterize crystallization. Typically the segmental relaxation, α is used as experimental probe to monitor the ordering process and its characteristics correlated with structural data extracted from scattering experiments. Pioneering DS experiments for PET showed that the dielectric strength of the β relaxation was inversely proportional to crystallinity[1]. Here we exploit this effect to attempt quasi real time crystallization experiments based only on DS. Fig.1 shows the evolution with crystallization time of both the α- and β-relaxation of poly(pentamethylene terephthalate) following a particular temperature-time protocol. Basically, it consists on a series of isothermal measurements starting by measuring the β-relaxation at low temperature. Then the temperature is raised up to the crystallization temperature, T_c, where the α-process is measured after a certain time,t_c. Subsequently, after cooling down, a new measurement of the β-relaxation is performed. By repetition of this method the crystallization process can be followed. On one hand, from the evaluation of the changes in the β-relaxation estimates of the crystallinity can be extracted. On the other hand, the evaluation of the α-process delivers information about the amorphous phase. Confronting both analysis fine structure-dynamics relations can be discussed



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Efect of High Pressure on the Crystallization Behaviour of Supercooled Liquids

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In recent years, there is a tremendous interest in manipulating and controlling crystallization behavior of molecular system which is an important issue in the field of material physics, chemical engineering, food and pharmaceutical developments. Among various strategies used to tune crystallization tendencies of glass-forming liquids one of the most intriguing is the application of high pressure. Under compression the molecular packing and intermolecular interactions of a given system are drastically modified, so as the key parameters governing the overall crystallization progress, i.e. kinetic and thermodynamic driving forces. However, quantifying the exact effect of pressure on the crystallization progress from the liquid state is very challenging task.

Here, we present results of high-pressure dielectric studies on the effect of hydrostatic pressure on the crystallization kinetics of low-molecular weight glass-forming liquids. To systematize our knowledge, we investigate crystallization behavior of molecular liquids with modified and non-modified intermolecular interactions as well non-racemic (pure enantiomer) and racemic systems. In our studies we have explored crystallization behavior of examinated materials at isochronal states only, which enables us to control molecular mobility factor and untangle thermodynamics effect from kinetics one. It is worth emphasizing that for a bulk phase this cannot be achieved by any other experimental attempt performed at ambient conditions.

Effect of Confinement on Polymer Crystallization and on the Local Polymer Dynamics

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The crystallization of polymers has been studied for more than 50 years, however, several issues/areas remain open. One such area is polymer crystallization under confinement. The aim of this study is to better understand how and why polymers crystalize under confinement. Since polymer crystallization affects polymer properties (i.e. optical and mechanical properties), controlling polymer crystallization has important technological apprications. Herein we report polymer crystallization under confinement provided by self-ordered nanoporous Alumina (AAO). We have investigated Poly (ethylene oxide)(PEO) [1], Poly(e-caprolactone)(PCL) [2] and double crystalline block copolymers of PEO-b-PCL[3] to AAO as a function of molecular weight, cooling/heating rate, pore size and surface functionality. In addition to this, we have also studied the effect of polydispersity, surface layer and mixing of oligomer using PEO as a model polymer [4]. Our results show a transition from heterogeneous nucleation to homogeneous nucleation below 65 nm diameter AAO. The strong molecular weight dependence of the homogeneous nucleation process (PEO) is reminiscent to the glass temperature suggesting a connection between homogeneous nucleation and heterogeneity at Tg. In this presentation, we will discuss the origin of heterogeneous and homogeneous nucleation in the process of polymer crystallization.

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Electrical and dielectric properties of composite materials: characteristic frequencies and scaling laws

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The composite approach represents a classical route of inducing a structuration process in the volume of materials, which can lead to enhanced mechanical and electrical properties. The global dielectric response of composite materials depends on the complex dielectric function of the constituting phases, on their volume fraction and their shape, on the local morphology given by the spatial distribution of the phases, and on their interfacial interactions. Due to local variations in conductivity across internal interfaces, the dielectric properties of composite materials are affected by the phenomenon of interfacial polarization, which leads to additional dielectric dispersions showing up in the dielectric spectra. Quite often, these dielectric dispersions take the appearance of relaxation processes and mask useful information arising from molecular fluctuations and charge transport processes. On the other hand, this phenomenon leads to an increase in the effective permittivity and can be used to design materials with giant permittivity, with possible applications in the field of energy generation and storage. The manifestation of interfacial polarization effects in dielectric spectra show several characteristic frequencies: (i) f_{on}, the onset of interfacial polarization effects; (ii) f_{max}, the full development of interfacial polarization; (iii) f_{MWS}, the frequency position of the Maxwell-Wagner-Sillars peak; (iv) f_i, the frequency where the increase in ε' show an inflection point. The present contribution will analyze in detail – in systematic dependence on local morphology, conductivity and volume fraction – the scaling laws of the characteristic frequencies observed in the dielectric spectra of composite materials. Furthermore, it will demonstrated how the phenomenon of interfacial polarization can be used to design materials with a huge value of permittivity.

Tailoring dielectric properties of bi-phasic polymeric materials by tuning their morphology

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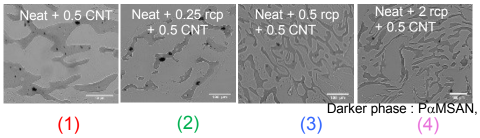
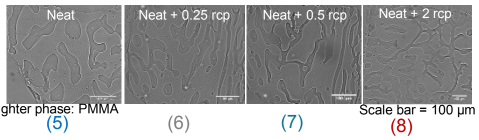
A systematic study of the effect of concentration of interfacially segregated copolymer (PS-r-PMMA) on the morphology refinement, accompanied by a huge increase in electrical conductivity of bi-phasic blends (PαMSAN/PMMA) was performed above the spinodal temperature (220 °C) as well as quenched to room temperature (Fig. 1 and micrographs 1-4). An ultra-low percolation threshold of MWNTs-PαMSAN composite (0.5 wt % MWNTs and 0.25 wt % compatibilizer) mimicked percolating structure (2 wt % MWNTs) at 220 °C. “Conductivity free” dielectric loss spectra were used to study the temperature and composition dependence of the relaxation time, and dielectric strength of interfacial polarization (Fig. 2). The former allowed determining the localized motions of interfacial relaxation, and the latter in predicting the refinement in morphology (see micrographs 5-8). Knowledge of the morphology-dynamics relationship in combination with structural mixing models allowed probing the interface between PαMSAN/PMMA and CNT/PαMSAN. Close agreement between the shape factors obtained from optical micrographs and dielectric mixing rules validated the source of detected interface, and the connectivity of PαMSAN.



Optical micrographs of immiscible blends with 0.5 wt % MWNTs and increasing copolymer concentration (rcp)



Optical micrographs of immiscible blends with increasing copolymer concentration

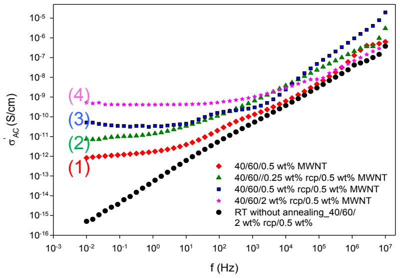


Fig. 1: Room temperature conductivity of bi-phasic 40/60 blend

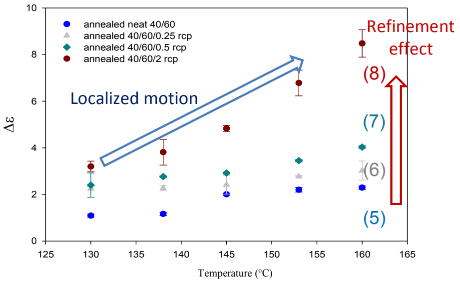


Fig. 2: Effect of copolymer concentration on temperature dependence of dielectric strength of interfacial polarization

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Dielectric Spectroscopy of macroscopic sample resonances for all-electrical measurements of electro-mechanical, electrical and mechanical properties in polymeric ferro- or piezoelectrets

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Dielectric resonance measurements have been proposed not only for inorganic piezoelectric materials, but also for piezoelectric polymers such as PVDF [1] or piezoelectrets [2]. In 2003, Axel Mellinger provided a comprehensive overview [3] of dielectric resonance spectroscopy (DRS) on macroscopic piezoelectric samples and its use with ferroelectric polymers and – in particular – with polymeric ferro- or piezoelectrets [4]. The method relies on the electrical excitation and detection of mechanical sample resonances and differs from the more recently proposed **atomic** dielectric resonance spectroscopy (ADRS) [5] in the relevant frequency range (typically between kHz and MHz) and the underlying physical mechanism of the observed **acoustical** resonances. Fitting the experimental resonance peaks with straightforward model calculations yields e.g. the respective components of the elastic modulus, the piezoelectric tensor or the electromechanical coupling factor – as well as other relevant materials parameters if the geometry and the boundary conditions of the sample are known. DRS has become a standard tool for assessing heterogeneous polymer foams and systems with electrically charged internal cavities that may be considered as macroscopic deformable electric dipoles. DRS can be employed to assess the temperature dependence of the mechanical, electrical and electro-mechanical parameters of piezoelectric polymer samples and to study the influence of various external factors such as humidity or radiation on their properties. In this contribution, we will briefly review typical examples for the successful use of DRS on various ferro- and piezoelectrets for determining essential applications-relevant properties.

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Nanostructured Ferroelectric Polymers. Implications on ferroelectricity and relaxation

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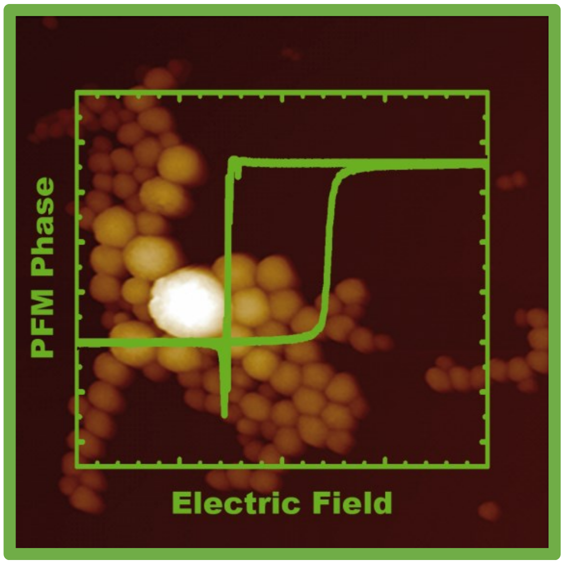
Ferroelectric polymers represent a unique class of functional insulating materials due to their long-chain rather than ionic-crystal nature. In recent years, the piezoelectricity, ferroelectricity, and pyroelectricity of ferroelectric polymers such as poly(vinylidenefluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) have been widely investigated, both from a fundamental point of view and from their potential applications in tactile sensors, solar cells, field-effect transistors, nonvolatile memory devices, etc. In these applications, the increasing demand for miniaturization, ferroelectric nanostructures have attracted considerable practical and theoretical interest. In this contribution we show how the ferroelectric behavior is modified when ferroelectric polymers are nanostructured. In particular, the ferroelectric response of nanostructured polymer surfaces and nanospheres has been characterized by piezoelectric force microscopy. The molecular dynamics of nanostructured PVDF-TrFE has been studied by broadband dielectric spectroscopy.



AFM image of PVDF-TrFE nanoparticles and out of plane hysteresis loop on a single particle measured by piezoresponse force microscopy)

Dielectric properties of biological cells and macromolecules: an overview with some new insights

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This talk will begin with an overview of the main principles of the time-honored Maxwell-Wagner relaxation theory as applied to the study of living cells. Particular emphasis will be placed on how nano-scale (i.e., molecular organization) and mesoscale structures of the cell is reflected in the measured dielectric dispersion spectra in the audio through the radio-frequency range. It will be then discussed how this knowledge may be used to probe the physical, chemical, and physiological properties of cells in suspension or within larger macromolecular aggregates. An interesting, more recent off-shot of this kind of work is detection of the binding of certain molecules (i.e., ligands) to receptor proteins on the plasma membrane or other molecules and organelles in the cell, which may trigger certain biological responses. This particular application of dielectric spectroscopy will be illustrated by presenting results from our recent investigations of the impact of the interaction between a G protein-coupled receptor – the Sterile2 α-factor receptor protein (Ste2p) – and its associated agonist ligand – the α-factor pheromone – on the dielectric properties of the plasma membrane and the cytoplasm of living yeast cells (*Saccharomyces cerevisiae*). The current knowledge in this field is that the agonist binding to the receptor Ste2p leads to internalization of the receptor-ligand complex, and triggers a cascade of signaling events inside the cell. Surprisingly, in our study, the changes observed in the electrical properties of some of the cellular compartments indicated that the cells respond to the ligand α-factor even when no receptor is present in the cell and therefore no ligand binds to the membrane. A possible explanation for the surprising effects that the agonist (α-factor) has on cells is proposed, which has already been confirmed using two-photon microscopy. These results confirm that not only is radiofrequency dielectric spectroscopy able to quantitatively study otherwise known biological structures and processes, but it may also lead to discovery of new and interesting structures and processes, as with Höber's original inference that an insulating layer (now known as the plasma membrane), must be covering the exterior of biological cells.

Polar order and collective relaxation mode in biaxial nematic phase of bend core molecules

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Many of current liquid crystal (LC) electro-optics and display applications use thermotropic uniaxial nematics (N_u) showing anisotropy of physical properties with two principal directions, along and perpendicular to the director. The nematic phase, in which the uniform alignment of the longest axes of the molecules, is accompanied by uniform orientation of the short axes is the so-called biaxial nematic (N_b) phase. The biaxial nematics are expected to speed up the electrooptic response as compared to their uniaxial counterparts. The identification of the relation between the molecular structure and phase symmetry is often a difficult and requires one to use multiple experimental techniques, especially those that probe the local order [1]. The main reason for the absence of a large biaxial order over macroscopic sizes is the fact that elastic constants associated with long range biaxial order are weak thus gets disturbed by thermal fluctuations. In context of the continuum theory, the field-induced transition from a local biaxial to a macroscopically biaxial state can be interpreted in terms of the quenching of low-energy orientational fluctuation modes associated with macroscopic biaxial order. Indications of field-induced transitions to a biaxial state under the action of moderate electric fields or under the action of surface anchoring can support the cluster picture [2] i.e. the existence of fairly sizeable clusters. Electro-optical and dielectric investigations exhibit ferroelectric-like polar switching. In some cases, presence of a moderately large threshold field may indicate polar order induced by the electric field. The most intriguing is appearance of the low frequency peak (at 10-100Hz) with rather large dielectric strength ($\Delta\varepsilon$=200-300) in dielectric spectra of A103, 2,5-bis-(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) and for 1,2,4-oxadiazole 4-cyanoresorcinol. This can be interpreted as a collective process due to the quenching of low-energy orientational fluctuations associated with macroscopic biaxial order. The results will be presented on correlation lengths of biaxial and polar order for selected bent core materials calculated on the basis of XRD and dielectric data.

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Adsorption of Poly(ethylene terephthalate)-chains to an aluminium substrate studied via pyroelectric depth profiling and dielectric spectroscopy

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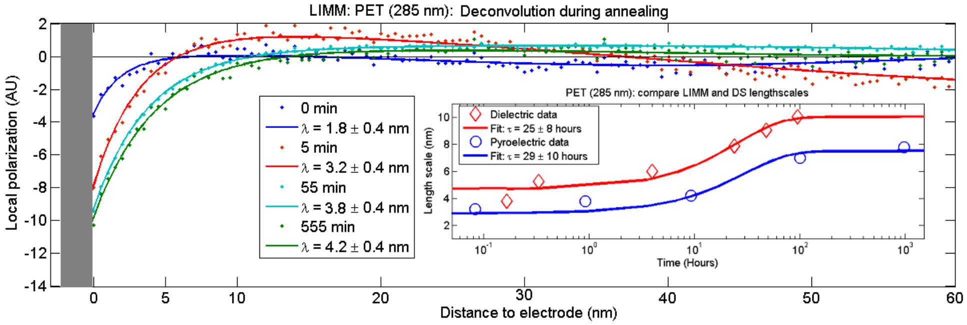
Thermal annealing of thin films of polyethylene terephthalate (PET) leads to irreversible adsorption of parts of the polymer chain to a solid substrate[1]. The resulting absorbed layer shows a reduced mobility that manifests as a decrease in the dielectric strength of the film. A first visualization of this adsorbed layer is obtained via washing experiments, appearing as a Guiselin brush structure, where the polymer backbones are oriented perpendicular to the substrate plane[2]. More detailed information on the orientation of the polymer chain is gathered using a photothermal technique known as Laser Intensity Modulation Method (LIMM)[3], where the metal-polymer interface is probed by high frequency photothermal waves excited in the range of 25 kHz to 25 MHz. In the event of macroscopic orientation of the terephthalate dipole moments, this thermal perturbation induces a pyroelectric current, proportional to the degree and direction of polymer chain orientation. To this end, a wide spectrum of thermal waves is used to deconvolute the pyroelectric response spectrum to a polarization depth profile with nanometer resolution, using an innovative Monte-Carlo algorithm. Figure 1 displays the polarization profile of PET at different annealing times, visualizing growth of the adsorbed layer as annealing time increases, indicative of the polymer chain orienting parallel to the substrate plane near the interface. The insert compares the timescale of evolution as measured with the LIMM setup with dielectric data on a sample from the same batch revealing an excellent match of the timescales, suggesting both techniques show different aspects of the structural evolutions process, ie. mobility and macroscopic orientation. This combination of dielectric spectroscopy with photothermal probing opens new ways towards a better understanding of polymer adsorption at solid interfaces.



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Molecular dynamics of confined poly(ethyl methacrylate) investigated by Broadband Dielectric Spectroscopy

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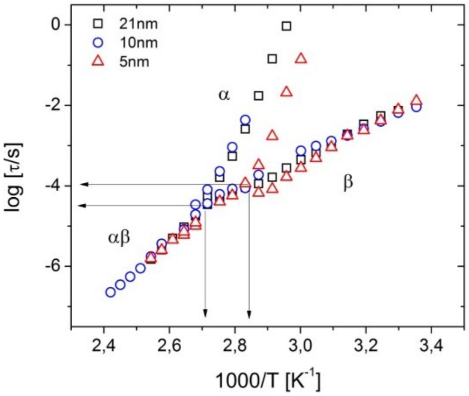
The local and cooperative dynamics of capped ultrathin films of poly(ethyl methacrylate) (PEMA) were investigated by broadband dielectric spectroscopy in a frequency range of 0.1 Hz up to 1 MHz and a temperature range from 233-423K. 1D-confinement was investigated using films of thicknesses down to 3.5 nm. While local dynamics was almost unaffected by reduction of the film thickness, the cooperative dynamics showed strong confinement effects, including a severe reduction in the strength of the process, indicating irreversible chain adsorption and a reduction in the relaxation time implying enhanced segmental mobility. This rather counterintuitive scenario confirms that the presence of an adsorbed layer does not necessarily provokes slower dynamics [1,2], and requires the development of a novel theoretical framework to describe the structural relaxation under confinement where the segmental mobility is related to the perturbations in interfacial packing density due to chain adsorption [3]. We identified a characteristic lengthscale h* (~ 10 nm), corresponding to the thickness of the layer irreversibly adsorbed after long annealing time, below which the αβ-process is more stable against against cooling and the onset of cooperativity (αβ-*splitting*) occurs at temperatures lower than in bulk. We discuss the implications of this intriguing feature in relation to the recent models on vitrification and on the cooperative character of the glassy dynamics.



