PREFACE

Welcome to the 20th European Symposium on Polymer Spectroscopy (ESOPS20).
The European Symposia on Polymer Spectroscopy, which were founded in Cologne in 1969, give opportunity to share knowledge of current research and development on the spectroscopic characterization and analysis of polymer systems. The ESOPS 20 symposium is going to address both interesting highlighted polymer systems probed by selected spectroscopic techniques as well as interesting highlighted spectroscopic methods applied to selected polymer systems. Thus, ESOPS 20 aims at bringing together not only specialized analytical and polymer scientists in academy and industry but also those aiming to be inspired by recent developments.

Topics

- Polymers/Copolymers/Blends
- Nanoparticles/Colloids/Fibres in Polymers
- Thin Films/Interfaces
- Biopolymers/Biomaterials
- Carbon Allotrops
- Polymer Processing
- Polymer Electronics
- Handheld Instruments/Miniaturization

Methods

- Methods FTIR/RAMAN/NIR/Terahertz
- NMR/EPR
- UV-VIS/Fluorescence/Circular Dichroism
- Spectroscopic Imaging
- Mass Spectroscopy
- XPS
- Dielectric Spectroscopy

ORGANIZATION

Conference Chairpersons
Dieter Fischer
Martin Müller
Klaus-Jochen Eichhorn
(all IPF Dresden, Germany)

Organizing Institute
Leibniz-Institut für Polymerforschung Dresden e. V.
(Leibniz Institute of Polymer Research Dresden - IPF)

International Advisory Board
Mischa Bonn, Mainz, Germany
Klaus-Jochen Eichhorn, Dresden, Germany
Vasilis Gregoriou, Athens, Greece
Sergei Kazarian, London, United Kingdom
Yukihiro Ozaki, Nishinomiya, Japan
Christian Pellerin, Montreal, Canada
Monika Schönhoff, Münster, Germany
Jiří Spěváček, Prague, Czech Republic

Local Organizing Committee:
Dieter Fischer Martin Müller Klaus-Jochen Eichhorn Kerstin Wustrack Juliane Bendzko

The organizers gratefully acknowledge the generous financial support by

DFG Deutsche Forschungsgemeinschaft

GENERAL INFORMATION

Venue and registration/conference office
Dorint Hotel Dresden
Grunaer Str. 14, 01069 Dresden
Phone: +49 351 4915-0 www.hotel-dresden.dorint.com

The conference office is located in the first floor.
Phone: 0160/97216924

Opening hours:
Sun, Sept. 11, 2016: from 17:00 to 20:00
Mon, Sept. 12 from 7:30 throughout all sessions
Tue, Sept. 13 to Thu, Sept. 14, 2016: from 8:00 throughout all sessions

Contact
Leibniz-Institut für Polymerforschung Dresden e. V.
Hohe Str. 6, 01069 Dresden
Phone: +49 351 4658-282 Fax: +49 351 4658-214

Technical Organization:
Kerstin Wustrack: wustrack@ipfdd.de
Juliane Bendzko: bendzko@ipfdd.de

Scientific Affairs:
Klaus-Jochen Eichhorn: kjeich@ipfdd.de
Dieter Fischer: fisch@ipfdd.de
Martin Müller: mamuller@ipfdd.de

Website: www.ipfdd.de/ESOPS20

Coffee and lunch breaks
Drinks, snacks and a lunch buffet are included. Drinks and snacks during the short breaks are served in the poster and industrial exhibitions neighbored to the lecture hall; the lunch is served in the banquet area opposite to the conference area (first floor, left of the staircase).

Internet
WLAN/WiFi access is possible for participants during the meeting and is free of charge.
Name of the wireless network: **dorint**
Password: **dresden2016**
In addition, you may use an internet terminal at the conference office.

Ticket for public transportation
A ticket for tram and buses (not for S-Bahn) within Dresden, valid from Sept. 11 to 14, 2016, will be handed over to the participants along with their conference materials. The ticket must be stamped in the machine inside the bus or tram when you use it for the first time.
We appreciate to get back tickets you do not use.

Book of abstracts
The book of abstract (hard copy) includes the short abstracts of all papers and posters and will be published with the ISBN number 978-3-9816007-4-2.

PRESENTATIONS

Oral presentations
To upload your oral presentation, please contact one of our student helpers in the session hall. You should do that in advance, at the latest in the break before your presentation.

Posters
Posters will be up for the whole duration of the symposium.
Please fix your poster as early as possible after your check-in and remove it by 14:30 on Wednesday.

AWARDS

Awards will be handed over for the two best posters.
The awards are sponsored by Wiley VCH Macromolecular Journals.

EXHIBITION

The following companies are present as exhibitors in the hall *Lohengrin*:

PHYSICAL ELECTRONICS GMBH
BRUKER
WITec focus innovations
neaspec see the nanoworld

FURTHER SPONSORS

HORIBA Scientific
DE G DE GRUYTER
Macromolecular Journals
Springer ANALYTICAL & BIOANALYTICAL CHEMISTRY

SOCIAL EVENTS

- **Welcome Mixer**
  Sunday, September 11, 2016, 19:00 to 21:00
  Dorint Hotel Dresden (symposium venue)
  You may enjoy some snacks and drinks while having the first talks to your colleagues.

- **Sightseeing and Conference Dinner**
  Tuesday, September 13, 2016, 16:30 to 22:30
  Guided tour of the Königstein Fortress (Festung Königstein) in the heart of Saxon Switzerland and subsequent dinner in the Restaurant “In den Kasematten” located in the fortress (bus shuttle available).
  Meeting time: 16:20 (Departure: 16:30)
  Meeting point: Lobby of the hotel

No special dressing code. Registration is required (no extra charge for active participants and officially registered accompanying persons) – make sure you have the voucher in your conference bag and bring it along.