The shift in splitting temperature of the αβ-process for thinner films. For films down to h* ~ 10 nm the splitting temperature is constant while it gradually decreases for h < h*.

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Poster
contributions

Novel themoresponsive systems based on poly(methoxy diethylene glycol acrylate) copolymers

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Stimuli-responsive polymers have attracted considerable scientific interest due to their unique properties and potential applications [1]. The transition of the temperature-responsive polymers, in particular, has been related to the competitive results of hydrogen bonding and hydrophobic interactions [2].

In the present work we employ Dynamic Light Scattering (DLS), Small-Angle Neutron Scattering (SANS), Differential Scanning Calorimetry (DSC) and broadband Dielectric Relaxation Spectroscopy (DRS) techniques in order to study the thermoresponsive transition and the organization of water in a series of thermoresponsive polymers and di- and tri-block copolymers based on poly(methoxy diethylenglycol acrylate) (PMDEGA)[3]. In the copolymers, the thermoresponsive blocks are tethered to short polystyrene (PS) blocks, which form the hydrophobic core of the micelles above the critical micelle concetration (CMC) [3].

In particular, Dielectric Spectroscopy ,which has been widely used in the investigation of the hydration properties of materials [4] and recently also for the investigation of the thermoresponsive behavior of polymers [5], was carried out on polymer/water mixtures with wide range of water content, aiming, both, at the study of the thermoresponsive transition and the organisation of water in the system at temperaτures below the LCST.

The combined study gives us results on the kinetics of the transition and long-range morphology as a function of temperature and water content.

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Role of H-bonds in the dynamics of concentrated solution of PDMAEMA

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In recent works we have investigated the component dynamics in concentrated aqueous solutions of polymeric macromolecules (poly(vinyl methylether)(PVME), poly(dimethylaminoethylmethacrylate) (PDMAEMA) and polyamides (PA)). We have found a similar peculiar phenomenology of the dynamics, including extreme stretching and deviations from Gaussian behavior. In our interpretation of the results, the existence of structural heterogeneities is one of the essential ingredients: invoking a distribution of mobilities derived from heterogeneous environments, we can explain the water behavior; an analogous distribution gives also account for the polymer response. In the case of the polymer motions, we also find that the formation of H-bonds with water plays a crucial role. An important arising question is whether the heterogeneities are a consequence of the H-bond formation. Trying to address this question, we have studied the PDMAEMA in concentrated solution with tetrahydrofuran (THF), where hydrogen bonds are absent, using dielectric spectroscopy. The system has been studied at different concentrations (dry, 15%wt, 30%wt, 40%wt, 48%wt, 58% wt). The dry polymer shows two different dynamics: an α-like component at high temperature and a β-like one at low temperature. Adding THF, two new dynamics appear in the low temperature region. The slower is related to the dynamics of the THF interacting with the polymer, while the faster is related to the motion of the solvent molecules. The β-like component of the polymer results to be slightly faster in presence of THF. The energy activation and the relaxation times of such dynamics don’t change increasing the solvent concentration. The dependence on the concentration of the α-like dynamics and the β-like component related to the THF suggests a saturation reached around 50%wt. This is supported by the study of the sample with 58%wt of THF where crystallization appears at low T, suggesting the presence of free THF molecules. In order to clarify the results we obtained using dielectric spectroscopy, we have characterized these concentrations by calorimetry. Moreover we have investigated the sample PDMAEMA/THF 30%wt by neutron scattering, using deuterium labeling to focus our attention in one component at a time. To complete our study, we performed dielectric spectroscopy measurements on the aqueous solutions.

Adhesion analysis of Alfa fibres reinforced unsaturated polyester hybrid composites using the dielectric analyzer and the tensile testing

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Adhesion of Alfa fibres in unsaturated polyester matrix was investigated by means of the dielectric analyzer and the tensile testing taking into account the presence of wool fibres and thermo-binder fibres. Two composites #1 and #2 having 17:2:1 and 17:1:2 as a relative fraction of Alfa/wool and thermo binder (Pe/Pet), respectively, have been characterized in this study. Furthermore, the diameter of Alfa fibres in this reinforcement was 89.95 µm. Analysis of dielectric relaxations at high temperatures, using the Havriliak–Negami model, revealed that adhesion of the reinforcement in the matrix was depended on the relative proportions of wool fibres and thermo-binder fibres. Indeed, interfacial polarization was hidden by the conductivity in the case of the composite #1 whereas its presence was detected in the composite #2. Hence the mechanism of adhesion in both composites was different. Tensile testing showed a better tensile properties and higher Young modulus in the composite #2. So the mechanism of adhesion in the composite #2 was better than that in the composite #1. Such results were consistent with our previous study [1].

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Conductivity, dielectric relaxation, and nanoscale organization in binary mixtures of amphiphilic molecules

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Broadband dielectric measurements on binary mixtures of surfactants reveal that, based on a suitable choice of the individual amphiphilic species, the conductivity of the mixture turns out to be several orders of magnitude larger than the conductivity of the pure components. In particular, focusing on liquid mixtures composed by bis(2-ethylhexyl)amine (BEEA) and octanoic acid (OA), a dielectric relaxation is observed in the MHz-GHz frequency range, whose average relaxation time is larger for the mixtures that exhibit higher conductivity. This behavior, which is opposite to that occurring for instance in neat molecular glass forming liquids as a function of temperature, could be explained considering that in OA:BEEA mixtures protonic conduction takes place, whereas polar head reorientations giving rise to the dielectric relaxation are controlled by breaking and reforming of hydrogen bonds. The formation of transient intermolecular networks of OA and BEEA molecules at the nanometer length scale would lead to larger relaxation times, and to higher viscosity, providing, at the same time, extended favourable paths for protonic hopping.

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Molecular dynamics of gradient poly(n-butyl acrylate-co-methyl methacrylate)

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It is well know that properties of polymers are determined by their molecular structure. The increasing importance of copolymer arises mainly from their unique properties, resulting just from details of their molecular structure. There are different types of copolymers in view of distribution of ingredient monomers along the chain. The random copolymers and block copolymers with homopolymer blocks constitute two extreme cases of these materials. Except these there are known copolymers with more sophisticated distribution of monomers such as tapered block copolymers and gradient copolymers. The composition in the gradient copolymers varies continuously along the chain. The gradient copolymers can be produced through controlled/"living" radical polymerisation. One of the most successful methods of such polymerisation is an atom transfer radical polymerisation, which allows to control of molecular weight, comonomer distribution and molecular architecture, i.e. all molecular parameters, which can influence physical properties of final copolymer.

In this work the series of gradient copolymers of n-butyl acrylate and methyl methacrylate with different composition was investigated. Additionally some block copolymers, containing besides one or two gradient blocks a homopolymer poly(n-butyl acrylate) block, also were studied.

The gradient copolymers, independently of composition, were homogeneous with one glass transition phenomenon, what was seen in DSC as well as in DMA and BDS measurements as the primary α relaxation. The values of glass transition temperature (T_g) were determined by ingredient of the comonomers – the higher content of butylacrylate the lower T_g and in consequence the α relaxation appeared at lower temperature range. The same tendency was observed, when the gradient block was bonded to homopolymer block. But in all investigated block copolymers a microphase separation was observed, what resulted in presence of second primary relaxation (second T_g) characteristic on pure poly(n-butyl acrylate).

Study of molecular mobility in poly(lactic acid) / silica hybrids

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In this work, the molecular mobility in porous organic-inorganic hybrids was studied. The hybrids were prepared by the addition of a silica inorganic phase inside the pores of polymeric membranes. Firstly, porous polylactid acid (PLA) membranes were obtained by freeze-extraction techniques and their surface was functionalized by an aminolysis reaction. The inorganic phase composed of silica was synthesized in-situ and inside the pores of the PLA membranes by sol-gel reactions in acidic medium using tetraethyl orthosilicate (TEOS) and glycidoxypropyltrimethoxysilane (GPTMS) as the silica precursors. GPTMS served also as a coupling agent between the organic phase and the silica network. The molar ratio of GPTMS with respect to TEOS in the sol-gel solution was varied between 0.05 and 1. The morphology study showed that the prepared hybrid materials present a microporous structure with a silica layer covering the walls of the pores and that the two phases are co-continous. Molecular mobility was investigated by Dielectric Relaxation Spectroscopy (DRS), in a frequency range between 10^{-1} Hz and 10^{6} Hz at temperatures from -150 ^{o}C to 100 ^{o}C, and by Thermally Stimulated Depolarization Currents (TSDC) technique. The main and secondary dielectric relaxations of each phase were followed. DRS and TSDC techniques are complementary to each other while the results obtained are in good accordance. The main α relaxation of PLA phase was found to be slower in PLA membranes modified by TEOS/GPTMS compared to pure PLA membrane. For hybrids with high amount of GPTMS the added phase exhibits an α relaxation at low temperatures related to the glass transition in accordance with Differential Scanning Calorimetry (DSC) results. The comparison with bulk samples prepared from TEOS/GPTMS showed that the relaxation of TEOS/GPTMS phase is faster in PLA+TEOS/GPTMS membranes. In addition, a Maxwell-Wagner-Sillars (MWS) relaxation was followed for the hybrids with high amount of GPTMS indicating the existence of a two-phase system.

Acknowledgements

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Dielectric relaxation in supramolecular polymeric systems

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Dielectric Debye-like relaxation has been observed in a model self-complementary AB type supramolecular polymer based on thymine and diamidopyridine triple hydrogen-bonding motifs.[1, 2] The dynamical behavior of this associating polymer is found to generally conform to those of type-A polymers, with a low-frequency chain relaxation and a high-frequency alpha relaxation visible in both rheological and dielectric measurements. The origin of the Debye-like dielectric relaxation has been discussed in the light of mono-alcohols. Recently, an AB_2 type hyberbranched supramolecualr polymer based on the same motifs has been further investigated by using broadband dielectric spectroscopy.[3] A distinct dielectric relaxation from that of the linear supramolecular polymer has been observed, which will be discussed in combination with other techniques.

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Broadband dynamics in mixtures of 2-ethyl-1-hexanol and 2-ethyl-1-hexyl bromide

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Binary solutions of 2-ethyl-1-hexanol (2E1H) with 2-ethyl-1-hexyl bromide (2E1Br) is studied by using broadband dielectric spectroscopy at ambient pressure and at elevated pressures up to 1,8 GPa over a broad range of temperatures. We investigated mixtures $(2E1H)_x(2E1Br)_{1-x}$ with alcohol concentrations x=0,4 and x=0,69. For both mixtures two well separated two loss maxima are seen in $\varepsilon''(f)$. The lower-frequency relaxation, corresponding to the Debye-like process. However, for sample with lower alcohol concentration (x=0,4) this process is much smaller and wider than the α-relaxation witch shows up at higher frequencies. For the alcohol rich samples (x=0,6) the situation is different. Here the Debye-like process exhibits the larger amplitude. Furthermore, it should be emphasized that in both cases, althoug the time separation between the relaxation processes exhibit a well resolved at ambient pressure, but with compression time distance between process markedly decrease. In light of these results, we show that the Debye-like process can be studied not only in neat monohydroxyalcohols but also in mixtures with non associated solvent.

Molecular Dynamics of Linear Poly(N-isopropylacrylamide) in Water Below and Above the Phase Transition: A Broadband Dielectric Relaxation Spectroscopy Study

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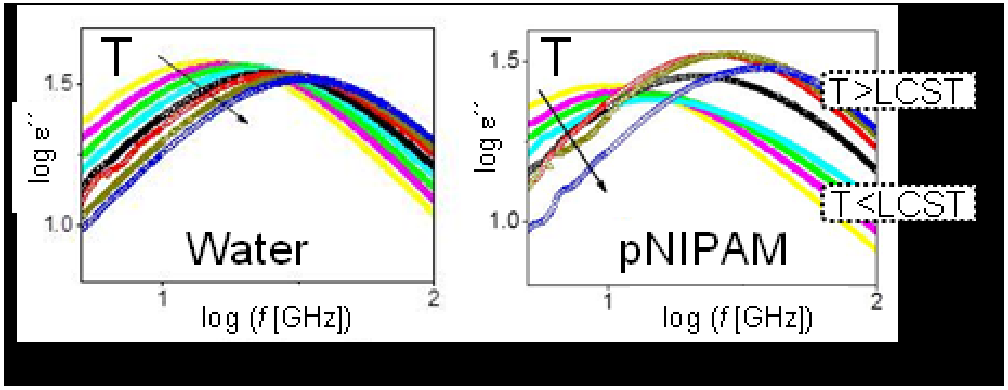
The molecular dynamics of linear poly(N-isopropylacrylamide) (pNIPAM) in aqueous media are investigated using dielectric relaxation spectroscopy in a frequency range from 0.1 Hz to 100 Ghz at temperatures between 15 and 50 °C. Below the lower critical solution temperature (LCST) two relaxation processes are observed located in the MHz and GHz region assigned to the reorientation of dipoles of the solvated polymer segments (p-process) and water molecules (w-process), respectively. Both relaxation processes are analyzed using the Havriliak-Negami (HN) functions taking special attention to the w-process. Above the LCST the dielectric spectra of the pNIPAM solutions resemble that of pure water showing only the high frequency relaxation process of the water molecules with more or less Debye-type behaviour. The non-Debye behaviour of the w-process below the LCST is mainly induced by the interactions between water and pNIPAM chains via hydrogen bonding. The relaxation time and strength of the w-process is studied in dependence on the concentration, temperature and the polymer chain length. The information obtained is useful for a deeper understanding of the dehydration behavior at the phase transition. The suggestion of dehydration of the pNIPAM chains at the LCST is confirmed by calculating a dehydration number.



Reference: M. Füllbrandt et al. *J. Phys. Chem. B* **2014**, *118*, 3750−3759.

Dielectric properties of organic photovoltaics based on polymer:perylene diimide blends

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Organic photovoltaic devices (OPV) with photoactive layers of polymer:perylene diimide (PDI) blends have recently attracted attention despite the lower performance as compared for example to polymer:fullerene OPV devices [1][2]. Here we report on the interplay between self-assembly and dynamics in different polymer:PDI blends [3]. The polymers (donors) are the F8BT and PBDTTT whereas the acceptor is solely PDI. We first compare the photophysical properties of both systems (photoluminescence quenching, charge carrier mobilities) with the hierarchical organization within extruded fibers obtained from X-rays. In a second step we employ DS and investigate the segmental and ion mobilities in the same systems. F8BT shows segmental dynamics with a strong T-dependence and with a liquid-to-glass temperature. In contrast, blending results in new dynamic processes exhibiting an Arrhenius temperature dependence with low activation energies reflecting properties of the heterojunction inrterfaces.

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Calorimetric glass transition of ultrathin poly-2-vinyl pyridine films

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Specific heat spectroscopy utilizing AC-chip calorimetry in the frequency range from 1 Hz to 1 kHz with a sensitivity of pJ/K was employed to study the dynamic glass transition behavior of ultrathin poly-2-vinyl pyridine (P2VP) films with thicknesses from 405 nm down to 10 nm. The amplitude and the phase angle of the complex differential voltage as a measure of the complex heat capacity were obtained as a function of temperature at a given frequency simultaneously. Both spectra were used to determine the dynamic glass transition temperature as a function of the film thickness. As main result no thickness dependence of the dynamic glass transition temperature was observed for P2VP thin films down to a film thickness of 10 nm within the experimental uncertainty of ±3K. Further, the width of the glass transition is independent on the film thickness, which indicates that the extent of the cooperativity is essentially smaller than the lowest thickness of 10nm.

Physical insight into kinetics of tautomerization of Etoricoxib drug

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In the last years, a great effort has been expended into consideration the impact of tautomerization in drug design and the biological consequences of this phenomenon. Some of the compounds, for which tautomerization is possible, may be a mixture of two constitiutional isomeric forms (tautomers) which exist in equibilirium with each other, although one of the forms is usually found in a greater amount than other. It is important not to neglect the properties of tautomers, which exact ratio may vary depending on solvent polarity, pH or temperature [1]. This phenomenon seems to be particularly important in the case of pharmaceuticals or compounds with a large biological importance. The most convincing example is the tautomerization of adenine, the basic building blocks of DNA and RNA, leading to faulty nucleobase pairing and consequently promoting potentially harmful mutations in the cells genome.

Herein we discuss the kinetic aspects of tautomerisation of Etoricoxib drug (ETB). In general ETB is orally administrated anti-inflammatory painkiller and acts as selective inhibitor of cyclo-oxygenase-2 enzyme (COX-2). It is applied in a treatment of various pain conditions like arthritis, gout, chronic back pain or postoperative dental pain [2].

To observe tautomerization reaction associated with intramolecular proton transfer, we prepared supercooled sample by melting the crystalline ETB and subsequently fast cooling to the temperature below its melting point. To get insigt into kinetics of tautomerization we applied broadband dielectric spectroscopy (BDS). It is well known that the amorphous materials with different tautomers ratio may be characterized by different glass transition temperature values or the average dipole moment [3]. Consequently, the kinetics of ETB tautomerisation process can be described by monitoring the time evolution of structural relaxation preak, dc-conductivity or dielectric relaxation strength. We recorded the dielectric loss spectra of supercooled ETB drug in a wide temperature range. Next we performed the time-dependent dielectric measurments at ambient pressure in different temperature conditions (342K - 348K). These data enable us to determine the activation energy of the tautomerization reaction of ETB. The kinetic parameters describing the ETB tautomerization reaction by means of BDS technique were compared with the results of infrared spectra analysis (FT-IR spectroscopy) and DFT calculations.