Program

Monday, September 12		
08:00	Registration	
09:00	Opening	
09:10	IL1 - Christian Pellerin	Orientation in polymers studied by vibrational spectroscopy
09:50	CL1 - Marie Richard-Lacroix	Raman spectroscopy investigation of orientation and disentanglement in single electrospun fibers
10:15	CL2 - Alessandra Vichi	Depth profiling of synthetic polymers of interest for cultural heritage with ATR-FTIR spectroscopic imaging
10:40	CL3 - Andreas Furchner	Amide-water hydrogen-bond interactions in polymer brushes at the solid-liquid Interface
11:05	*Coffee break/Exhibition*	
11:35	IL2 - Mischa Bonn	A molecular view on composite materials
12:15	CL4 - Vincent Ball	Spectroscopic characterization of "polydopmaine" formation in solution and on surfaces as a function of the used oxidant: Towards a structure-property relationship
12:40	CL5 - Tibor Nagy	Ionization of non-polar polyizobutylene derivatives by DART and ESI ion sources
13:05	*Lunch/Exhibition*	
14:00	IL3 - Polycarpos Pissis	Dielectric spectroscopy on nanostructured polymer-based materials
14:40	CL6 - Ulrich Scheler	Solid-state NMR in hybrid materials
15:05	CL7 - Thomas E. Müller	Dynamics of polyethercarbonate polyols in comparison to polyether polyols
15:30	CL8 - Uwe Lappan	Segmental dynamics of poly(acrylic acid) in polyelectrolyte complex coacervates studied by spin-label EPR spectroscopy
15:55	*Coffee break/Exhibition*	
16:25	IL4 - Miriam Unger	Nanoscale infrared spectroscopy and imaging of polymeric fibres and thin films
17:05	CL9 - Timur Shaykhutdinov	IR nanopolarimetry on biaxially anisotropic supramolecular structures
17:30	CL10 - Ute Schmidt	The power of confocal Raman-AFM imaging in polymer research
17:55 -18:20	CL11 - Andreas Huber	Nano-FTIR-quantitiative infrared imaging and spectroscopy at 10nm spatial resolution
18:30 -20:30	Poster Discussion/Exhibition with beer and snacks	

Program

Tuesday, September 13		
08:00	Registration	
09:00	IL5 - Harumi Sato	THz and low-frequency Raman spectroscopy of polymers
09:40	CL12 - Ulrich Künzelmann	Novel micro-structured silicon single reflection elements: Their design, fabrication and application for in situ ATR-FTIR investigations of the influence of ammonia on the structure of PEDOT/PSS composite layers
10:05	CL13 - Sascha Morlock	Chemically sensitive SEC detection with FTIR and QCL-IR spectroscopy
10:30	CL14 - Severine Bellayer	Chemical imaging of filled polymers with wavelength dispersive spectrometers
10:55	*Coffee break/Exhibition*	
11:25	IL6 - Martin Kraft	On-line Raman spectroscopy for polymer process analysis
12:05	CL15 - Gabriele C. Eder	Fluorescence spectroscopy and imaging on aged polymeric PV encapsulantes
12:30	CL16 - Zuzana Moravkova	In-situ Raman spectroscopy during electrochemical oxidation of aniline
12:55	*Lunch/Exhibition*	
14:00	CL17 - Sebastian Primpke	Automated analysis of µFTIR imaging data for microplastic samples
14:25	CL18 - Andrea Käppler	Investigation of microplastics in marine samples by FTIR and Raman microspectroscopy
14:50	CL19 - Barbara M. Scholz-Böttcher	Pyrolysis gas chromatography mass spectrometry (Py-GCMS) for simultaneous trace analysis of nine common plastics in environmental samples
15:15 -15:40	CL20 - Robin Lenz	Microplastic analysis below 100 µm: Raman microspectrometry to correct visual countings
16:30	Sightseeing and Dinner: Bus shuttle-start 16:30, Return 22:30 (Königstein), arrival to Dresden 23:15	

Wednesday, September 14		
08:00	Registration	
09:00	IL7 - Monika Schönhoff	Diffusion NMR in polymer systems
09:40	CL21 - Jiri Spevacek	NMR and FTIR study of thermoresponsive block copolymers in aqueous solution
10:05	CL22 - Marcin Pastorczak	Initial stages of coil-to-globule transitions of stimuli-responsive polymers in water
10:30	CL23 - Peter Werner	New process spectroscopic approaches for the coil-to-globule/ globule-to-coil transformation in a concentrated PNIPAM suspension
10:55	*Coffee break/Exhibition*	
11:25	IL8 - Heinz W. Siesler	Vibrational spectroscopy with handheld instruments: Instrumentation, applications and future aspects
12:05	CL24 - Elena Sagitova	Low-frequency Raman spectra of propylene copolymers and polymorphs of polypropylene
12:30	CL25 - Enrico Pigorsch	FTIR spectroscopic and Raman imaging investigations of cellulose graft copolymers
12:55	CL26 - Frank Windrich	Monitoring the cure process of thin films polymers for microelectronic packaging applications by rapid scan in-situ FTIR spectroscopy
13:20	Closing session and Awards	
13:35	*Lunch and Farewell*	