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Dielectric Relaxation in Pure Amines through Time Domain Reflectometry Technique

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Dielectric relaxation study of liquids is one of the most important approaches to understand its molecular behavior. To compare the influence of the different polar groups in the relaxation mechanism, we have considered it interesting to perform an analogous treatment such as that carried out for primary amines, substituting the one-alkyl group by the amino group. The series of amines and diamines of which positional isomers with same and also different molecular sizes are selected to understand the effect of amino and methyl side group on the dielectric parameters, where the significance is based upon the tetrahedric nature of the NH_2 group. The existence of the NH_2 group contributes to the formation of hydrogen bonds of N-H….N type with its neighbors. The presence of such complexes is manifest in infrared spectroscopy techniques, with the appearance of absorption bands at 3450 and 3550 cm^{-1}. The positions of these bands do not change with the length of the aliphatic chain. Consequently, we cannot establish priori any one type of hypothesis concerning the association in these amines. This association must be dependent on the aliphatic chain or, at most, on some carbon atoms close to the aminated end, where the nearest bond to the dipolar group must play a decisive role in the molecular confirmation. The dielectric dispersion (permittivity) ε' and dielectric loss ε'' of amines and diamines were measured by employing the Time Domain Reflectometry technique over a frequency range 10 MHz to 20 GHz. The accuracy in the measurement of the ε' and ε'' values obtained from this technique is within ±5%. All these measurements were carried out at twelve different temperatures starting from 5 to 55°C, and being controlled by using thermostat with ±0.5°C. To evaluate various dielectric parameters, the frequency dependents complex permittivity ($\varepsilon^* (\omega) = \varepsilon' - j\varepsilon''$) data viz., dielectric constant (ε_0), relaxation time (τ) and permittivity at high frequency (ε_∞) were fitted by the non-linear least-squares fit method to Debye expression. Temperature dependent dielectric constant (ε_0), relaxation time (τ), Kirkwood correlation factor (g) and thermodynamical energy parameters have been determined and discussed in terms of the effect of amino (-NH_2) and methyl side-group (-CH_3) on molecular dynamics and intermolecular hydrogen bonds. Further the variation in dielectric parameters and molecular reorientation due to addition of either –NH_2 side-group or CH_3 side-group in the molecular structure has been explored by comparing the values of dielectric parameters of diamine series.

Theoretical investigation of dielectric relaxation in ice H_20 Ih

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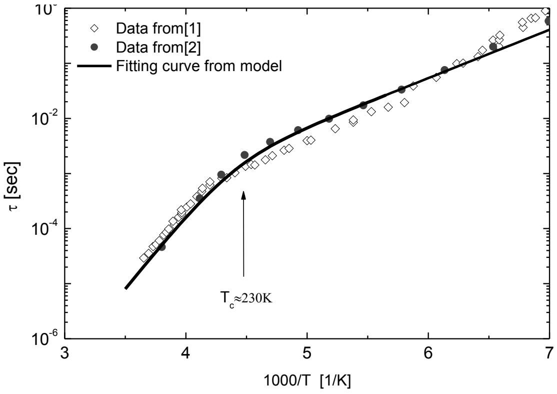
In spite of the intensive study of electrical properties of ordinary hexagonal ice (Ice Ih) for the last century, the main relaxation mechanism and its temperature dependence is still remains unclear. The most interesting and still unexplained feature of ice is the presence of the dynamical crossover in relaxation time behavior around T_C=230±7K [1, 2]. It is well known that there are no any kinds of phase transition in ice at this temperature (first or second order). Therefore, we cannot assign the origin of the crossover with any structural change. Here we are presenting the model, in which the crossover of the realxation temperature dependence is expelined by the change of the polarization mechanism. The dielectric relxation driven by the diffusion of orientation L-D Bjerrum's defects (at high temperature) is changed to another one where the diffusion of intrinsic ionic $H3O^+/OH^-$ defects is dominated (at low temperature). A similar idea was proposed early by Bilgram & Granicher [3], but it was not disseminated.

In the framework of the developed model, we propose the analiycal equation for complex dielectric permittivity, which takes into account the contribution of both types of defects. Moreover we can obtain analitycal expression for temperature dependences of time relaxation and Cole-Cole broadening parameter α. Also the obtained equation for α helps us to explain the phenomenon of the loss peak broadening increase with temperature decrease in ice [1]. The figure is presented the experimental data [1, 2] and the fitting curve, which was predicted by our model.



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Linear and nonlinear impedance in BiV ceramics and BiV-SBO glass-ceramics

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The linear and nonlinear ac complex conductivity of ferroelectric ceramics and glass-ceramics were studied as the function of frequency and temperature. Four sets of samples were prepared. Reference sample- ferroelectric bismuth vanadate ceramic (BiV) was synthesised via a conventional solid state reaction route. Bismuth-vanadate glass-ceramics were prepared by conventional melt technique. Moreover two groups of strontium-borate glasses doped with ferroelectric bismuth vanadate were prepared: first one from Bi_2O_3, V_2O_5 and pre-prepared SrB_4O_7 (SBO) and the second one from pre-prepared BiV and SBO. Next BiV-SBO glasses were subjected to crystallization in order to obtain glass-ceramics. The effect of preparation method, composition, used substrates and crystallization process on dielectric behaviour is analyzed.

The nonlinear impedance studies of ferroelectric BiV showed that the ratio of third harmonic to base frequency of conductivity reached more than 0.2. These materials gave the response deviated significantly from the linear. Therefore measurement only a linear impedance was insufficient to fully describe their electrical properties. The conductivity determined only on the basis of standard method, neglecting nonlinear effects was subjected to sufficient errors. Linear and nonlinear electrical properties of BiV-SBO glasses and glass-ceramics were compared with ferroelectric BiV.

Structure and Dynamics of Poly(styrene-*b*-1,4-isoprene) Diblock Copolymers under 1- and 2-D Confinement

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The impact of 1- and 2-dimentional (2D) confinement on the structure and dynamics of poly(styrene-*b*-1,4-isoprene) P(S-*b*-I) diblock copolymers are investigated by a combination of Grazing-Incidence Small-Angle X-ray Scattering (GISAXS), Atomic Force Microscopy (AFM) and Broadband Dielectric Spectroscopy (BDS). 1D confinement is achieved by spin coating the P(S-*b*-I) in nanometer thin layers while in the 2D the polymer molecules are confined in cylindrical anodized aluminum oxide (AAO) nanopores. GISAXS and AFM reveal hexagonally packed cylinders of PS in a PI matrix. Using BDS (Fig. 1), three relaxation processes are observed, which can be assigned to the two segmental modes of the styrene and isoprene blocks and a relaxation process related to the normal mode of the isoprene block. The dynamic glass transition related to the segmental mode of the styrene and isoprene blocks is independent on the dimensionality of the restricting space while the normal mode becomes faster under 2D confinement [1].

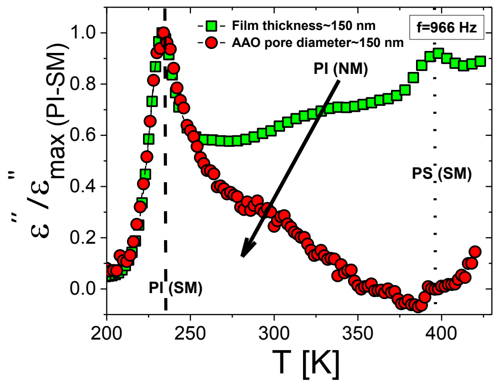

Fig. 1 Isochronal dielectric loss spectra normalized with respect to the maximum of the segmental mode (SM) of isoprene block of P(S-*b*-I) with f_{PI}=0.73. Filled squares corresponding to film thickness of 150 nm while the filled circles represent the confined P(S-*b*-I) in AAO nanopores with pore diameter ~150 nm. Vertical dashed and dotted lines indicate the positions of the segmental modes of the isoprene and styrene blocks while the arrow refers to the normal mode relaxation of the isoprene block.

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Water-rich glycerol mixtures; The origin of the liquid-liquid transformation

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Water/glycerol mixtures for the last decade have left many open questions regarding the relaxation processes that are observed in wide frequency and temperature ranges [1-3]. Special attention has been paid recently to the low temperature region, leading to a variety of physical explanations of water/glycerol structures and Liquid-Liquid Transition (*LLT*) [4], depending on the pre-treatment of the solution (see Figure 1).

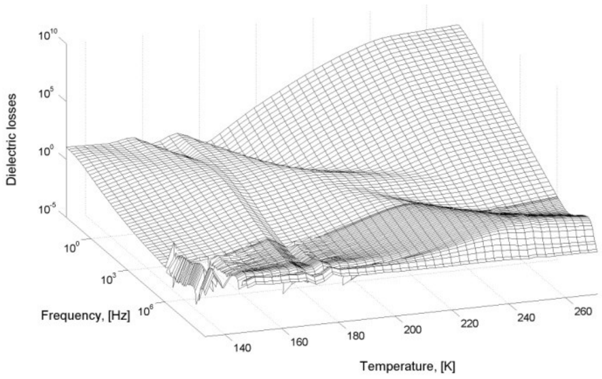

Figure 1. 3-D plot of the temperature and the frequency dependence of the dielectric losses for the 20 mol% water glycerol solution.

Here we present the new consideration of the dielectric relaxation at the concentration of 20 mol% that appeared to be critical between the spinodal or nucleation and growth scenario of the ice formation. The special temperature/time protocol was designed for the dielectric study for the clarification of these phenomena. The sudden change of the relaxation spectra at 172 K associated before to the LLT is explained.

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Segmental and local dynamics of stacked thin films of poly(methyl methacrylate)

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The glass transition temperature and the alpha-process of thin polymer films have widely been investigated by many researchers over 20 years. Recently, the glass transition dynamcis of the stacked films of polystyrene and poly(2-chlorostyrene) have been investigated and the significance of the interfacial interaction on the glass transition dynamics in thin film geomtries [1]. In this study, the glass transition temperture and the dynamics of the alpha- and beta-processes have been investigated using defferential scanning calorimetry and dielectric relaxation spectroscopy during successive annealing processes above the glass transition temperature for stacked thin films of poly(methyl methacrylate) (PMMA) of various thickness [2]. The glass transition temperature decreases and the dynamics of the alpha-process of stacked thin films of poly(methyl methacrylate) becomes faster than those of bulk states in almost similar way to that in single thin film geometry. Annealing at high temperature causes the glass transition temperature to increase from reduced value, and causes the dynamics the alpha-process to become slower approaching those of the bulk. Contrary to the segmental motion, the relaxation time of the beta-process (local motion) of the stacked PMMA thin films is almost equal to that of the bulk PMMA state, and is unaffected by the annealing process. However, the relaxation strengths of both the alpha-process and beta-process show a strong correlation between each other. The sum of the relaxation strenghs remains almost unchanged, while the individual relaxation strengths change during the annealing process. This suggests that there is the coupling effect between alpha-process and beta-process during the annealing process. The fragility index of stacked thin films before annealing is lower than than that of the bulk state, and increases with annealing time.

In this poster repsentation, the results obtained by the neutron reflectivity measurement, which will be a collaboration with K. Sadakane and S. Yamada, will also be shown, if the analysis is finished.

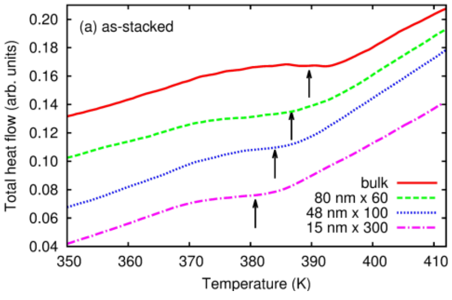

Fig.1 Temperature dependence of total heat flow for stacked PMMA thin films before annealing with various single thickenesses, from 15nm to the bulk.

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Ultra-stable glass properties studied by simultaneous dielectric and ac-calorimetric measurements

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Two approaches are typically used to prepare glasses; namely ultrafast cooling to quench the liquid below the freezing temperature and preparing amorphous films directly from the vapor phase by condensing the molecules onto a cold substrate. It has been found that glasses produced by physical vapour deposition well below the bulk glass transition temperature (T_g) exhibit extraordinary properties including low heat capacity, high kinetic stability and high density. These glasses can be referred to as "ultra-stable" glasses. The high density of stable glasses implies a more efficiently packed glass.[1,2] The present work aims to explore the stability of vapour deposited glasses of 2-Ethyl-1-Hexanol using in-situ simultaneous broadband dielectric spectroscopy and ac- calorimetric measurements. Dielectric spectroscopy reveals the molecular dynamics of the glasses, with an aim of studying the correlation between glass density and local order. [3] By means of calorimetry; the dynamic aspects of C_p and its relation to kinetic stability is investigated. [4] The effect of substrate temperature and deposition rate in introducing or preventing orientational order is also investigated.

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Kinetics of cold crystallization of 4-cyano-3-fluorophenyl 4-butylbenzoate (4CFPB) glass forming liquid crystal in microscopic, DSC and dielectric studies

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Investigation of liquid crystalline substances, especially glass formers, is one of the most interesting subjects in condensed matter physics. The substance 4CFPB is characterized by the nematic phase near room temperature and shows rich polymorphism of solid state: two crystalline phases and glass of nematic [1]. Additionally, liquid-like smectic phase was induced in high pressure dielectric spectroscopy experiment [2].

DSC heat flow data allow to present temperature dependence of volume fraction $A(T)$ of a solid phase growing in the supercooled nematic. Pure metastable CII crystal grows for heating rates greater than 5 K/min – otherwise a mixture of CII and CI crystals was detected. Similar temperature dependence of degree of crystallization was calculated basing on microscopic observations for 8 K/min rate. Using Augiss-Benett model to the DSC data the barrier for CII phase crystallization was estimated. The Ozawa model, applied for the non-isothermal crystallization process, instead of Avrami model used thoroughly for isothermal processes, allows us to calculate the rate of crystallization and the parameter describing what is the type of crystallization. TTT diagram was also constructed. Dielectric relaxation allows to check the isothermal crystallization (Fig.1). Evolution of degree of crystallization at 255K is shown in Fig.2. For isothermal experiment $A(t) = \{\varepsilon''_{\max}(0) - \varepsilon''_{\max}(t)\}/\varepsilon''_{\max}(0)$, where $\varepsilon''_{\max}(t)$ means dielectric loss corresponding only to the flip-flop rotations of molecules. Precession of molecules detected in the nematic phase is still present in the metastable CII phase while β-relaxation is stopped.

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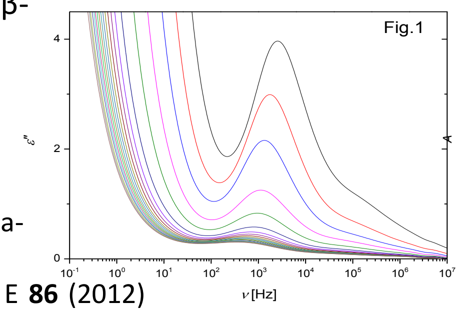
Fig.1

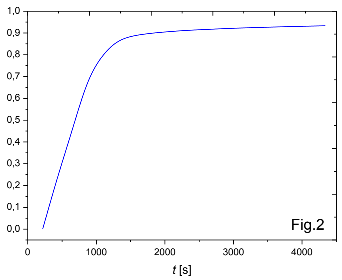
Fig.2

Fragile-to-strong transition of water and glass transition temperature in aqueous mixtures

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and Shin Yagihara

Department of Physics, Tokai University

Recently, molecular dynamics of glass transition phenomena on aqueous mixtures are widely investigated by various techniques such as NMR, neutron scattering, MD simulations, calorimetric measurements and broadband dielectric spectroscopy. Several investigations have demonstrated that relaxation process of water which we called ν process shows fragile-to-strong transition (FST). Some of the recent studies suggest that the FST of water in aqueous mixtures occurs at the glass transitions temperature, T_g of structural α relaxation process.[1, 2] The other studies on confined water and protein hydration water suggest that the FST occurs at 225 K.[3] However, molecular dynamics on polymer and partially crystallized systems, in which part of water crystallized at subzero temperatures, are still incompletely understood. In this study, we discuss the FST of partially crystallized gelatin-water mixture[4] and uncrystallized poly(vinyl pyrrolidone) and poly(vinyl methyl ether)-water mixtures studied by broadband dielectric spectroscopy with comparison to that of various uncrystallized sugar and alcohol aqueous mixtures. Figure shows relationship of T_c and T_g for various types of aqueous mixtures. It clearly shows T_c agrees well to T_g. The results suggest that driving force of FST of water in mixtures is glass transition of α process.

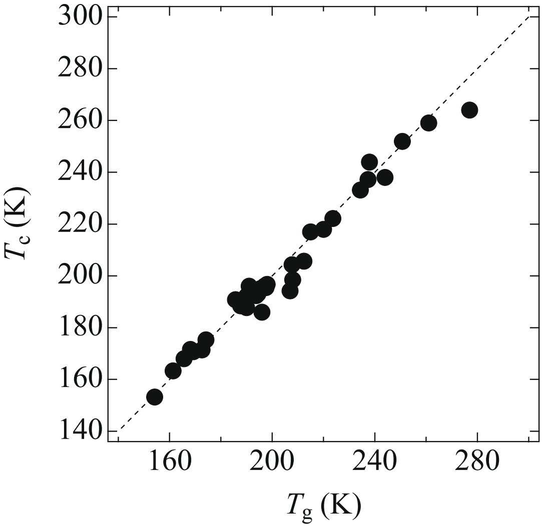

Figure Relationship between T_g and T_c of various aqueous mixtures.

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Polymeric materials with giant permittivity

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One essential aspect related to the increasing demand for alternative energy sources represents the need to develop systems with enhanced capacity of energy storage. In this context, polymeric materials with high values of permittivity occupy an important place. Two different strategies to increase the global permittivity of materials are presented in the current contribution:

(i) one approach relies on inducing – using the phase separation phenomenon of block-copolymers – local variations in electrical conductivity across internal interfaces. The self-structuration process driven by a disorder-order transition specific to this class of polymers leads to well–defined morphologies on the nanometric length-scale resulting in a huge density of interfaces. The incompatibility between the two polymer phases and the large difference in the miscibility toward an ionic liquid offers the possibility of an asymmetric doping leading to a nano-structuration process of the local electrical properties. This gives rise to a well-defined sequence of insulating and conductive polymer phases on the nanometric length-scale. In the present contribution we show that this approach can be used to produce materials exhibiting a giant permittivity (Fig. 1).

(ii) the second approach relies on controlling the distribution of fillers in composite polymeric materials by means of an applied magnetic field. Here we show that this can lead to a permanent increase in the global permittivity of composite materials.

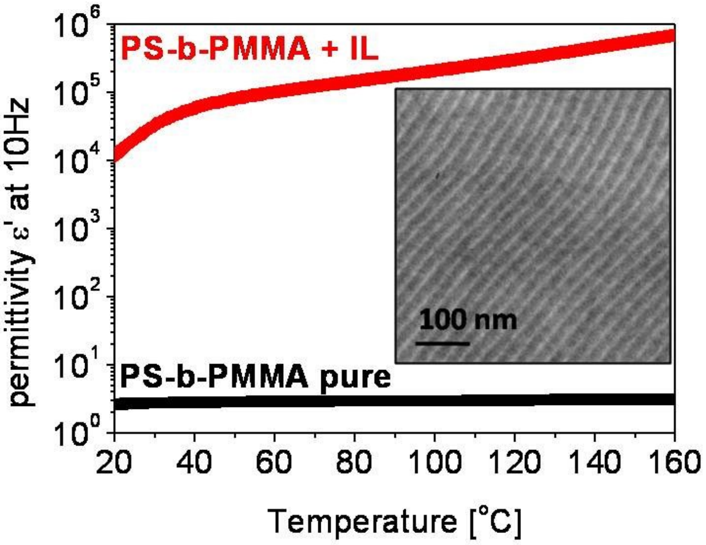

Fig. 1: the permittivity value of pure PS-b-PMMA and of PS-b-PMMA doped with an ionic liquid. Inlet: sequence of insulating and conductive polymer nano-layers.

Electrode polarization vs. Maxwell-Wagner-Sillars interfacial polarization: scaling laws, similarities and differences

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The Maxwell-Wagner-Sillars interfacial polarization and the electrode polarization phenomenon are analyzed by considering the global dielectric response of a system consisting of a conductive and an insulating layer of different thicknesses (d_c and d_i, respectively). The manifestation of these phenomena in dielectric spectra is marked by several characteristic frequencies: (a) f_{on}, the onset of polarization effects; (b) f_{max}, the full development of polarization effects; (c) f_{MWS}, the frequency position of Maxwell-Wagner-Sillars peak; (d) f_i, the frequency where the increase in ε' shows an inflection point. In the present work, the scaling laws governing these characteristic frequencies are derived and compared, in systematic dependence on conductivity and volume fraction x of the insulating layer ($x=d_i/L$, where $L=d_i+d_c$). Large similarities and notable differences are found between the scaling laws of the electrode polarization phenomenon and those of interfacial polarization effects.

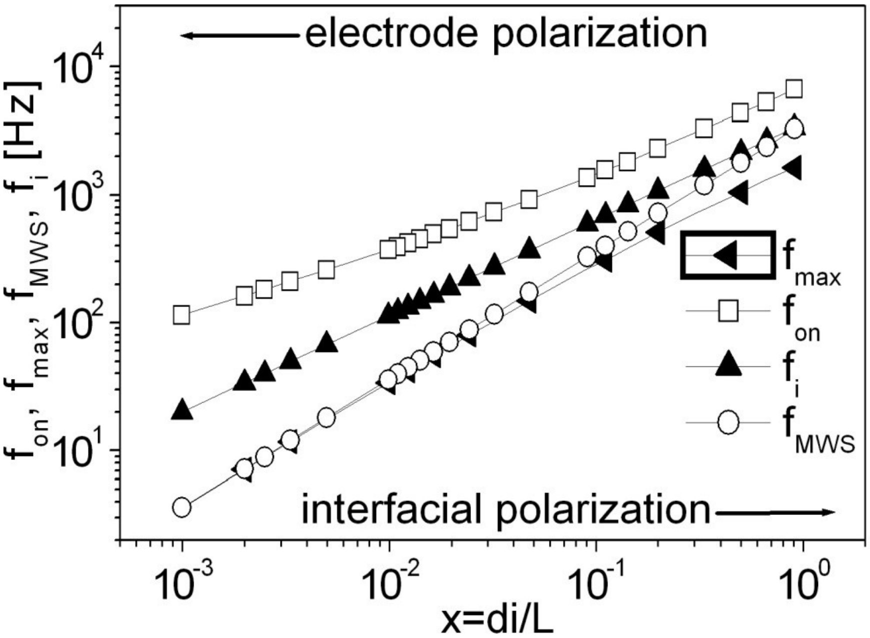

Fig. 1 : the characteristic frequencies of electrode polarization and interfacial polarization effects in dependence on the volume fraction of the insulating layer.

Temperature-Volume Entropic Model for Structural Relaxation Times and Viscosities of Glass Formers

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In this presentation, an entropic model recently formulated by Mauro et al. [1] for the temperature dependence of viscosity in glass-forming materials is generalized [2] to describe the temperature-volume dependences of structural relaxation times and viscosities near the glass transition. We found out that the generalization shows limitations of its temperature precursor. The extended model describes well structural dielectric relaxation times $\tau_\alpha(T,V)$ of supercooled van der Waals liquids and satisfactorily predicts the pressure dependence of the isobaric and the isochoric fragility parameters. The obtained results are discussed in the context of the thermodynamic scaling law for molecular dynamics of viscous systems, because the newly proposed function $\tau_\alpha(T,V)$ satisfies this scaling law.

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Influence of DC bias electric field on a low frequency dielectric relaxation in a transformer oil based ferrofluid

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Ferrofluids or magnetic fluids (MF) are liquid dispersions of nanosized (≈ 10 nm in diameter) magnetic particles covered with surfactants[1]. Transformer oil based ferrofluids (TOMF) may show extraordinary cooling and dielectric properties with a higher breakdown voltage than that of pure oils, what is still not sufficiently understood[2]. By measuring a dielectric response of such TOMF, a remarkable dielectric relaxation has been observed in low frequencies. The process can be associated with a double-layer polarization on the particle surfaces or with rearrangements and movements of the particles forming percolation clusters. In this study we point out the formation of particle clusters induced directly by DC bias electric field. That is indicated by decrease in the relaxation frequency with the increasing bias voltage V_B. Moreover, variations in real permittivity and losses may be clearly seen as dependent on both, the amplitude and duration of the applied bias field. In order to observe the time evolution of the cluster formation, each measurement at a certain V_B was repeated 5 times one after the other in 5 minutes period (Fig. 1). The initial formation of clusters in the low bias field and their response to the probing field caused the increase in dielectric losses. At a higher bias field, the cluster growth and its reducing response ability due to the DC energy barrier is manifested by the decreasing losses. Finally, such particle cluster formation may help to understand the higher ferrofluid breakdown voltage[3].

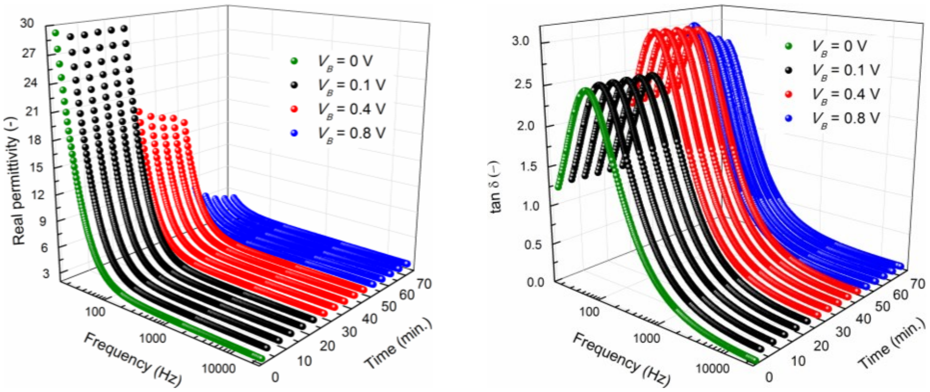

Fig. 1 DC bias field influence on real permittivity (left) and dissipation factor (right) spectra measured in the time dependence. The electrode separation distance d = 1.7 µm, the probing AC voltage V = 85 mV.

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Method for Estimating Oil Viscosity via Dielectric Spectroscopy

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Canada's reserve of bitumen (i.e. extra-heavy oil or asphalt) is the third largest source of petroleum in the world. Due to the remote location, bitumen is transported from reserve locations to refineries via ambient temperature pipelines, requiring dilution. The high viscosity of bitumen has been attributed to interactions between its asphaltene particles. The physical properties of asphaltenes are therefore a topic of consistent interest in the field of oil, gas, and mining. In this study the relationship between bitumen viscosity and the rotation of asphaltene nanoaggregates was empirically explored via dielectric spectroscopy. Particle size was found to be independent of concentration, and dielectric spectroscopy was found to be a reliable means to predict viscosity in neat bitumen and concentrated solutions. Due to the simplicity and portability of modern impedance analyzers, this technique offers a unique method for estimating a wide range of oil viscosities in the field ($<10^1$ to $> 10^5$ cP) and even offers the possibility of *in situ* oil viscosity monitoring in pipelines or oil-lubricated mechanical systems.

Electrical and dielectric properties of composite materials: the role of interfaces and interphases

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A general route to adjust 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 electrical and dielectric properties of multiphase composite materials in systematic dependence on morphology and volume fraction. 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.

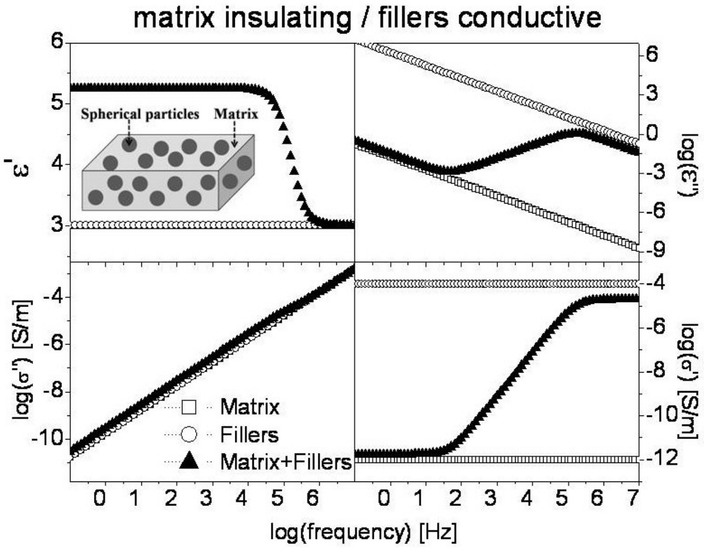

Fig. 1: complex dielectric permittivity and complex conductivity of an composite material consisting of an insulating matrix and conductive spherical fillers. The volume fraction is 20%. Conductivity values of 1e-4 S/m and 1e-12 S/m were considered for the conductive and for the insulating phase, respectively.

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A Dielectric Spectroscopy Study of Quenched Milk

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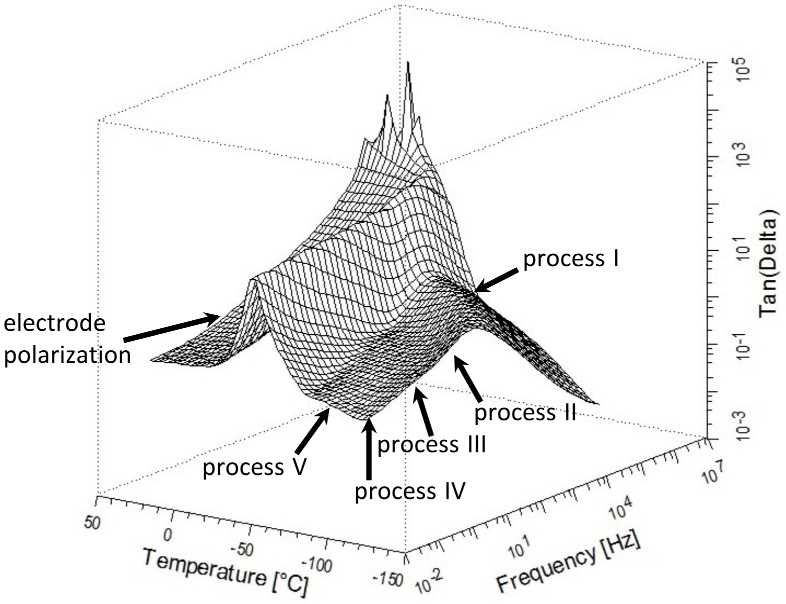
Bovine milk is a major constituent of the human diet, hence it is extensively studied. Most of the work in this field pursues practical goals such as the determination of milk's freshness [1], adulteration [2] or fat content [3]. However, despite the importance of and a plethora of research, milk is still poorly understood [4]. This is especially true when considering its dielectric properties. Specifically, the mechanisms of a multitude of dielectric relaxation processes need to be elucidated in terms of their molecular dynamics.

In this work we present dielectric measurements of quenched raw bovine milk in a wide range of temperatures and frequencies (10^{-1}-10^{6} [Hz], 173-242 K). We were able to observe five distinct processes. Based on dielectric relaxation behavior and existence of critical temperature points, we may tentatively link one of the processes to the presence of cooperative water-lactose complexes. Another process may be considered as the response of bulk ice, while the others are probably associated with milk proteins and electrode polarization.



3D representation of tanδ for a typical raw milk sample as a function of frequency and temperature.

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Effect of fish skin collagen on selected electric parameters of human skin *in vivo*

[1]Gauza M., [1]Kubisz L., [2]Dańczak-Pazdrowska A., [2]Polańska A.,
[1]Hojan-Jezierska D., [2]Adamski Z., [2]Osmola-Mańkowska A., [1]Pankowski E.

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The paper describes effects of fish skin collagen on selected electric parameters of human skin.
Collagen was achieved from fish skin by acidic hydration, the method permitting a protection of the native structure of collagen macromolecule. This property was controlled in another experiment. Such collagen is considered as biologically active protein. Collagen in a form of hydrogel of 9% protein content, was applied within the same skin region - flexural site of the left upper extremity. Measurements of electrical properties of the skin were carried out by means of Hioki 3532-50 LCR in the frequency range 0,5Hz-5MHz. The comparison of recorded spectra of collagen treated forearm (left) and control forearm (right) permits to conclude on the influence of collagen on human skin.
In the experiment the biophysical skin properties, including transepidermal water loss (TEWL), skin hydratation (corneometry), skin pH as well as skin viscoelasticity (cutometry), were assessed using Cutometer MPA 580 (Courage+Khazaka Electronics, Cologne, Germany) according to the guidelines. The assessment of skin thickness and mean skin echogenicity were determined with a high frequency ultrasound scanner (Dermascan C ver. 3, Cortex Technology, Hadsund, Denmark). This instrument operates at a frequency of 20 MHz, with a resolution of 60 µm × 200 µm (axial × lateral) and approximately 15-mm penetration.

Dielectric Spectroscopic Study on Hydrated Stratum Corneum

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2) L'OREAL Research & Innovation, Aulnay-sous-bois, France

Water is capable of being absorbed and dissolved by a variety of materials and thereby yields essential plasticizing effects. This is often associated with dynamic properties of a variety of soft materials, such as expression of protein functionality and viscoelastic and electric properties of hydrogels. In order to understand these dynamic properties, interaction between water and hydrophilic guest materials has to be elucidated. Recently, universal properties among a variety of hydrophilic material are debated from the view point of common dynamics of water [1,2]. To test the applicability of this idea, we studied dynamics of stratum corneum (SC), which is a top layer of skin, at a variety of hydration conditions. Moreover, the interaction between SC and water is important also from the view point of cosmetic and medical application.

Dielectric spectra of SCs were measured as a function of hydration level. Examined SCs exhibit the similar relaxation process assigned to dielectric response of the hydrated water. It shares several common properties: (i) the process is very broad in its spectral shape, reproduced by Cole-Cole function with similar values of small stretch exponent: (ii) the process exhibits crossover in the temperature dependence of the relaxation time and similar values of activation energies are observed below the crossover temperature. Hydration level dependence of this process and a relation between the crossover and glass transition are to be discussed in detailed.

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Dielectric properties of juices and their variation over time during storage

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Dielectric spectroscopy was proven to be a successful tool in investigating properties of various complex materials and processes [1]. One of the fields in which the method is applied is food science [2]. Dielectric properties serve as an indicator of the origin, maturity, freshness, type or additives content of food materials and products. They are also used for tracking the changes to which the materials are subjected or which they are undergoing spontaneously. The aforementioned applications of dielectric techniques show that they are also promising in the context of investigating quality factors of foods. The examined materials were six pure natural juices (chokeberry, black elder, nettle, sea-buckthorn, plum and cranberry) and their samples with sodium citrate and ascorbic acid as low-concentrated additives. The dielectric permittivity spectra were collected with the use of an open-ended coax probe within the frequency range from 200 MHz to 20 GHz. The readings were taken at temperature equal to 20±1°C. The conductivity and pH value of each sample were measured independently. The experiments were performed fourfold within eight weeks and the samples were stored at room temperature between the measurements. The obtained spectra were elaborated for the differentiation among the tested samples and the variations of dielectric parameters of the investigated materials over time were characterised.

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Specific electric conductivity dispersion of vena saphena magna

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Introduction

Pathologically changed structure of the vein wall causes the change of its electrical properties such as conductivity, **σ** and electric permittivity, **ε**. The presented results concern on different parts of pathologically changed great saphenous vein. Studied samples of vein were at different state of pathology. The proximal and terminal part of extracted vein had very similar electrical properties whereas other parts differed significantly. The change of conductivity as a function of temperature for the fixed frequency allowed to examine the thermal denaturation process of proteins contained in the vein wall.

Material & method.

The aim of our study was to determine the electrical properties of the vein wall for the great saphenous vein characterised as C2,Pr. In this vein the venous insufficiency concern the whole thigh and the upper part of shank.

The extracted vein was divided into 6 even parts. Number one means the most proximal part of the vein. From the every part, the 10 mm diameter sample was prepared and placed between capacitor plates. Measurements were carried out by means of automatic RLC bridge HIOKI in the frequency range 100 Hz – 5 MHz and the temperature range 20°C - 120°C. The fixed temperature was maintained with the accuracy of $\Delta t = \pm 0.3°C$.

Results

The results obtained at the temperature 30°C revealed the great electric conductivity and dielectric permittivity dispersion in the frequency range of 100 Hz – 10 kHz. For the frequency range 10 kHz – 5 MHz, the dispersion was not observed. The regions of the greatest change of **σ** were almost the same for all parts of vein.

Comparing the results obtained for all parts of the vein one could conclude that smallest value of **σ** revealed the part #3 and the biggest parts # 6 and #4.

The values of **ε'',** related to dielectric losses, for all parts of vein (except the part #1), above 10 kHz frequency were close to 1.

The part #3 revealed the minimal dispersion of **ε'** and **ε''**, which both, were close to 1.

The increase of temperature caused the increase in **σ** for all parts of vein. The characteristic maximum was observed for all curves, except the part #4. The sharper maximum was presented the functions of **ε'**(T) and **ε''**(T).