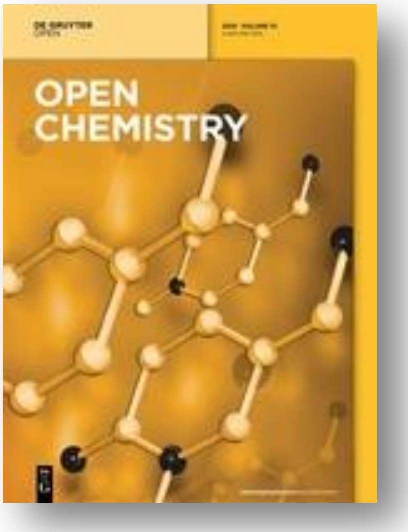
ESOPS20

Poster list

Status: as of August 19, 2016

Nr	Title	Authors
1	Synthesis and characterization of polymeric ionic liquids by AB step growth polymerization	M. Suckow, M. Roy, K. Sahre, L. Häußler, N. Singha, B. Voit, **Frank Böhme**
2	Hydrolytic degradation of biodegradable films based on poly(lactic acid)/poly(butylene succinate)/fatty acid blends	N. Ratsameetammajak, R. Molloy, **Dieter Baurecht**, R. Somsunan
3	Effect of additives on the crystallization behavior of poly(hydroxybutyrate-co-hydroxyhexanoate)	**Shuhei Suzuki**, H. Sashiwa, H. Sato
4	NMR studies to probe the interaction between thermoresponsive polymers and model drugs	**Frank Termühlen**, Monika S.
5	Phase separation behaviour of poly(ethylene glycol) and poly(propylene glycol) studied by ATR-FTIR spectroscopy	**Hideyuki Shinzawa**, J. Mizukado, S. G. Kazarian
6	Polarized ATR-IR spectroscopy investigation of supramolecular complexes of block copolymers into ultra-thin films	**Marie Richard-Lacroix**, K. Borozenko, C. G. Bazuin, Ch. Pellerin
7	Polymers as templates for Au and Au@Ag bimetallic nanorods: Investigation by surface enhanced Raman spectroscopy (SERS)	**Dieter Fischer**, R. Contreras-Caceres, C. Dawson, P. Uhlmann
8	Temperature-dependent FT-IR and Raman imaging spectroscopy investigation of phase separation in the polymer blend PHB/PLA	**Dieter Fischer**, M. Unger, H. Sato, Y. Ozaki, H. W. Siesler
9	Identification of microplastics in marine samples by Raman microspectroscopy	**Dieter Fischer**, A. Käppler, J. Muche , S. Oberbeckmann, M. Labrenz, K.-J. Eichhorn, B. Voit
10	Turbidimetry and fluorescence study of effect of hyaluronan addition to cationic micellar solution	**Tereza Pilgrová**, P. Holínková, M. Pekař
11	Fluorescence anisotropy study of microstructural changes of hyaluronan-cetyltrimethylammonium bromide hydrogel	**Petra Holínková**, F. Mravec, M. Pekař
12	Functionalization of SEIRA substrates towards biosensing	F. Rösicke, Ch. Kratz, T. Shaykhutdinov, J. Rappich, **Karsten Hinrichs**
13	Polymer and hybrid photonic crystals	**Giovanni Manfredi**, P. Lova, C. Bastianini, P. Giusto, D. Comoretto
14	in-situ-ATR-FTIR Spectroscopy at polypeptide and polyelectrolyte based coatings	**Martin Müller**, B. Urban, D. Vehlow, B. Torger, M. L. Möller
15	FTIR detection of drug release from polyelectrolyte complex coatings	**David Vehlow**, B. Urban, M. Möller, B. Torger, M. Müller
16	Characterization of thin bioinspired polydopamine films by in-situ-ATR-FTIR spectroscopy	D. Vehlow, B. Urban, **Martin Müller**
17	Nanostructured biocomposites based FLAX Fibers	**Rabiaa Hajji**
18	Singlet oxygen dynamics and bactericidal effect of photofunctional polymer	**Kang-Kyun Wang**, Y.-R. Kim
19	Appropriate operating conditions of cyclones for HDPE drying process	S. A. Razavi Alavi, **Ebrahim Nemati Lay**, S. K. Afzali
20	In-situ FT-IR study of the reaction kinetics of divinyl siloxane bis-benzocyclobutene in solid state and modeling of the polymerization process	F. Windrich, **Mikhail Malanin**, K.-J. Eichhhorn, B. Voit

21	Sulfur-overrich polythiophenes for BHJ solar cells	**Elisabetta Salatelli**, F. Di Maria, M. Lanzi, M. Marinelli, L. Zuppiroli
22	Raman structural characterization of "neck region" for films of single-crystal mats of ultrahigh molecular weight linear polyethylene	K. A. Prokhorov, **Elena A. Sagitova**, G. Yu. Nikolaeva, P. P. Pashinin, S. N. Chvalun
23	Adhesion control in semiconductor processing via Fourier transform infrared spectroscopy	**Marko Omazic**, G. Oreski, M. Pinczolits, M. Erceg, G. Pinter
24	Stretch-induced crystalline phase transition of poly(butylene succinate) by Terahertz spectroscopy	**Seika Tatsuoka**, Y. Ozaki, H. Hoshina, H. Sato
25	Nano-scale morphological analyses of PEG-based polyacrylate gel	**Bing Wu**, M. Tian, J. Xu, J. Li, D. Brougham, V. M. Litvinov
26	Investigation of rubber network structure by using low-field nuclear magnetic resonance spectroscopy	**Beatriz Basterra-Beroiz**, R. Rommel, F. Kayser, S. Westermann, J. L. Valentín, G. Heinrich
27	NMR study of thermoresponsive polyoxazoline homopolymers and copolymers in aqueous solution	**Rafał Konefał**, J. Spevacek, P. Černoch
28	L-NMR used for the characterization of polymers	**Monique F. H. Ensinck**, H. Linssen
29	FCS Nanorheology of biopolymeric hydrogels - a novel approach to study passive rheology of hydrogels	**Jakub Mondek**, M. Pekař
30	Mapping the nanostructural heterogeneity of network polymers using AFM-IR and nano-thermal analysis	**Suzanne Morsch**, S. Gibbon, S.t Lyon
31	Characterization of poly (ε-caprolactone) by using terahertz imaging	**Chihiro Funaki**, T. Toyouchi, H. Hoshina, Y. Ozaki, H. Sato
32	IR/NIR spectroscopic birefringence imaging of polymeric spherulite	**Yuta Hikima**, R. Mitsui, M. Ohshima
33	Matrix-assisted laser ionization/Desorption mass spectrometric study of the 4,4`-diphenyl-methane-diisocyanate and polyol uncatalyzed reactions	**Borbála Antal**, T. Nagy, A. Dékány-Adamoczky, J. Karger-Kocsis, M. Zsuga, S. Kéki
34	Easy access to the characteristic ratio of polymers using ion-mobility mass spectrometry	**Shinsuke Kokubo**, Ph. Vana
35	XPS depth profiling by cluster ion sources for characterization of polymers, organic and composite materials	Andrey Lyapin, **Stefanie Zauzig**



Open Chemistry
formerly Central European Journal of Chemistry

IMPACT FACTOR 2015: 1.207
5-year IMPACT FACTOR: 1.272

EDITOR-IN-CHIEF:
Miguel Yus,
University of Alicante, Spain

MANAGING EDITOR:
Bozena Bittner-Wróbel
Bozena.BittnerWrobel@degruyteropen.com

Open Chemistry is a peer-reviewed open access journal that provides an international medium for the publication of research results and reviews in all areas of Chemistry. We value and promote every single paper and assure the global circulation and worldwide visibility of your research work by the implementation of our attractive and efficient promotional techniques.

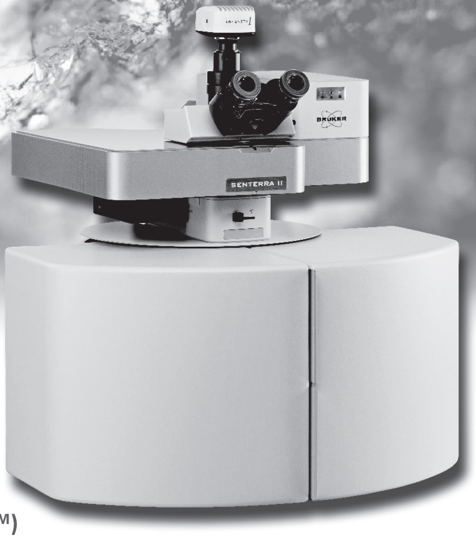
As an Author of Open Chemistry You can have a range of benefits:
- fast and constructive peer review,
- convenient, web-based submission and manuscript tracking system – Editorial Manager,
- high-quality electronic publication technology,
- you retain the copyright to your papers.

In order to sustain the production of our fully-refereed open access journal, each article accepted for publication in Open Chemistry is subject to an Article Processing Charge of €1000. However, for the conference participants we offer high discounts in APC to publish in recently launched Topical Issue on Polymer Science.

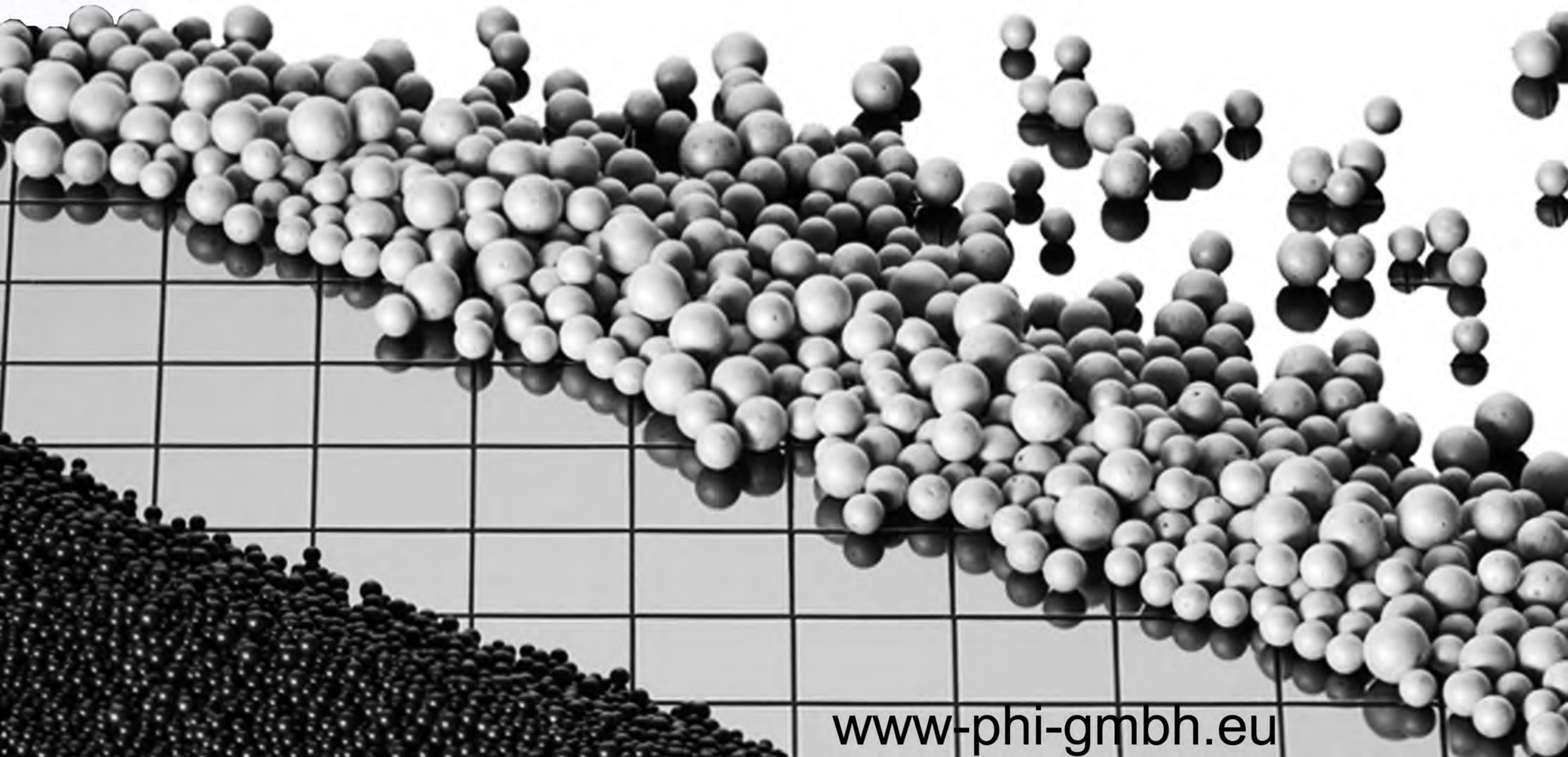
Additional information related to editorial policy, paper writing guide, reference citation, scope of journal can be found at http://www.degruyter.com/view/j/chem.