Hydration of complexes between sodium copper chlorophyllin and serum albumines

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This study is designed to examine the hydration effects accompanying the interaction between sodium copper chlorophyllin (CHLN, Fig. 1), a potent inhibitor of experimental carcinogenesis, and the most abundant plasma proteins - serum albumins (human (HSA) and bovine (BSA)) in aqueous solutions using differential dielectric method. The method applied in the work allows studying both dielectric characteristics and hydration of the compounds under investigation. It is based on the direct measurement of the difference of attenuation (Δα) coefficients and phase shift (Δβ) coefficients between water and aqueous solutions of compounds under investigation.

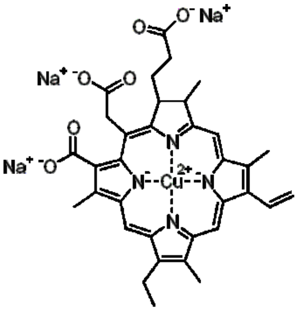

Fig. 1. Structural formula of chlorophyllin

Measurements of the complex dielectric permittivity of water solutions of the substances are carried out in the range of millimeter wavelengths (λ = 7.6 mm) using an original high–sensitivity EHF differential dielectrometer.

Estimating the decrement of the dielectric permittivity using the values of Δα and Δβ obtained directly in the experiment and basing on some known models, we can calculate the extent of hydration of the compounds.

We show that for both BSA-CHLN and HSA-CHLN complexes the process of complex formation is accompanied by changes of dielectric parameters. Results of calculations of the hydration of proteins and their complexes with ligand are presented in table 1 (for each protein its concentration both in the solutions of proteins and in the solutions of complexes is the same).

We found that formation of CHLN complex with fatty acids free BSA is accompanied by a significant decrease of hydration. It can be contributed to the redistribution of free and bound water molecules in system and serve as an evidence of BSA–CHLN interaction.

We observed only a slight tendency towards some decrease of hydration accompanying formation of CHLN complex with HSA containing fatty acids. This result might indicate that such complexation is unfavorable due to the presence of fatty acids that bind with HSA with higher affinity than CHLN.

Table 1. Hydration (ω) of CHLN, BSA, HSA, BSA-CHLN and HSA-CHLN complexes

Substance	ω, g/g
CHLN	0.21
BSA	0.38
BSA-CHLN	0.30
HSA	0.27
HSA-CHLN	0.25

The dynamics and kinetics of water in a protein hydration shell

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One of the most intriguing questions in biological physics is the hydration mechanism in biological systems. It is well known that water is not a passive solvent in biology, but plays an active role in many biomolecular and cell processes, interactions and can even have catalytic effect on important functions. The dielectric study of water in protein hydration shell can clarify its structural and dynamic interaction with the protein. The dielectric spectrum of protein's hydration shell is symmetrical and can be described by a Cole-Cole (CC) function.

The dielectric properties of protein hydrated powders were measured in wide frequency and temperature ranges. Comparison between diffrent hydrated biological and other complex systems like hydrated clays and glasses is presented. The dielectric study of water in a variety of complex systems can clarify its structural and dynamic interaction with such systems. Thus the dipole-matrix interaction of the protein's hydration shell is discussed.

Dynamics of cis-1,4 Polyisoprene and 1,4 Polybutadiene confined to Nanoporous Alumina

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We study the effect of confinement of two flexible polymers ,one with attractive interactions with the pore walls (cis-1,4 Polyisoprene) and one with repulsive imteractions (cis-1,4 Polybutadiene), as a function of molecular weight, pore diameter, temperature and frequency. Polyisoprene is a type-A polymer (Stockmayer) and as such it has a dipole moment parallel and perpendicular to the backbone. We employ molecular weights in the range from 300-20.000 g/mol and as confining medium we use self-ordered AAO templates with diameters in the range 400-25 nm. Our main interest is on the effect of confinement on the normal modes and segmental mode. Dielectric spectroscopy measurements over a broad range of frequencies and temperatures revealed a significant broadening of both modes on confinement and a slow-down of the normal mode dynamics in the lowest molecular weight. For the Polybutadiene case we study its behavior under the same confining media using molecular weights in the range from 500-55.00 g/mol. The feature that makes this case different of that of PI is that the segmental mode speeds-up as with decreasing pore diameters.

Dynamics and phase transitions of zeptograms of matter

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Investigations on zeptograms of matter (1 Zeptogram = 1e-21 gram) open the possibility of exploring the transition between nanoscience and molecule physics. Measurements on this scale require sample cells having all three dimensions on the nanometric length-scale. Based on the concept of employing nanocontainers as experimental cells (Fig. 1), a novel experimental development allowing dielectric measurements down to the level of zeptograms is demonstrated in the present contribution. This approach enables one to crystallize tiny amounts of matter under high electric fields (Fig. 1), with the goal of inducing a macroscopic coherence of molecular functionalities. This could give rise to new material properties, not naturally available in the case of bulk materials.

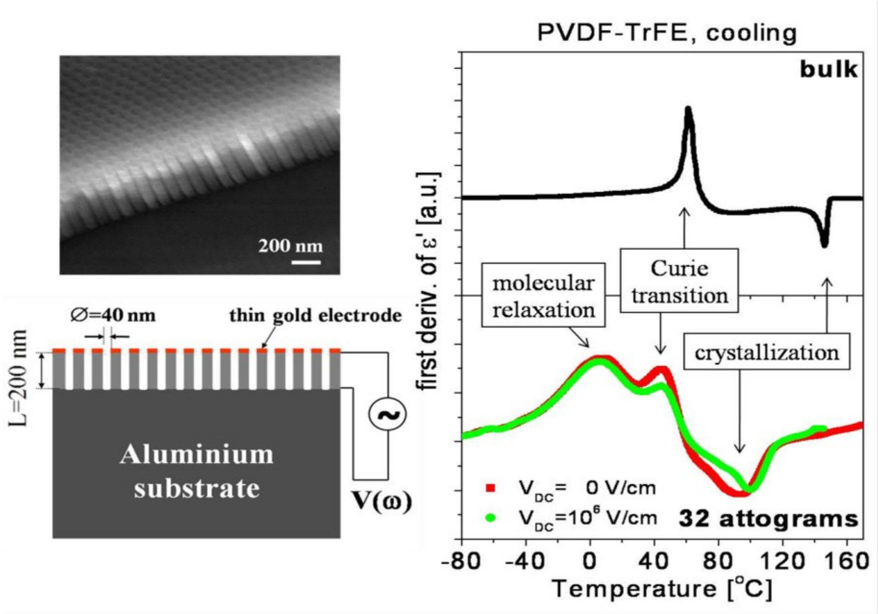

Fig1. (left) highly ordered arrays of identical, independent, additive nano-containers employed to hold and measure samples down to the level of zeptograms; (right) phase transitions measured for PVDF-TrFE in the bulk and for 32 attograms of material. A shift to higher temperatures is observed for the crystallization process of 32 attograms when a DC-bias is applied upon cooling.

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Relaxation phenomena and electrophysical properties vs. structural organization of the electroactive hybrid polymers containing ionic liquids

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The development, investigation and implementation of electrolyte systems of different nature, notably organic liquid electrolytes, ionic liquids, polymer electrolytes and inorganic solid electrolytes, are of interest. In brief polymer electrolyte systems can be conditionally divided as follows: polymer + organic liquid (polymer gel); polymer + ionic liquid; polymer + inorganic solid electrolyte + ionic liquids; polymer electrolyte + ionic liquid; polymer electrolyte + ionic liquid + liquid organic electrolyte; ionic liquids + liquid organic electrolyte; polymer electrolyte + inorganic solid electrolyte.

The blends consisting of two and more mentioned components are used and studied for obtaining electroactive polymer materials EaPM with combined merits of selected products.

The present work shows (by WAXS, FTIR, DSC, TOM and POM) that the doping of the hybrid organic-inorganic polymer systems (HOIS) based on urethane oligomers (UO) and metal silicate (MS) by the molecules of ionic liquids (IL) based on morpholine leads to destruction of the mineral phase with the simultaneous formation of new crystalline structures due to MS/IL reactions. Contrariwise, synthesis of EaPM based on UO and IL results in amorphous grain-oriented structural organization and formation of the ion conducting cluster with the high conductivity level $\sigma_{DC} \sim 10^{-3}$-10^{-4} S/cm, AC conductivity level $\sigma' \sim 10^{-2}$-10^{-3} S/cm and permittivity $\varepsilon' \sim 10^{5}$-10^{6} (by the results of BDS and cyclic VA spectroscopy).

Structure-Property relationships of Nanocomposites Based on Epoxy and Layered Double Hydroxides

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Two kinds of organically modified MgAl Layered Double Hydroxides (MgAl-LDH) were synthesized and reaction blended with an epoxy system (EP) to obtain polymerbased nanocomposites. The organic modification of the MgAl-LDHs were by sodium dodecylbenzene sulfonate (SDBS) modified and own synthesized SACC. The two kinds of nanocomposites were investigated by a combination of differential scanning calorimetry (DSC), small- and wide-angle X-ray scattering (SAXS and WAXS), and broadband dielectric spectroscopy (BDS) in dependence of the concentration of the nanofiller. The differences observed for the both kinds of nanoparticles are discussed in detail.

Structure-Property relationships of Nanocomposites Based on Polylactide and Layered Double Hydroxides

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Polymer based nanocomposites prepared by melt blending of synthesized NiAl layered double hydroxides (NiAl-LDH) and polylactide (PLA) were investigated by combination of differential scanning calorimetry (DSC), small- and wide-angle X-ray scattering (SAXS and WAXS) and broadband dielectric spectroscopy (BDS). In the case of NiAl-LDH based nanocomposites the degree of crystallinity at first increases and then decreases as a function of LDH concentration. By extrapolation a limiting concentration of NiAl-LDH ca.15% where the crystallization of PLA is completely suppressed by the nanofiller. The dielectric spectra of the nanocomposites show several relaxation processes related to dynamic glass transition and localized fluctuations were identified and analyzed in detail to understand the morphology. The results of the PLA based nanocomposites with NiAl-LDH as nanofillers were further compared with PLA based nanocomposites with MgAl-LDH as nanofillers.

Orientational degrees of freedom of pure and water-containing fullerene derivatives

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We employ broadband dielectric spectroscopy to study the dynamical behavior of the solid phases of two high-symmetry fullerene derivatives, fullerol ($C_{60}(OH)_{24}$) and oxofullerene ($C_{60}O_4(OH)_{14}$), both of which have basically zero net dipole moment and are strongly hygroscopic. These fullerene solids display relaxation phenomena due spatial charge relaxations associated with charge-transport processes, and, when present, to the reorientation of H_2O molecules. We investigate in particular the orientational dynamics, both of the water present in the organic matrix and of the quasi-spherical fullerene units.

In fullerol we observe three different types of water-related relaxations. Of these, the faster two derive from non-equivalent water molecules inside the fullerol matrix, one corresponding to intermolecular water clusters and one to water molecules directly attached to the hydroxyl (OH) groups of the fullerol units.[1] The slowest relaxation could be due to the re-orientational motion of fullerol-water complexes, and would then be the signature of a plastic phase in fullerol similar to that of Buckminster fullerene (C_{60}). [2]

Oxofullerene (which contains hydroxyl groups as well as epoxy/carboxy oxygens) displays two main rotational phase transitions between room temperature and 373 K (in the absence of water). The pure material exhibits a dielectric loss that stems from the sample's heterogeneity and is closely related to charge transport.[3,4] Both the conductivity and the related dielectric loss show important changes across phase transitions. The first transition at 323 K involves the breaking of the hydrogen bonds between hydroxyl and epoxy units of neighboring molecules, and is accompanied by a dramatic increase of the dielectric strength of the conductivity-related loss feature. The second transition around 370K results in a higher rotational lability of the oxofullerene molecules probably including the motion of polar side groups, which leads to a partially dipolar character of the loss feature.

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Molecular Dynamics of nanometric Poly(2-Vinyl-Pyridine) brushes with varying grafting density

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Broadband Dielectric Spectroscopy (BDS) combined with nano-structured electrode arrangements is employed to measure the molecular dynamics of poly(2-vinyl pyridine) (P2VP) brushes (M_w=43.8kg/mol) with a grafting density varying between 0.09 - 0.12chains/nm².

The grafting of P2VP on a highly conductive silicon layer is realized in a two-step "grafting-to" preparation. A thin layer (~2.5 nm) of poly(glycidyl methacrylate) (PGMA) serves as anchors for carboxyl terminated poly(2-vinylpyridine) (P2VP-COOH). By applying different annealing times, P2VP-brushes with different grafting densities are formed. In the present study P2VP-brushes with three different grafting densities (0.09 - 0.12chains/nm²) and layer thicknesses from 5 nm to 7 nm were investigated. This corresponds to distances between the grafting points of about 3-4 nm (smaller than Rg $\sim$ 5 nm). The quality and homogeneity of the P2VP layers is checked by Atomic Force Microscopy (AFM) and Ellipsometry.

For the dielectric measurements a nanostructured electrode arrangement is used. Two highly conductive silicon electrodes (ρ < 0.01 Ωcm, bottom electrode: 10x20mm², top electrode: 1x1mm²) are assembled to form the capacitor. Silicon dioxide pistons having a height of 35 nm serve as spacers, leading to a distance of around 40-50 nm between the solid surfaces of the electrodes.

Two well separated relaxation processes are observed, a β-relaxation attributed to PGMA and the dynamic glass transition of the grafted P2VP layer showing a Vogel-Fulcher-Tammann temperature dependence similar to bulk P2VP.

P-42

Dielectric behaviour study of silica-containing polyimide and poly(amide imide) hybrid films

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The present paper describes the preparation and characterization of polyimide and poly(amide imide) films containing different amounts of silica, having the thickness in the range of tens of micrometers. Polyimide/silica hybrid films were prepared using two poly(amic acid)s and tetraethoxysilane via sol-gel technique and thermal cyclodehydration. The poly(amic acid)s were synthesized by the reaction of 4,4’-oxydiphthalic anhydride with 1,3-bis(4-aminophenoxy)benzene or with a mixture of the later and 3,5-diaminobenzoic acid, followed by end-capping with an aminosilane coupling agent, 3-aminopropyltriethoxysilane. The poly(amide imide) hybrid films were prepared by sol-gel technique using tetraethoxysilane and a polymer having hydroxyl groups, resulting from solution polycondensation reaction of a mixture of 4,4’-diamino-4”-hydroxytriphenylmethane and 1,3-bis(4-aminophenoxy)benzene (molar ratio 3/7) with a fluorinated diacid chloride containing imide rings, 2,2-bis[N-(4-chloroformylphenyl) phthalimidyl]hexafluoroisopropane. To improve the compatibility between the polymer matrix and silica, the pendant hydroxyl groups of the polymer were reacted with 3-(triethoxysilyl)propyl isocyanate.

A study of the thermal and electrical behavior of the hybrid films is presented. Broadband dielectric spectroscopy and dinamic mechanical analysis were employed to emphasize the influence of silica in the polymer matrix. The surface morphology of the films was investigated by scanning electron microscopy and atomic force microscopy. The polymer films exhibited good thermal stability having the initial decomposition temperature above 420°C, high glass transition temperature and dielectric constant in the range of 2.64-3.89, at 20°C and 10 kHz. Two subglass transitions, γ and β, were evidenced by broadband dielectric spectroscopy. At higher temperature, a conductivity relaxation process was noticed. On increasing the concentration of silica a decrease of dielectric constant and thermal stability were observed.

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Dielectric Relaxation Behavior of Thin Films of Polyamide Random Copolymers

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We investigated the relaxation behavior of thin films of polyamide random copolymers 66/6I using broadband dielectric spectroscopy. There are four dynamical modes, i.e., alpha-, beta-, gamma-processes and electrode polarization[1]. The peak position and the height of electrode polarization at a given frequency is shifted to lower temperature with decreasing film thickness. We have analysed the dynamical behavior of the relaxation process related to electrode polarization to elucidate the glass transition dynamics. The temperature dependence of the relaxation time of electrode polarization can be described by Vogel-Fulcher-Tammann law and strongly depends on film thickness. This result suggests that the relaxation process due to electrode polarization is associated with the alpha-process. The Vogel temperature determined by data fitting slightly decreases with decreasing film thickness. The Vogel temepratture obtained thus for the bulk system is 303 K, which is by about 50 K lower than the thermal glass transition temperature obtained by DSC. Therefore, the dynamics of the alpha-process can be evaluated through the analysis of the relaxation behavior due to the electrode polarization. Such analysis shows that this system has higher mobility in thin film than in the bulk. Furthermore, the fragility index was evaluated from the Angell plot of the temperature dependence of the relaxation times due to the electrode polarization. Fragility index increases with decreasing film thickness, i.e., the system shows a crossover from strong to more fragile glass with decreasing film thickness. This thickness dependence is different from that of thin polystyrene films [2]. The observed difference of the thickness dependece of the fragility between the amorphous polyamide and polystyrene may rely upon the difference of the microscopic structure.

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Water–Triggered Conduction and Polarization Effects in a Hygroscopic Fullerene Salt

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Impedance spectroscopy is employed to probe the frequency-dependent conductivity and dielectric response of the crystalline $C_{60}O_{24}Na_{24}$ fulleride and of its hydrate of chemical formula $C_{60}O_{24}Na_{24} \cdot 16\ H_2O$, which is stable only below 390 K. Charge conduction in the pure material is mainly electronic in the whole temperature range studied.[1] Exposure of the pure material to humid atmosphere results in an increase of the room-temperature conductivity by four orders of magnitude due to the surface hydration of the crystalline grains, a situation encountered in many other weakly conducting systems.[2] The surface water desorbs upon heating to 330 K.

The conductivity of the hydrate is dominated between 320 and 390 K by a water-related contribution, possibly due to proton shuttling. Due to such contribution, at 360 K the hydrate's conductivity is higher than that of the pure material by almost two orders of magnitude.

A dielectric loss feature is visible in both hydrate and pure material. The loss feature in the pure material is found to have a conductivity origin (conductivity-induced loss [3]), but its frequency and intensity are affected by the presence of water. The structural (bulk) water molecules in the hydrate do not display any dynamic relaxation, in agreement with the expectation for a crystalline hydrate with a rigid hydrogen-bond network. The adsorption of hydration (surface) water in the hydrate leads, on the other hand, to the appearance of an intense dipolar loss feature in the radiofrequency region. Such loss feature displays a non-monotonic temperature dependence, similar to that found in other water-containing systems.[4]

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The role of size and charge delocalization in dissociation and charge transport in solvents of low polarity

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The high lattice enthalpies of salts make them insoluble in most solvents. In addition, even when they are soluble, they only partly dissociate in nonpolar solvents because of the high free energy of dissociation. For liquids of low polarity ($\varepsilon_S < 11$) and for inorganic salts such as NaCl, KCl, and KNO_3, the energy of dissociation is many times the thermal energy k_BT. One consequence of the low degree of dissociation is that dispersions in nonpolar solvents cannot be stabilized by electrostatic or electrosteric repulsion.