HOW TO SUBMIT:
www.editorialmanager.com/openchem

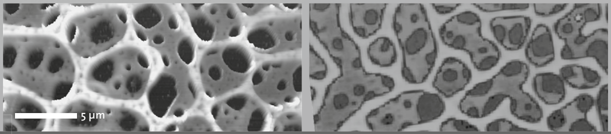
www.openchemistry.com

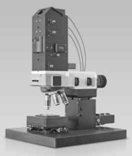


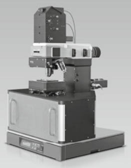

ANASYS
INSTRUMENTS
nanoIR2



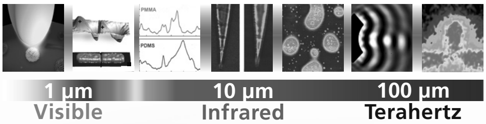

WITec
focus innovations


5 µm





nea!spec see the nanoworld



Introducing nano-FTIR

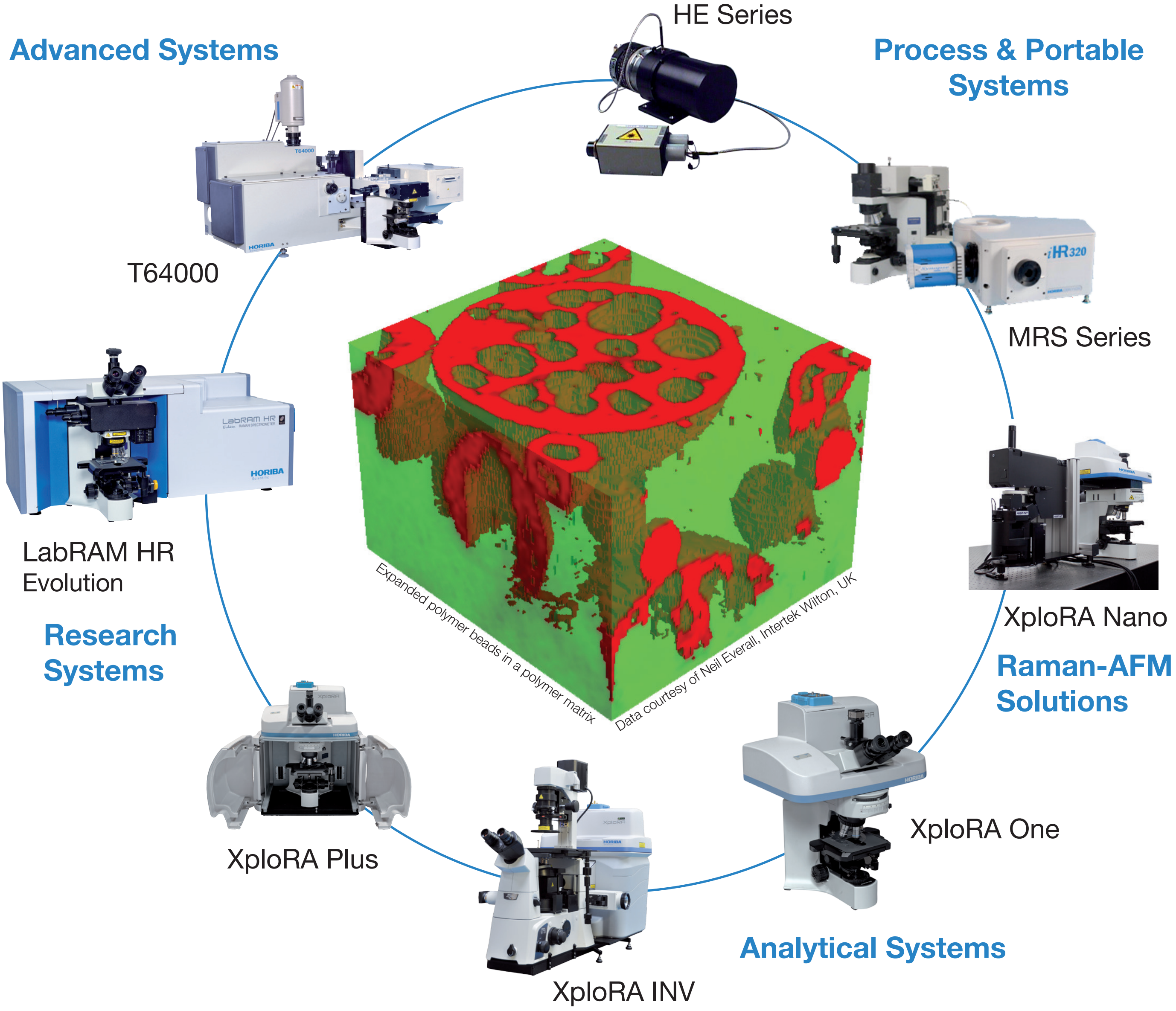
Imaging & Spectroscopy at 10 nm Spatial Resolution