From a thermodynamic viewpoint, charging in a liquid is controlled by the Bjerrum length, λB. In liquids of low polarity such as toluene or even THF, the Bjerrum length is 20.4 and 7.4 nm, respectively. Ion dissociation in such solvents is limited unless the ion size approaches the "escape distance" set by λ_B. Hence extensive research was made on increasing the size and bulkiness of molecular anions that led to a new class of compounds known as weakly coordinating anions (WCAs).

In addition to the systematic variation of the anion or the cation size, another approach emphasized the effect of delocalization of the anion charge. It is thought that the spreading of the anion charge to a larger area is responsible for the weaker coordination.

Octaacetylmaltose - a very effective agent to improve physical stability of amorphous indomethacin

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Most of recent investigations concerning amorphous pharmaceuticals are focused on finding new ways to stabilize it. Here we have demonstrated a very effective and easy way of stabilization of amorphous indomethacin (IMC) by preparing binary mixtures with octaacetylmaltose (acMAL). Detailed studies on the physical and thermodynamical properties of binary systems with different concentrations of acMAL were performed using Dielectric Spectroscopy (DS), Differential Scanning Calorimetry (DSC), Raman Spectroscopy, X-ray Diffraction (XRD), Infrared Spectroscopy (FTIR) and Quantitative Structure–Activity Relationship (QSAR).

Our research have revealed that indomethacin mixed with acetylated saccharide forms homogeneous mixture with only one value of the glass transition temperature, T_g. Interestingly, even a small amounts of modified maltose (25 wt %) prevents recrystallization of amorphous IMC. Moreover, it has been shown there is no phase separation in examined binary samples. In order to describe the dependence of the glass transition temperature vs concentration of indomethacin, Gordon-Taylor equation was used. The negative deviation of the experimental data from the ideal behavior predicted by the Couchman-Karasz model suggested that there are definitely strong intermolecular interactions between indomethacin and octaacetylmaltose. In fact FTIR measurements confirmed that the concentration of indomethacin dimers is significantly affected by the presence of modified carbohydrate. Hence, with increasing the amount of acMAL in the system we may expect that molecular interactions between matrix and API become more dominant over the IMC-IMC ones. The same conclusions were derived from the QSAR calculations. Structural investigations with the use of X-ray diffraction have demonstrated that indomethacin does not recrystallize upon storage at room temperature for more than 1.5 year. Finally, solubility analysis revealed that acetyl derivative of maltose not only stabilizes the amorphous API, but also enhances its solubility.

Dielectric and thermal study of the interfacial dynamics and crystallization in polymer nanocomposites

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Polymer crystallization and, in particular, annealing of polymer nanocomposite materials induced by crystallization are in the center of interest in the present work. Broadband Dielectric Spectroscopy (BDS) and Differential Scanning Calorimetry (DSC) were employed for the quantitative investigation of the different polymer phases in two series of samples. The first series of samples was constisted of poly(L-lactic acid) (PLLA, *MW*~100,000) matrix filled with different types of inorganic fillers (silica, graphene oxide [1], CNTs) (1D-3D geometry). The second series was consisted of polydimethylsiloxane (PDMS) polymer both, (a) crosslinked and filled with *in situ* generated silica and titania particles [2] and (b) sorbed mainly onto the surfaces and pores of silica and titania particles forming the so called '*core-shell nanoparticles*' [3-4].

Molecular mobility of bulk polymer chains and of those confined within polymer crystals (Rigid Amorphous Phase, RAF_{cryst}) or located in the polymer-particles interfacial layer (RAF_{filler}) was studied by performing, mainly, isothermal crystallization experiments (annealing procedure). The mobile polymer chains were investigated by the simultaneous monitoring of the segmental, *α,* relaxation process and the degree of crystallinity. Isothermal annealing measurements at standard temperatures resulted in similar crystalline structures and enchanced degree of crystallinity [1]. BDS in semicrystalline polymers was found to be more sensitive in monitoring the formation of RAF_{cryst} and in following the first stages of crystallization procedure (nucleation) as compared to DSC [5]. RAF_{cryst} was estimated to vary between 0.14 and 0.44 wt of the whole polymer.

In the case of PDMS based nanocomposites, the interafacial polymer dynamics has been investigated by monitoring a specific relaxation process appearing only in the nanocomposites (α' relaxation) [2-3]. The interfacial polymer was found to be responsible for the initial suppression of α relaxation in the nanocomposites as compared to neat polymer, all of them being fully amorphous [2-4]. The Effects of annealing induced by crystallization on the PDMS molecular mobility in bulk and at the interfaces were investigated. Our results suggest that these are independent on both, the type and the dimensions of the filler [4].

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Dielectric properties and conductivity of the crosslinked elastomeric polyurethane containing the small additions of the single-wall carbon nanotubes

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In this paper, to clarify the nature of the effect of influence of single-walled carbon nanotubes (SWNT) (0 - 0.018 wt.%.) [1] on the properties of crosslinked polyurethane elastomer (PU) applied methods of broadband dielectric spectroscopy.

Samples were prepared by the method described in [1]. The volume fraction of the dispersed phase of polyamide-6 in flexible polyurethane matrix is about 10%. Dielectric measurements were performed on a broadband dielectric spectrometer «Novocontrol» in the frequency range f = 10^{-3}-10^{5} Hz and temperatures from 133 to 453 K.

Studies have shown that the direct current conductivity σ_{dc} dependences on temperature significantly deviated from the Arrhenius equation and satisfactorily described Vogel-Fulcher-Tamman equation $\sigma_{dc} = \sigma_{dc0} \exp\{-DT_0/(T-T_0)\}$, where T_0 - temperature Vogel, D - strength parameter. Nonmonotonic dependence of the strength parameter D concentration with a maximum in the region of 0.002 ÷ 0.008 wt. % was observed. The influence SWCNTs on the relaxation times in main and impurity phase of the composite were opposed. Relaxation times of the α-relaxation in the temperature range in polyurethane phase increased with the introduction of SWCNTs. This effect is apparently due to the decreasing of the free volume, identifying the α-relaxation times of the polyurethane. In contrast, in α-relaxation for polyamide phases relaxation times were reduced when introduction of SWCNTs. These results are agreement with previously published results on the effect of en SWCNTs on the physico-mechanical characteristics of PU [1]. The main results will be published in {2,3].

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Impact factors on the mutarotation process in supercooled monosugars

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Mutarotation phenomenon, sometimes called tautomerization in sugars is studied more than 200 years, however it is still not known any correct description of this process in the condensed matter. Mutarotation process is a transition of one anomer form to another by opening cyclic ring form until equilibrum state beetwen them is reached (Fig.1).

Sugars tautomerization is dependent on both temperature and pressure. Methods, which allow to explore and clarify this fascinating interconversion in sugars is broadband dielectric spectroscopy, infrared spectroscopy, Raman spectroscopy, DFT-calculations.

Moreover, molecular dynamics in carbohydrates can be observed by refraction index changes. In addition to temperature and pressure, interesting impact factors on this process are also alcohols, acids and bases.

The main purpose of the research is to explain the interconversion in monosugars, finding factors that affect a speeding up or slowing down of mutarotation undergone via different methods and under different conditions. By analyzing kinetic cuves at several temperatures, we determined the reaction rate constatnts for the several temperatures and we calculated the activation energy for this reaction by fitting to the Arrhenius equation.

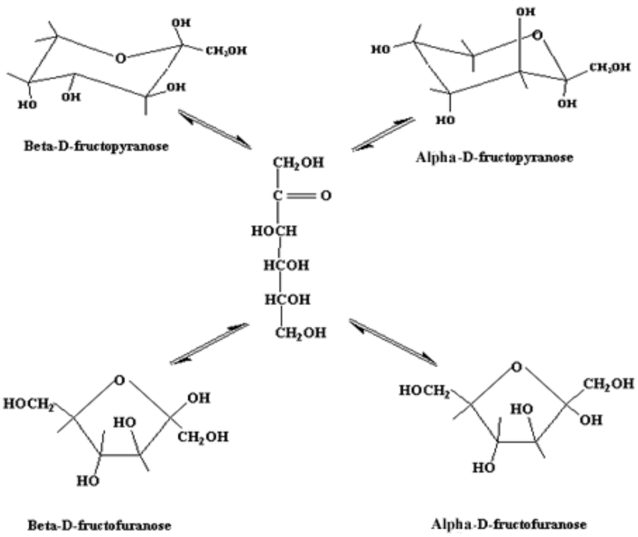

Fig.1. Mutarotation in D-fructose.

Molecular dynamics of itraconazole at different thermodynamic conditions

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Comprehensive molecular dynamics studies of vitrified and cryogrounded Itraconazole (Itr), a triazole derivative with broad-spectrum antifungal activity and a poor solubility, were performed at different thermodynamic condition. DSC measurements yielded beside of melting and glass transition observed during heating and cooling of both samples two further endothermic events around T=363 K and T=346 K. FTIR measurements revealed that order parameter variation in Itr shows typical sequence of liquid crystal phases with axially symmetric orientational order; i.e. nematic phase in the temperature range 361.7 K to 346.5 K and Smectic A phase below 346.5. Moreover, dielectric measurements demonstrated that except of structural relaxation process, there is also slower mode above the glass transition temperature in the both vitrified and crygrounded samples. For the dielectric data collected at elevated pressure, evolution of the steepness index versus pressure was determined. Finally, the pressure coefficient of the glass transition temperature was evaluated to be equaled to 190 K/Gpa. Moreover, we performed Pressure-Volume-Temperature (PVT) measurements and determined the value of the γ exponent of this compound and tested the thermodynamic scaling law.

Isothermal cold crystallization kinetics study of sildenafil

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Isothermal cold crystallization of sildenafil, which is used as API of *Viagra*, was investigated by dielectric spectroscopy, differential scanning calorimetry, optical microscopy and X - ray diffraction. To analyze the kinetics of crystallization Avrami and Avramov approaches were used. These two models enabled to characterize basic parameters such as crystallization constant rate (*k*), dimensionality (*n*) and activation energy of the crystallization process. Moreover, we found that the activation energies for the crystallization process obtained from the applied methods are comparable. From the optical measurements, it was possible to estimate the time of the nuclei formation, the nucleation density, sizes of the forming embryos and crystals at each temperature as well as the crystal morphology and habit. Additionally, monitoring the crystallization process by optical microscopy, we observed unexpected corrugations of the sample surface before the nucleation begins. This behavior can be related to the phenomenon of intermolecular proton transfer between molecules of sildenafil.

Further, the physical stability and molecular dynamics of amorphous sildenafil are investigated in both the liquid and glassy states. Molecular mobility are very important in context of recrystallization during its long-term storage at room temperatures of amorphous pharmaceuticals.

Key words: sildenafil, crystallization kinetic, isothermal measurements, molecular mobility, dielectric spectroscopy, differential scanning calorimetry, X – ray diffraction, optical measurements.

Photodielectric Properties of the Poly[NiSalen] Metallopolymer Structures

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Polymer structures based on Ni(II) complexes of the [NiSalen] type are attractive from the standpoint of the miniaturization of electronic components and the development of microelectronic devices on a supramolecular level, capable of performing complex functions involving directional charge and energy transfer. We present the results of the experimental investigation of the photodielectric properties of metal-containing polymer films synthesized using electrochemical polymerization of the initial [NiSalen] monomers. The samples of polymer films with a thickness of about 1 μ m were prepared on polished glass substrates with a conducting SnO_2 layer (bottom electrode). The temperature–frequency dispersion of the dielectric parameters for the sandwich structures formed was determined on an E7-20 immitance spectrometer in the frequency range $f = 10^3–10^5$ Hz at temperatures $T = 293–360$K. The samples were irradiated with light from an incandescent lamp with an intensity of 1.5 μW cm^2 in the visible range. To avoid heating of the thin film structures, the infrared part of the spectrum was filtered off with the use of a system of the corresponding light filters.

The analysis of the dispersion curves has demonstrated that, in the frequency range under investigation, the illumination of the polymer film leads to a positive photodielectric effect, i.e., an increase in the dielectric parameters of the sample.The suppression of the photodielectric effect with variations in temperature is caused by the probable thermal injection of charge carriers from metastable defects of the structure, which decreases the role of the photogeneration process. Moreover, there occurs an enhancement of the thermostimulated activity of the recombination on defects of the polymer chain, the number of which increases with increasing temperature due to the breakage and rearrangement of bonds in the system of π-conjunctions. The results obtained in this study allowed us to draw a conclusion regarding the photoactivity of the structure of the poly[NiSalen] metallopolymer outside the electrolytic medium from measurements of the dielectric characteristics under light excitation in the visible range. The revealed photodielectric response is integral in character due to the photoconduction process stimulated by electron transitions in the system of π-bonds of the polymer and owing to the probable change in the charge state of the nitrogencontaining coordination site of the [NiSalen] monomer. The temperature–frequency dispersion of the dielectric parameters of the metallopolymer films under exposure to light undergoes most pronounced changes in the range of low frequencies $f = 10^3–10^4$ Hz and temperatures $T = 300–340$ K. When the photoexcitation is removed, the kinetics of photodielectric response in the poly[NiSalen] structure exhibits a photomemory effect.

Dielectric spectroscopy of bismuth niobate powders prepared by solid state reaction

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Multilayer microwave devices have been developed to reduce the size of devices in mobile radio communication systems. $BiNbO_4$ is a dielectric material that presents high dielectric constant values in the GHz region. In this work, $BiNbO_4$ ceramics were prepared by solid state reaction. The as-prepared samples were treated in controlled conditions at temperatures between 600 and 1200 ºC.

The samples structure was analyzed by XRD and Raman spectroscopy. Morphology was studied using SEM. The dielectric properties of these samples were measured in the frequency range between 100 Hz and 1 MHz and after, using the low-perturbation resonance cavity method, at 2.7 GHz, at room temperature.

The samples heat treated at temperatures above 800 ºC present the $BiNbO_4$ crystal phase, being the predominant phase on the samples treated above 950 ºC. The samples treated below 900 ºC present the $Bi_5Nb_3O_{15}$ phase, which seems to be responsible for the highest dielectric constant values observed at room temperature. The sample treated at 1100 ºC, which presents $Bi_5Nb_3O_{15}$ and $BiNbO_4$ phases, presents the lowest value of dielectric constant (4.1 @ 2.7 GHz). At this frequency, the dielectric losses of all samples are always lower than 10^{-4}.

Impedance and modulus studies of ceramic oxide $Ba_2Co_2Fe_{12}O_{22}$(Co2Y) doped with V_20_5

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With the recent development of satellite communications and consequent mobile applications, the miniaturization and high efficiency of devices for information andcommunication technology have been required, especiallyon multilayer components. This rapid development of wireless communication necessitates the design of new ceramics,sinterable at low temperature, and exhibiting good dielectricproperties[1,2,3]. Polycrystalline samples of a layered magnetic ceramic oxide, $Ba_2Co_2Fe_{12}O_{22}$(Co_2Y), doped withBi_2O_3were prepared by the solid state reaction method. The dielectric impedance properties werestudied over the range of frequency between 1 Hz–1MHz and in the temperature range of 313–493K, using the modulus formalism. The impedance plot showed a first semicircle at high frequencythat wasassigned to the grain intrinsic effect and a second semicircle, at lower frequencies,which corresponds to grain boundary polarization (conduction phenomenon). A complex modulusspectrum was used to understand the mechanism of the electrical transport process, which indicatesthat a non-exponential type of conductivity relaxation characterizes this material. The values of theactivation energy of the compound (calculated from both dc conductivity and the modulusspectrum) are very similar, suggesting that the relaxation process may be attributed to the sametype of charge carriers. The dielectric measurements were studied, including the conductivity parameters. The studydemonstrates that the investigation of dielectric relaxation, conductivity, and loss of the ferritematerials, as a function of temperature, are essential for future microwave absorption applicationsof this material.

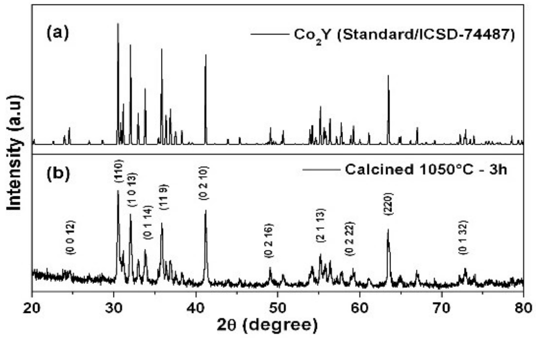

Fig. 1.(a) XRD standard (ICSD/74487) of Co_2Y powders and (b) processes (1050°Cfor 3 h) (CuK, λ= 1.5405 Å).

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Study impedance spectroscopy of MgO addition on the ceramic matrix BBT

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In this word a study of MgO addition (0, 2, 5 and 10 wt.%) and its effects in the impedance spectra of$BaBi_4Ti_4O_{15}$ (BBT)ceramic matrix was carried out. The structural, dielectric properties of the addition in the BBT matrix were discussed. In the preliminary structural studies, X-ray diffractograms of the samples were recorded at room temperature with X-ray powder diffractmeter with Cok_a. The Rietveld refinement method were usedandconfirmed themonoclinicstructureforpure sample.The results show that the synthesis of BBT was effective from 800 °C, showing nanosize particles (35–45 nm) with tetragonal symmetry. The dielectric properties of BBT presented high values of dielectric permittivity for radiofrequency range. The dielectrical behavior (complex impedance - Z^* and complex modulus - M^*) were studied over a frequency and temperature ranges of 1 Hz – 1 MHz and 300 K – 733 K, respectively. BBT was prepared by ceramic method with the precursor oxides Bi_2O_3 (Aldrich 99%), TiO_2 (Aldrich 99%), BaO (Aldrich 99%). They had been previously milled in stoichiometric quantities in a planetary mill for mixing and reduction of particle size for 6 h. The mass of reagent weighted in was in according with a stoichiometric reaction proposed: $Bao_{(solid)} + 2Bi_2O_3(solid) + 4TiO_{2(solid)} \rightarrow BaBi_4Ti_4O_{15(solid)}$ The obtained products from the milling process had been calcined in air different temperatures. X-Ray Diffraction and Raman Spectroscopy were the techniques used for the structural characterization of the products obtained from calcination and sinterization process showing the present phase. The pellets and ceramic cylinders were prepared in a metallic mold under constant pressure. An organic agglutinate (Alcohol Polyvinyl – PVA), with 5 wt%, was necessary for a better conformation of the pellets. The sinterization process in a furnace at 950 °C/3 h at air temperature was utilized for densification of ceramics.

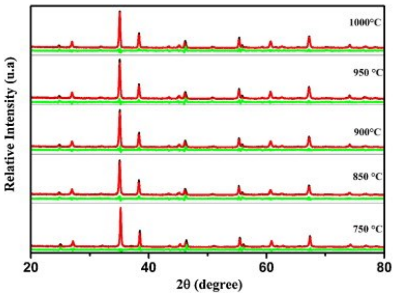

Fig. 1 Refinement Rietvield for BBT calcined in 750, 850, 900, 950 and 1000 °C.

Reference

Radiofrequency and microwave properties study of the electroceramic $BaBi_4Ti_4O_{15}$
P.M.O. Silva, T.S.M. Fernandes, R.M.G. Oliveira, M.A.S. Silva, A.S.B. Sombra, http://dx.doi.org/10.1016/j.mseb.2013.11.017

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Dielectric properties of $(Bi_{1-x}Fe_x)NbO_4$ ceramics prepared by Sol-Gel method

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In recent years, new dielectrics materials, in particular low temperature-cofired ceramics (LTCC), have been studied in RF and microwave frequency range, in order to produce miniaturized devices [1,2].

Bismuth-based dielectric ceramics are well known as low-firing materials and have been studied for multilayer capacitors. Various attempts have been undertaken to improve the dielectric properties of $BiNbO_4$, such as the addition of oxides or the substitution of Bi by lanthanides [3-6].

In this work, $(Bi_{1-x}Fe_x)NbO_4$ (x = 0.25, 0.50 and 0.75) samples were prepared using the Sol-Gel method. The fine particles were pressed into pellets and then treated at temperatures between 350 and 650 °C. The structure was studied by XRD and the morphology by SEM. The dielectric properties were analysed in the frequency range between 10^2-10^6Hz, in function of temperature (200–400 K), and in the microwave region, at 2.7 and 5 GHz. For treatment temperatures above 500 °C and with x = 0.25 and 0.5, $Bi_{1.34}Fe_{0.66}Nb_{1.34}O_{6.35}$ phase was observed. The dielectric constant value seems to be improved with the increase of the $Bi_{1.34}Fe_{0.66}Nb_{1.34}O_{6.35}$ phase.

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Dielectric measurements on Er^{3+}/Yb^{3+} co-doped tungsten-Yttrium tellurite glasses

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TeO_2 based glasses with molar composition $(70\text{-}x\text{-}y)TeO_2\text{-}20WO_3\text{-}10Y_2O_3\text{-}xEr_2O_3\text{-}yYb_2O_3$, where x = 0 and 0.5 mol% and y = 0, 0.5, 1, 2 and 4 mol%, were prepared by the melt quenching technique. At room temperature all the samples are transparent, mechanical and thermally stable. The XRD results showed the amorphous nature of all the samples and the Raman spectra showed a band distribution related with Te-O and W-O bond vibrations. The structural effects of the minority components, Y_2O_3, Er_2O_3 and Yb_2O_3 were regarded as small perturbations. The introduction of WO_3 results in a bandwidth substantially larger when compared to SiO_2 based glasses and even other TeO_2 based glasses, making this vitreous system promising for Raman optical amplification. The presence of WO_3 in the tellurium glass matrix can also modify the electrical properties of the glasses due to the promotion of the electronic conductivity contribution.

In this work, the measurement and analysis of the electrical properties of the $TeO_2\text{-}WO_3\text{-}Y_2O_3\text{-}Er_2O_3\text{-}Yb_2O_3$ glass system was made. It was found that the hopping of small radius polarons, for small concentrations of networks modifiers, is the dominant process in the charge transport mechanism for the DC conductivity. For higher concentrations of ions structurally inserted in the glass network, the ionic conductivity starts to have an important role in the transport mechanism. The AC conduction mechanism was attributed to a dipolar process between the interstitial modifier cations and the nonbridging oxygen ions. For all samples, the dielectric constant is practically temperature and frequency independent, tending to decrease with the increase of the concentration of Yb^{3+} cations.

Magneto-Dielectricity and Quantum fluctuations in $Ca_{0.90}Li_{0.10}Cu_3Ti_4O_{12}$

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In recent years, magneto-dielectric coupling phenomenon is being a trend in the materials science because magneto-dielectric materials are very useful in many applications like four storage devices and spintronics [1]. The magnetic degree of freedom (spins) can be coupled to electrical degree of freedom (dipoles) via spin lattice coupling. In the present work, we report an observation of competition of quantum fluctuations and spin-lattice coupling driven magneto-dielectricity in the Li doped $CaCu_3Ti_4O_{12}$ (CCTO) abbreviated as LCTO. The parent material CCTO is famous for high dielectric constant without any ferro-electric phase transition [2]. CCTO shows an anti-ferromagnetic transition [T_N] at 25K due the ordering of the Cu spins. The dielectric constant shows a drop below T_N a signature of magneto-dielectric coupling. The CCTO has similar structure as that of $CaTiO_3$ which is famous quantum para-electric material but additionally CCTO also has a magnetic atom Cu. But till now no report are available in the quantum para-electrcity of CCTO because of that the quantum para-electric behavior (intrinsic) in CCTO is masked by its huge dielectric constant originate from nano-scale charge disorder, site anti-site disorder of Ca and Cu.

We have unmasked the quantum para-electric nature of the CCTO by doping of Li at the Ca site which alter the disorder efect in CCTO and change its dielectric and magneto-dielectric behaviors. However the magnetic ordering temperature is not much affected by Li doping (23K). The temperature dependence of dielectric constant of LCTO is well fitted by the Barrett formula [3] down to magnetic ordering temperature which is signifying the quantum paraelectric nature of LCTO. The dielectric constant shows a frequency dependent drop near to T_N indicate a magneto-dielectric coupling are present in LCTO. The frequency dependent drop in dielectric near to T_N is indicating that there is no log range electrical ordering induced by the magnetic ordering. Because the quantum fluctuation oppose any long range ordering but spin phonon coupling want a long range electrical ordering in the system and as a compromise a disorder electrical state is established as a signature in frequency dependent dielectric peak near to T_N. The frequency dependent transition in dielectric constant near T_N is a direct consequence of the competition of Magneto-dielectricity and quantum fluctuations in material.

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Linear Dielectric Dispersion as a General Phenomenon in Solid Dielectrics

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This work is devoted to the study of mechanisms of linear dispersion, which is frequently observed in low-frequency range in different ferroelectric polymers and crystals with hydrogen bonds. This phenomenon is caused by non-marcovian processes: a following event (dielectric response) depends on a previous state, which has not caused a system to reach equilibrium for the time between two events [1]. Linear dielectric response is found to be typical for a wide range of materials with different structures far from equilibrium state (for example, near phase transition points, or after application of external mechanical and electrical fields).

It was found that in many dielectrics with hydrogen bonds ε''(ε') diagram consists of two parts - a Debye-type semicircle and linear dispersion region at ultra-low frequencies. Common diagrams were obtained for several crystallohydrates (Erbium (Fig. 1), Yttrium, Holmium Formates) [2,3]. These compounds contain hydrogen bonds that are 0.26-0.29 nm in length. It was showed by dielectric spectroscopy method, that the region of linear dispersion, where ε''/ε'=const, is be related to the multipositional hopping proton conductivity.

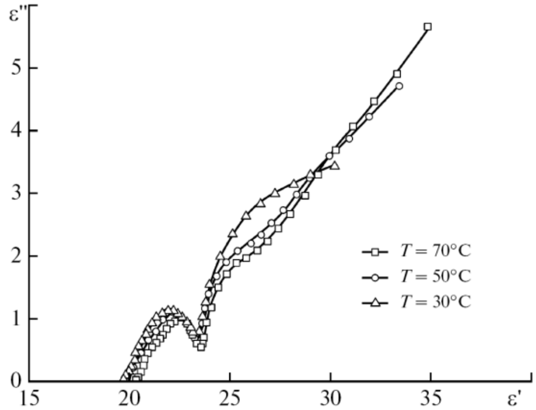

Figure 1. Cole-cole diagrams for Erbium Formate at several temperatures indicated on the plot [3].

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Effect of electrode material on space charge relaxation in ferroelectric Vinylidene Fluoride – Tetrafluoroethylene copolymer

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Broadband dielectric spectroscopy method (10^{-1}-10^{7} Hz, 20-160°C) has been used to study processes of space charge relaxation in isotropic films of Vinylidene Fluoride – Tetrafluoroethylene (71:29) copolymer prepared in acetone solution. Electrodes of Al (I) and Au (II) were deposited by vacuum evaporation. Comparison of dielectric and conductivity spectra for films with different electrodes shows difference in low-frequency part of spectra. In this class of polymers strong low-frequency dispersion is usually observed at temperatures over 100°C [1-3]. Comparison of dielectric spectra of samples I and II shows that low-frequency value of dielectric permittivity ε' is by order of magnitude lower in sample II. At the same time analysis of dielectric loss ε'' and electric modulus M'' spectra shows that the number of relaxation processes and their parameters are different for samples I and II.

This result may be explained by feasible chemical changes in the surface of the studied copolymer during depositing of various metals. This hypothesis was verified via X-ray photoelectron spectroscopy. It is shown that in case of Al electrodes, new Al–C, Al_2O_3 and other organometallic bonds are formed which are not typical for the polymer. Similar changes were found in other copolymers [4]. It means that Al electrodes are partially blocking and this will increase electrode polarization, as we see in our experiments.

In case of Au no chemical changes in the surface are detected, but the Au4f line is shifted to higher binding energy with respect to pure gold. This effect may be explained by formation of a dipole layer at the Au/polymer boundary. Comparison of relaxation processes for films with Al and Au electrodes shows that in case of Au an additional relaxation process with high relaxation times is observed.

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Dielectric properties of thermosensitive polyelectrolyte hydrogels

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Smart polymers, which are able to change their properties in response to surrounding factors, have recently attracted special attention from researchers. Systems characterized by a conformational transition induced by an insignificant variation in the parameters of the surroundings are of interest for both fundamental research and practice. Special attention is attracted to sensitive hydrogels, which are able to react on changes of temperature, light, media content, electric field. In thermosensitive gels, the transition between a swollen gel and a collapsed gel is induced by a variation in temperature. Poly(N-isopropylacrylamide) (PNIPA) and poly(N-vinylcaprolactam) are the best studied thermosensitive polymers.

It was found earlier [1] that after drying and reswelling thermosensitive hydrogels based on copolymers of NIPA and sodium salt of vinylsulfonic acid (VSA) P(NIPA-VSA) recover their weight incompletely. Because the swelling of weakly crosslinked gels characterizes the 3D structure of the gel network, it may be assumed that a decrease in the degree of gel swelling after drying is associated with the changes in the network structure. The concentration of polymer chains in the networks of P(NIPA–VSA) gels in the dried state results in the formation of ion pairs and their multiplets because the average permittivity of the medium becomes low and not all multiplets disintegrate during repeated swelling. The multiplets function as additional crosslinks and stipulate a decrease in repeated gel swelling.

Dielectric spectroscopy method (10^{-1}-10^{7} Hz) has been used to study dielectric properties and conductivity of hydrogels based on copolymers of NIPA and sodium salt of styrenesulfonic acid (SSA) P(NIPA-SSA) containing 5 and 10% of ionogenic groups at cyclic drying/swelling. Experiments showed that dielectric spectra are typical for systems with high concentration of charged carriers. Typical values of dc conductivity were $\sim 10^{-4}$ $(\text{Ohm*cm})^{-1}$. Comparison of data on swelling behaviour of hydrogels after reswelling and values of dc conductivity allowed to draw a conclusion that part of charge carrires are localized in ionic pairs and multiplets.

Acknowledgements.
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Broadband Dielectric Relaxation of P(VDF-TrFE) Ferroelectric Nanoparticles

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Nanoparticles of Poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) (56:44, VDF:TrFE content) have been prepared by the dialysis nanoprecipitation method[1]. The morphology of the Nanoparticles was studied by Atomic Force Microscopy (AFM). The ferroelectric nature of the nanoparticles was corroborated by Piezo-response Force Microscopy (PFM), Wide Angle X-ray Scattering (WAXS) and calorimetry (Fig.1(right)). Similar as for the bulk polymer the Nanoparticles exhibit a ferroelectric-to-paraelectric transition as evidenced by WAXS and broadband dielectric spectroscopy. In the paraelectric phase the Nanoparticles show an intense dielectric relaxation process associated to the rotational motion of the dipoles within the paraelectric crystalline phase whose relaxation time is shown in Fig.1 (left). The nature of this dielectric process is similar to that of the bulk. Potential application on these Nanoparticles as elements for non-volatile memories will be discussed.

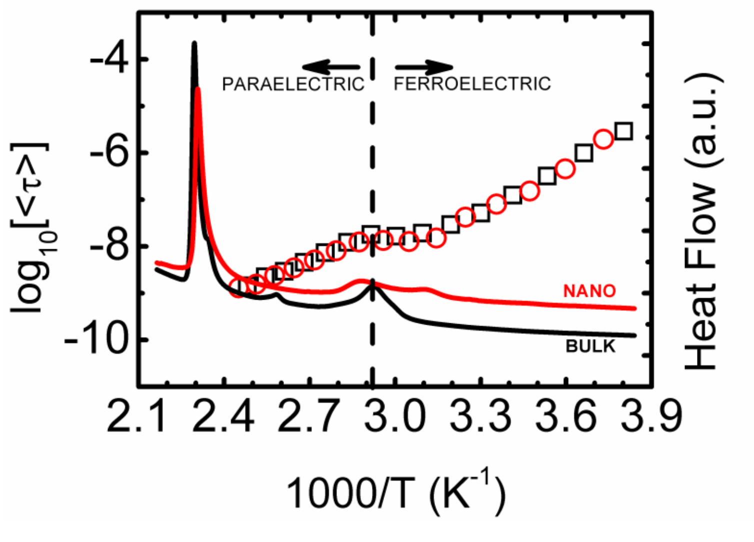

Fig.1 Relaxation plot (Left) and calorimetric trace (Right) for P(VDF-TrFE) Nanoparticles (red circles) and bulk polymer (black squares)

[1]Zhang et al. Macromolecular Rapid Communications. 2012. Vol 33, 1798-1803

Water dynamics in phosphoric acid-based geopolymers

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Geopolymers are a new class of porous materials, with amorphous to semi-crystalline nature, formed by the condensation of aluminosilicates and silicates from natural minerals or industrial wastes. Phosphoric acid based geopolymers were made with metakaolin and phosphoric acid in presence of water. In fact, in the whole process of geopolymer synthesis, water plays an important role since it takes part in the dissolution, hydrolysis and polycondensation reactions during geopolymer synthesis. Besides, water released in geopolymerization reaction is not only expelled after reaction and further curing, but also permits the formation of discontinuous pores in the geopolymer which is beneficial to its performance. Consequently, geopolymer materials are characterized with a highly porous network so that they can be used as an adsorbent with well-developed pore structure. In this work, thermal behavior and dielectric response of water confined in geopolymer materials was studied using differential scanning calorimetry (DSC) and dielectric spectrometry, respectively. DSC thermogramms showed that water can be presented in geopolymers with many types. Moreover, by dielectric measurements, we have investigated phase transitions and dipolar relaxations related to water molecules.

Dielectric properties of nanocomposites based on acrylic copolymer and cellulose whiskers

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Nanocomposites based on poly (styrene- co -2-ethylhexylacrylate) copolymer and cellulose whiskers as the nano-size filler were prepared by in situ miniemulsion polymerization. The dielectric response of the nanocomposites was examined by means of broadband dielectric spectroscopy .Two relaxations processes were identified in the case of copolymer matrix which are the α relaxation associated with glasse rubbery transition of the polymer and the relaxation process associated with conductivity occurring as a result of the carriers charges diffusion for high temperature above glass transition and low frequencies. The incorporation of nanofiber cellulose (NFC) is responsible for other relaxation processes. A first phenomenon is due to an interfacial polarization and a relaxation process associated to the presence of traces of water in cellulose. The effect of water is becoming increasingly important with NFC content.

The influence of cellulose nanowhiskers on the thermal and dielectric properties of natural rubber based nanocomposite films

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Natural rubber nanocomposites have attracted interest for dielectric applications. In this work, natural rubber, reinforced with different amounts of cellulose nanowhiskers, extracted from the rachis of date palm tree, was successfully characterized using impedance spectroscopy. The rubber matrix presents α relaxation processes, a water polarization relaxation and an ionic conduction phenomenon. The α relaxation, correlated with the mobility of the natural rubber polymer chains, is influenced by the interactions between the nanofiller and the matrix. The cellulose nanowhiskers are responsible for another relaxation phenomenon called "the interfacial polarization". This one leads to characterize the interfacial zone, reflecting the adhesion properties between the polymer matrix and the filler.

Effect of coupling agent on the dielectric properties of low density polyethylene / short palm lignocellulosic fibers composites

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In this work, the use of short palm tree lignocellulosic fibers as a reinforcing phase in the low density polyethylene (LDPE) matrix has been reported. Compatibilization of these fibers was carried out with the use of maleic anhydride copolymers. In order to investigate the coupling agent effect, the composites were studied by broadband dielectric spectroscopy (BDS). Dielectric parameters were measured in the temperature range from -100° C to 100 °C with the step of 10 °C / min and the frequency range from 0.1 Hz to 1 MHz. For the neat matrix, no relaxation has been detected in this temperature range and frequency. After the incorporation of cellulose filler, the dielectric losses increases and two relaxation processes appeared: a dipolar relaxation and the interfacial polarization. It was shown that the use of the compatibilizer improves the interfacial adhesion and the dielectric properties to a critical content of compatibilizer beyond which the dielectric properties decrease was observed.

Keywords
Composites; Low density polyethylene (LDPE); Lignocellulosic fibers; Coupling agent; Dielectric properties.