- › Chemical identification @10nm best in class spatial resolution
- › Highest imaging & spectroscopy speed without compromise on quality
- › nano-FTIR directly correlates with conventional FTIR spectra
- › Suited for all material classes, organic & inorganic samples
- › Easy-to-use with guaranteed performance by intelligent software design
- › Extendable to VIS, NIR, MIR & THz applications by modular system design

Visit us at our booth

neaspec GmbH
Bunsenstrasse 5
82152 Martinsried (Munich)
Germany

phone: +49 89 4524 206 - 0
fax: +49 89 4524 206 - 99
mail: info@neaspec.com
web: www.neaspec.com


Advanced Systems
HE Series
Process & Portable Systems
T64000
MRS Series
LabRAM HR Evolution
Research Systems
XploRA Nano
Raman-AFM Solutions
XploRA Plus
XploRA One
XploRA INV
Analytical Systems
Expanded polymer beads in a polymer matrix
Data courtesy of Neil Everall, Intertek Wilton, UK

Abstracts of the invited lectures

IL1

ORIENTATION IN POLYMERS STUDIED BY VIBRATIONAL SPECTROSCOPY

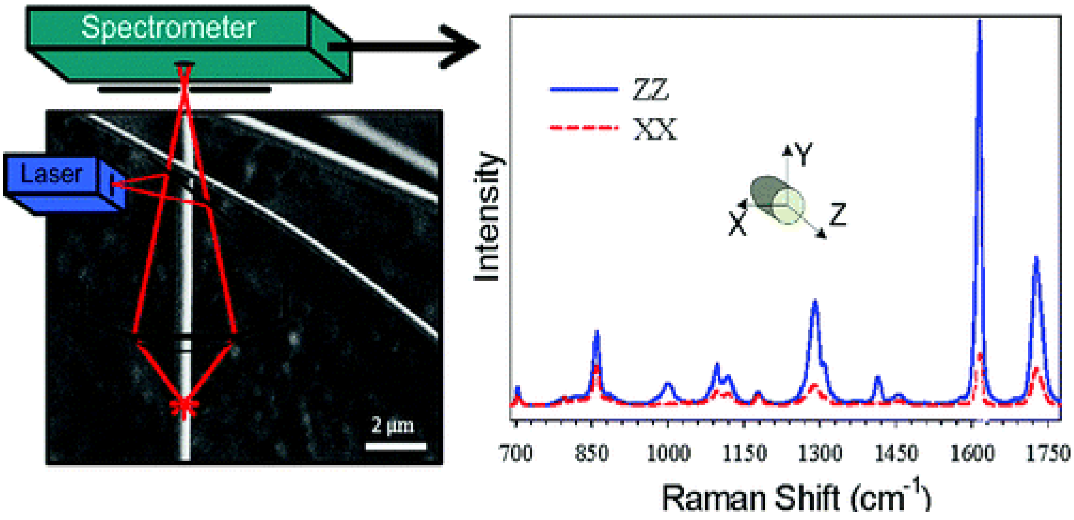
Christian Pellerin
University of Montreal, Canada

c.pellerin@umontreal.ca

The properties and function of materials depend on their molecular structure and orientation. Our group develops and applies polarized infrared and Raman spectroscopy to gain insight into the structure of soft materials such as electrospun polymers, ultrathin films, molecular glasses and azomaterials. In this presentation, we will highlight our recent work on two classes of materials.

Electrospun fibers show unusual properties that are poorly understood, such as an exponential increase of their modulus with a decreasing diameter. We used Raman spectroscopy at the single fiber level to show that this increase in modulus directly correlates with molecular orientation. We also probed the impact of the collection method on orientation development. Our results on polystyrene fibers further revealed a partial disentanglement that also correlates with fiber diameter. This work required the development of a new method to quantify orientation that circumvents some difficulties of the standard approach.

Azobenzene-containing materials can orient and even flow on a macroscopic scale when irradiated well below their glass transition temperature (Tg). We have used time-resolved polarization modulation infrared spectroscopy to probe the molecular orientation under polarized irradiation of supramolecular complexes of polymers with azo dyes. We also demonstrated that the photoinduced creation of free volume in azomaterials is heterogeneous at the submolecular level that helps to understand the puzzling phenomenon of photoinduced macroscopic flow upon illumination far below Tg.



Raman spectroscopy of individual electrospun nanofiber

IL2

A MOLECULAR VIEW ON COMPOSITE MATERIALS

Mischa Bonn, S. Parekh
Max Planck Institute for Polymer Research, Mainz, Germany

bonn@mpip-mainz.mpg.de

My presentation will highlight our efforts in connecting macroscopic elastic and rheological behavior to changes occurring on molecular length scales.

The first are composite materials that can bear large cyclic loads, such as those used for care tires. These materials typically employ nanoscale filler particles within a polymer matrix to enhance mechanical properties. While a clear connection exists between filler size and amount of reinforcement, substantially less is known about the nonlinear regime, particularly where strain-hardening begins to dominate the response. Here, using a combination of tension and spectroscopic measurements of polymer chain alignment, we show that strain-hardening is linearly correlated with polymer chain alignment and only depends on nanofiller amount, which is in contrast to linear elasticity where reinforcement depends on both amount and size of nanofillers.

In a second line of research, we investigate the molecular mechanics of fibrin. Fibrin biopolymer networks are crucial biomaterials that comprise the key component of blood clots. As natural wound dressing, this protein-based material must satisfy a rather unique set of mechanical requirements, needing to be both highly flexible under strain, yet sufficiently strong to not break under load. These combined properties are enabled by multiscale resistance to deformation, starting at fiber (i.e. protein assembly) level and proceeding down to the level of individual protein molecules. Label-free molecular microscopy that allows determining local protein structure reveals that for an initially molecularly uniform fibrin hydrogel, the protein structure in the network becomes spatially heterogeneous under strain, i.e. proteins collectively change their structural folding pattern in micron-scale regions, so that the material effectively transforms from a single component to a composite system.

IL3

DIELECTRIC SPECTROSCOPY ON NANOSTRUCTURED POLYMER-BASED MATERIALS

Polycarpos Pissis
National Technical University of Athens, Greece

ppissis@central.ntua.gr

Dielectric spectroscopy (DS) is widely employed to study polymer dynamics in polymer-based materials. The extremely broad frequency range of isothermal DS measurements of more than 12 decades in combination with temperature variation enables to follow on the same sample molecular motion in wide ranges of time scale and spatial scale, from tenths of nm to mm [1]. These features make DS especially suited for nanostructured materials.

After a brief introduction to DS and a few examples of application to various nanostructured polymer-based materials, including geometrically confined polymers, thin polymer films and polymer mixtures, the power of DS will be illustrated at the example of polymer nanocomposites (PNCs). By combining DS with calorimetry, we focus on structure/organization, thermal transitions and dynamics of the polymer in the polymer-filler interfacial layer, determined to be a few nm thick [2]. The basic system taken as example is poly(dimethylsiloxane) (PDMS)/silica nanocomposites, prepared by following different routes in wide ranges of composition. The strong (hydrogen bonding) polymer-filler interactions are found to affect significantly the mobility of PDMS and to suppress crystallization [2]. Four contributions to the segmental dynamics associated with the glass transition are observed and analyzed, arising, in the order of decreasing mobility, from confined, bulk, restricted between condensed PDMS crystals, and interfacial polymer [3]. Distinct similarities and differences to other PNCs based on rubbers, thermoplastics and thermosets, as well as correlations to results by other spectroscopic techniques will be discussed.

[1] F. Kremer, A. Schönhals (eds) Broadband dielectric spectroscopy, Springer, Berlin, 2002.
[2] D. Fragiadakis, L. Bokobza, P. Pissis, Polymer 2005, 46, 6001.
[3] P. Klonos, A. Kyritsis, P. Pissis, Polymer 2016, 84, 38.

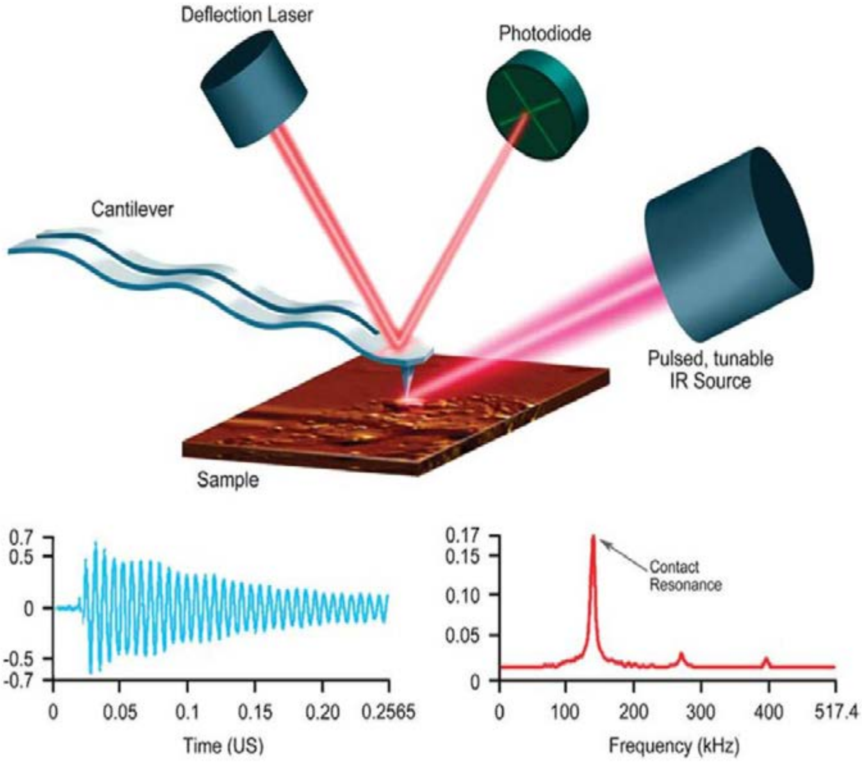
IL4

NANOSCALE INFRARED SPECTROSCOPY AND IMAGING OF POLYMERIC FIBRES AND THIN FILMS

Miriam Unger[1,2], *Curtis Marcott*[3]
[1)] *Anasys Instruments, Santa Barbara, CA, USA*
[2)] *Physical Electronics GmbH, Ismaning, Germany*
[3)] *Light Light Solutions, Athens, GA, USA*