Effect of magnetic field and lysozyme concentration on the dielectric properties of magnetic lyotropic liquid crystal

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Aqueous solutions of lysozyme (concentrations 0,3; 0.7 and 1.4 mM) with magnetic nanoparticles (concentration 10^{-2} wt.%) were studied. To enhance the action of the magnetic field we added magnetic liquid (ML) with pH=2.0 to some of the solutions. The published data show, that under the influence of the magnetic field in such solutions, the magnetic nanoparticles (MN) together with the lysozyme molecules are oriented in the direction of magnetic field[1]. Such ordering remains for a short time after switching off the magnetic field. Therefore, the solutions investigated by us are called magnetic lyotropic liquid crystals (MLLC). Oscilloscopic method with the frequency range 10^{-1}-10^{6} Hz was used. Amplitude of the voltage of measuring signal with triangular shape was 0.25 V. Measurements were performed with and without the action of a constant magnetic field with the induction 0.2 T at 293 K. The analysis of dielectric spectra in terms of complex conductivity was carried out. It was shown that all the dielectric spectra may be approximated by the Havriliak and Negami ratio.

$$\sigma^*(\omega) = -\frac{\sigma}{\left(1+(i\omega\tau_0)^{1-\alpha}\right)^{\beta}}$$

It was found that the parameter β differs significantly from 1 only for MLLC with the lysozyme concentration of 0.3 mM. The parameter α ranges from 0.7 to 0.9 in dependence on lysozyme concentration, presence of ML and action of the magnetic field. It was observed that the introduction of the ML into MLLC leads to a decrease of the parameter α. The magnetic field insignificantly reduces the magnitude of the parameter α only in solutions without magnetic fluid. The samples with the lysozyme concentration 0.3 mM had the maximum value of the parameter α. The relaxation time τ of the investigated MLLCs was within $2\cdot10^{-5}$-$3\cdot10^{-4}$ s. Addition of ML into MLLC, except for solutions of 0.7 mM of lysozyme, increased the τ value. Magnetic field resulted in a decrease of τ in the samples without ML. It was shown that the relaxation process is caused by exchange of electrons between ions of MLLC and electrodes. The Havriliak and Negami ratio may be one of the solutions of the continuity equation, taking into account Schottky emission through the near-electrode barrier. Except for MLLC with lysozyme concentration of 0.3 mM, the magnetic field leads to a decrease in the conductivity. The assumption is made that the reason of the decreasing conductivity is formation of MLLC and, as consequence of this decreasing, the mobility of charge carriers decreases. When ML is presented, MLLC is realized even at the lysozyme concentration 0.7 mM.

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Dielectric spectroscopy of Sodium Ferrite prepared by Sol-Gel method

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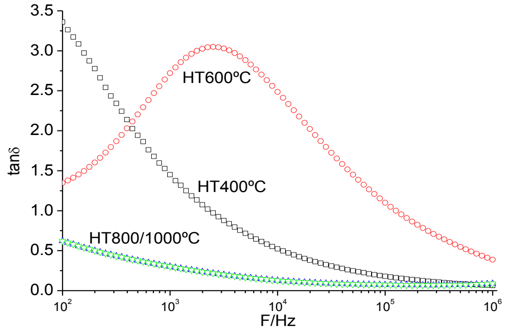
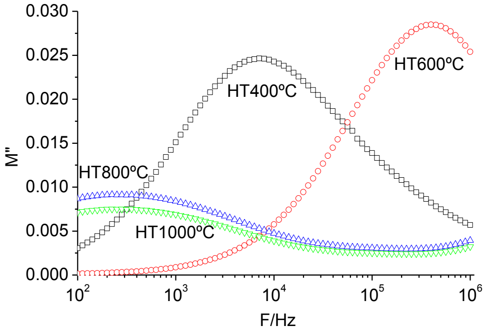
Applications of mixed metallic oxides, such as the alkali metal ferrites have attracted significant attention due to their potential applications in high capacity batteries, electrochromic displays, waste-water cleaning, low magnetization ferrofluids, intercalation electrodes in rechargeable batteries and as strong oxidizing agents [1-3]. Sodium ferrite is a potential candidate for these applications. It was firstly studied in the 1950s [4], but until nowadays this system has not yet been experimentally studied in detail.

In the present work, sodium ferrite powders were obtained by Sol-Gel. The fine particles were pressed into pellets and then treated at temperatures between 600 and 1100 ºC. The structure was studied by XRD and Raman spectroscopy and the morphology by SEM microscopy. The dielectric properties were analysed in the frequency range between 10^2-10^6 Hz, in function of temperature (200–400 K), and then in the microwave region. For treatment temperatures below 800 ºC, $NaFeO_2$ phase was observed and for higher temperature $Na_3Fe_5O_9$ crystal phase becames predominant. The dielectric constant value was improved with the growth of the $Na_3Fe_5O_9$ phase and a dielectric relaxation, which moves to higher frequencies with treatment temperature was also observed. All the data was related with the microstructure.





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Dielectric spectroscopy of the lacunar $Ca_2MnO_{4-\delta}$ system

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The frequency and temperature dependence of ac electrical conductivity (σ_{ac}), dielectric constant (ε'), dielectric loss (ε'') and loss tangent ($tan\delta$) in the temperature range 280 - 360 K and frequency range 40 Hz - 2 MHz have been made for $Ca_2MnO_{4-\delta}$ system (δ=0.00, 0.15, 0.20 and 0.30). The powder samples were used in the form of compressed pellets. The frequency dependence of σ_{ac} follows the universal law with the relation, $\sigma_{ac} = \sigma_{dc} + A\omega^S$, where *S* is the frequency exponent. The parameter *S* was found to decrease with increasing temperature. A comparison between values of this exponent with those numerically calculated from different conduction models reveals that Correlated Barrier Hopping (CBH) model is the proper model to describe the *ac* conduction mechanism. The maximum barrier height (W_m) and the minimum hopping distance (R_{min}) were calculated. It was verified that both dielectric constant and loss increased with the increase in temperature and decreased with the increase in frequency.

Temperature dependent dielectric anomalies in Te(IV) doped Calcium Copper Titanate ($CaCu_3Ti_{3.8}Te_{0.2}O_{12}$)

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Pervoskite structured dielectric ceramic $CaCu_3Ti_{4-x}Te_xO_{12}$ (CCTTO) was fabricated using the powder obtained from conventional solid state synthetic route. The room temperature XRD pattern for the x=0.2 modified sample was confirmed to possess double pervoskite structure with cubic space group I*m*-3 by Rietveld refinement. The scanning electron microscopy established the average grain size to be close to 15-20 µm. Oxidation states of atmos and the stoichiometry of elements are confirmed by XPS data analysis. The dielectric properties of these ceramics were studied over wide frequency range (40Hz-110MHz) at room temperature. The temperature response of dielectric properties and electrical conduction for $CaCu_3Ti_{3.8}Te_{0.2}O_{12}$ ceramics was monitored in the 25°C to 550°C temperature range. Three prominent peaks (150, 278 and 378°C) were observed in the dielectric variation with temperature at various frequencies. Around 278°C The dielectric constant (ε_r) is as high as $4X10^4$ though the room temperature value is about 700. Disappearance of polaronic stacking faults, due to substitution of Ti^{4+} by Te^{4+} in Calcium Copper Titanate ($CaCu_3Ti_4O_{12}$) matrix, is believed to be the origin of the low dielectric constant. Dielectric spectra for the samples sintered in N_2 atmosphere shows the peak arround the 278˚C retained. The unexpected dielectric behaviors observed for $CaCu_3Ti_{3.8}Te_{0.2}O_{12}$ ceramic samples sintered in both ambiant air and N_2 (reducing) atmosphere at higher temperatures are corelated with high temperrature XRD data , which indicates a lattice parameter change arround 278˚C.

Electrophysical properties of ionic-conductive polymer systems on the base of an aliphatic epoxy oligomer and $LiClo_4$

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Nowadays an urgent need in developing and creation of ion-conductive solid electroactive polymers for modern instrument engineering exists. For example, it is known that the use of such compounds as oligooxyethylene offers possible existence of ionic conductivity in dry conditions, which extends the range of operating conditions and, accordingly, the scope of their practical use. The presence of oxygen atoms with significant electro-donor energy in polyethylene oxide chains promotes the formation of bonds with cations. At the same time, an aliphatic epoxy oligomer (DEG) contains ether oxygen, i.e. its chemical structure is similar to the structure of polyethylene oxide (PEO). That enables to take it as a basic product for creation of ion-conductive (Li^+ by using $LiClO_4$) polymer materials [1].

In such materials cation transport from one "oxygen-area" to another under the impact of the external electrical field depends on segmental mobility of polymer chains, which is in turn a function of the glass transition temperature of the polymer matrix [5]. Such features of chemical structure and charge transport mechanisms in the proposed materials allow to obtain the high temperature ion-conductive materials.

Epoxy oligomer DEG and lithium perchlorate salt $LiClO_4$ were used for synthesis of ion-conductive epoxy polymer material. $LiClO_4$ content was varied from 0 to 20 phr, DEG content cases was 90 phr for all. Polyethylene polyamine hardener (PEPA) was used as a curing agent. The content of PEPA was 10 phr for all cases.Thermal characteristics as well as the impact of the $LiClO_4$ content on electrical and dielectric properties of the epoxy polymer systems obtained were studied. The conductivity multiplies more than two orders of magnitude with increasing the content of $LiClO_4$ and reaches maximum value σ '= 1,1 10^{-3} at T = 200 ^oC. The values of permittivity ε ' tend to 10^6. It is shown that the increase of lithium perchlorate content, on the one hand, leads to an increase in σ 'and ε' since $LiClO_4$ is a source of cations Li^+ and, on the other hand, it affects the hardening process of epoxy matrix (DEG) as evidenced from a significant increase in the glass transition temperature with increasing of $LiClO_4$ concentration in the reaction mixture.

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Application of imidazolium ionic liquids as conductivity and processing enhancers in the nitrile rubber composites

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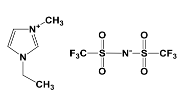
According to a definition of ionic liquids (ILs), organic molten salts composed entirely of ions that melt at or below 100 ºC are categorized as ILs.[10] The current interest in ILs is mainly driven by their negligible volatility, low combustibility, high ionic conductivity and chemical stability. Recently it has been reported that ILs may serve multiple functions in the preparation of elastomer composites. Their potential applications in elastomer composites include the use as processing aids for the melt processing of rubber/filler composites,[11] plasticizers that reduce the glass transition temperature of an elastomer matrix,[12] interfacial modifiers (compatibilizers, coupling agents for improving filler dispersion),[13] cure accelerators[14] or antistatic additives.[15] The high ionic conductivity enables ILs to act as ion reservoirs to increase the ionic conductivity of polymer composites.[16] However, due to their ~~the~~ complex effects on the polymer properties, almost each polymer system containing ILs should be individually examined. In this work hydrophilic and hydrophobic imidazolium ionic liquids in different concentration were applied in acrylonitryle-butadiene rubber (NBR) and carboxylated nitrile butadiene rubber (XNBR) to obtain composites which are characterized by good mechanical properties and improved ionic conductivity. The effects of anion type (hydrophilic thiocyante [SCN] and hydrophobic bis(trifluoromethylsulfonyl)imide [TFSI]) of imidazolium ionic liquid and the impacts of the length of alkyl chain of 1-n-alkyl-3-methylimidazolium [Cn-MIM][TFSI] on the conductivity, mechanical and morphological properties of nitrile rubber compounds were analyzed.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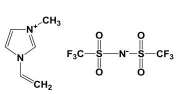
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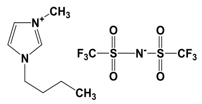
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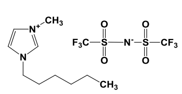
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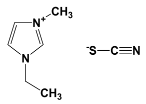
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Analysis of the conductivity of conjugated polymer/fullerene based blends by dielectric spectroscopy

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Poly alkyl thiophenes, including poly(3-hexylthiophene) (P3HT), show some of the highest carrier mobilities among organic electronic polymers. Studies of P3HT reveal a tendency to selforganization by forming a semicrystalline domain embedded in an amorphous matrix. Blends of P3HT with [6,6]-phenyl C71 butyric acid methyl ester) (PCBM) are widely used as active layer in plastic solar cells. In semiconducting polymers, the a.c. electric response is a superposition of any possible dipolar relaxation and the motion of the charge carriers. Understanding the role of each of these contributions becomes very important, since the frequency dependence of the conductivity has implications in the performance of devices such as field effect transistors.

In this work we have investigated the complex conductivity of pure P3HT and 50/50 P3HT/PCBM blend. Blending increases the DC conductivity (Fig.1). We will present results of the analysis in terms of the variable range hoping model for the pure polymer and for the blend. The role of the crystallinity of P3HT in both cases will be also discussed.

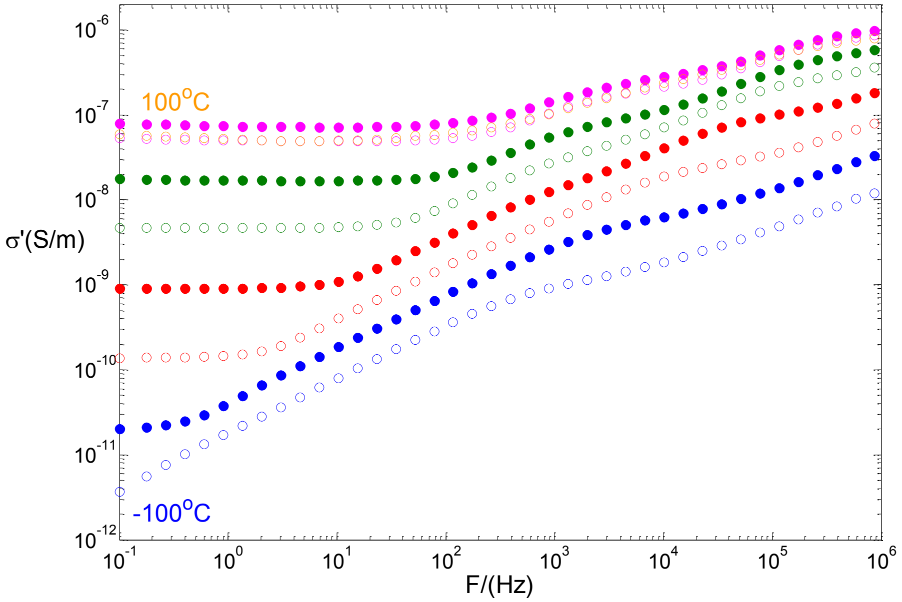

Fig. 1. Real Part of the complex Conductivity as a function of the frequency and temperature (in 25 °C steps) for P3HT prepared from solution cast.

The role of size and charge delocalization in dissociation and charge transport in solvents of low polarity

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The high lattice enthalpies of salts make them insoluble in most solvents. In addition, even when they are soluble, they only partly dissociate in nonpolar solvents because of the high free energy of dissociation. For liquids of low polarity ($\varepsilon_S < 11$) and for inorganic salts such as NaCl, KCl, and KNO_3, the energy of dissociation is many times the thermal energy k_BT. One consequence of the low degree of dissociation is that dispersions in nonpolar solvents cannot be stabilized by electrostatic or electrosteric repulsion.

From a thermodynamic viewpoint, charging in a liquid is controlled by the Bjerrum length, λB. In liquids of low polarity such as toluene or even THF, the Bjerrum length is 20.4 and 7.4 nm, respectively. Ion dissociation in such solvents is limited unless the ion size approaches the “escape distance” set by λ_B. Hence extensive research was made on increasing the size and bulkiness of molecular anions that led to a new class of compounds known as weakly coordinating anions (WCAs).

In addition to the systematic variation of the anion or the cation size, another approach emphasized the effect of delocalization of the anion charge. It is thought that the spreading of the anion charge to a larger area is responsible for the weaker coordination.

Electrophysical properties of solid polymer electrolytes based on epoxy oligomer and lithium perchlorate salt

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Ion-conductive epoxy polymer materials were synthesized using an epoxy oligomer, namely diglycide ester polyethylene glycol DEG, and lithium perchlorate salt $LiClO_4$ that was firstly dissolved in oligomer DEG. DEG-$LiClO_4$ solutions were prepared with content from 0 to 20 phr on 100 phr of DEG. Polyethylene polyamine hardener (10 phr) as a curing agent of DEG was used. The effect of $LiClO_4$ content on electrophysical properties of epoxy polymers has been studied by Differential Scanning Calorimetry (DSC), the Broadband Dielectric Spectroscopy (BDS) and Thermogravimetric Analysis (TGA). Synthesis of epoxy polymer in the presence of lithium perchlorate made possible to obtain an ion-conductive polymeric materials with a high level of ionic conductivity ($\sim 10^{-3}$ S/cm) and permittivity ($6 \cdot 10^5$) at elevated temperature (200 °C). According to TGA results weight loss at 200 is negligible, that indicates its usability at elevated temperatures. However, the conductivity at 100 °C is two orders of magnitude lower than at 200 °C. Increase in amount of injected $LiClO_4$ in reactive mixture from 0 to 20 phr leads to linearly increase of glass transition temperature of the synthesized polymers from -10 to 25 °C. It is shown that salt affects on structure of the epoxy DEG. Lithium ions form coordination bonds with DEG macromolecules that reduces molecular mobility of the polymer chains.

Dielectric relaxation in (acetamide+ lithium bromide/ nitrate) melts

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Recently, room temperature ionic liquids have attracted the attention of the scientific community for fascinating physics and application in the fields of catalysis, electrochemistry and material chemistry. Deep eutectics display close resemblance to room temperature ionic liquids in solubility and with wide range of liquidous state. These are mixtures of ionic and non-ionic solid compounds where melting temperature much lower than the pure compounds and offer suitable reaction media for chemical industry. It has been reported that aliphatic amides, when mixed with inorganic salts, yield liquids near room temperature with outstanding affinity to supercool. Acetamide is one of the most commonly used amides due to its exceptional solvating properties. These molten mixtures are characterized by glass transition temperatures (T_g) $\sim$ 190 K < T_g < 250 K range. Introduction of suitable cation and/or anion in these melts provide longer-ranged interactions (proportional to r^{-1}, r^{-2} and r^{-3}). This supercooling phenomenon and the associated application in chemical industry have encouraged the research for proper understanding of medium structural and transport properties.

In the present study, we have investigated the temperature dependent dielectric spectroscopy (BDS) of molten mixtures of acetamide with lithium nitrate and bromide with general formula 0.78 CH_3CONH_2 + 0.22[f*LiBr + (1-f)*$LiNO_3$], where fractions of the anions have been varied in order to study both the mixed anion effects. The data has been presented in modulus formalism to understand the conductivity relaxation phenomena. BDS technique allows the direct observation of the conductivity relaxation process which originates from the translational motion of ions. The conductivity relaxation follows Vogel-Fulcher-Tammann relation (VFT) and T_g increases on increasing f. Below T_g secondary processes (β and γ) were observed which are governed by Arrhenius behavior.

Index of Participants