marcott@lightlightsolutions.com

Nanoscale Infrared spectroscopy has been successfully demonstrated in an expanding range of applications in recent years due to significant increases in capability. One method of nanoscale infrared spectroscopy, atomic force microscope based infrared spectroscopy (AFM-IR) uses the tip of an AFM as a nanoscale detector of the expansion caused by absorption of IR radiation. AFM-IR can be used to obtain IR absorption spectra and chemical imaging with resolution as fine as the AFM tip radius, >100X smaller than spatial resolution limits of conventional infrared spectroscopy. The AFM-IR technique has demonstrated improvements in sensitivity, down to the scale of single monolayers, and speed with spectral acquisition times dropping by an order of magnitude. This presentation will highlight applications of nanoscale spectroscopy and chemical imaging in materials sciences. In particular, studies of cross sections of multilayer thin films, identification of polymer defects, and core-shell chemical differences in electrospun polymer fibres will be examined.



The AFM-IR technique uses a pulsed, tunable IR source to excite molecular resonances in the sample. Absorption of IR radiation by the sample leads to a rapid thermal expansion that excites resonant oscillations of the cantilever.

IL5

THZ AND LOW-FREQUENCY RAMAN SPECTROSCOPY OF POLYMERS

Harumi Sato
Kobe University, Graduate School of Human Development and Environment, Department of Human Environmental Science, Kobe, Japan

hsato@tiger.kobe-u.ac.jp

Recently, Terahertz (THz) spectroscopy has received an increasing interest from biomolecules, medicine, and polymer materials. Since the low-frequency vibrational modes reflect the higher order conformations of large molecules, it is a very powerful tool for the investigation of various material properties such as hydrogen bonding of the polymers. One of the most prominent characteristics of THz and low frequency Raman spectroscopy is these spectroscopy is that it is possible to detect the inter- and intramolecular vibrations and orientation of the polymer chains sensitively.

In the present study, we have investigated the characterization of the various biodegradable polyesters by using THz and low frequency Raman spectroscopy. Especially we focused on the changing of the THz spectra for crystallization process, thermal behavior, hydrogen bonding of the polymers. Moreover, we also have been investigated the correlation between low frequency spectra and the changes of physical behavior in polymer by comparing with ordinal spectroscopic methods, IR and Raman. The isothermal crystallization of polyglycolic acid (PGA) was studied by monitoring the temporal evolution of THz absorption spectra with 2DCOS analysis. These results indicated that the hydrogen bonding of PGA are initially formed before well-defined crystal structure are established.

IL6

ON-LINE RAMAN SPECTROSCOPY FOR POLYMER PROCESS ANALYSIS

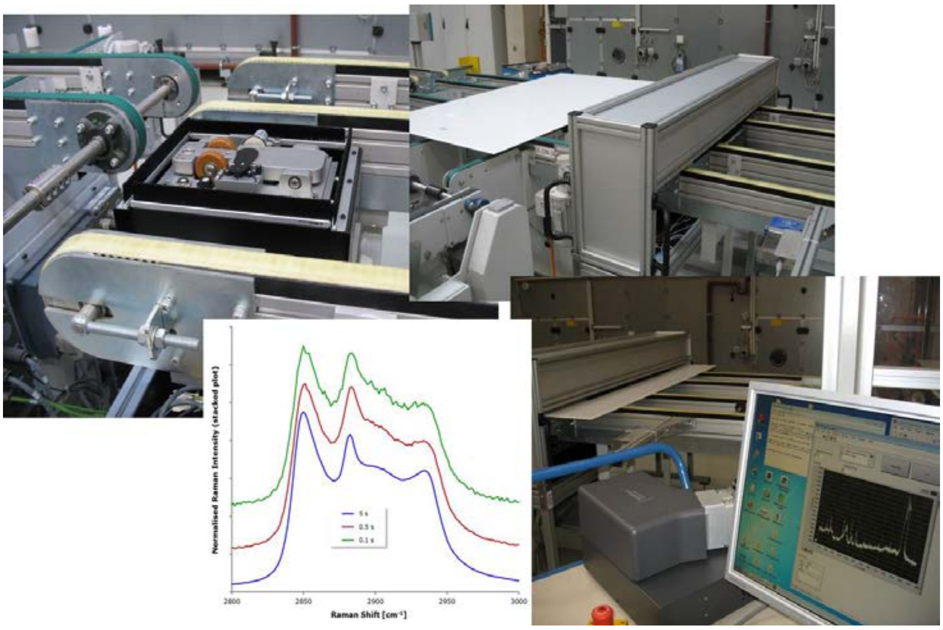
Martin Kraft[1], M. DeBiasio[1], L. Neumaier[1], G. Eder[2], Ch. Hirschl[1]
1) *CTR Carinthian Tech Research AG, Villach, Austria*
2) *OFI Technologie & Innovation GmbH, Vienna, Austria*

martin.kraft@ctr.at

The key advantage of Raman spectroscopy is the ability to acquire vibrational spectroscopic information using visible light, using standard optics and opto-electronics. Yet, while highly versatile, contact-free, non-destructive and providing direct material information, Raman spectroscopy is still mostly regarded as a laboratory technique. Recent developments, in particular of lasers and spectrometers, now change that rapidly. With measurement times down to 0.1 s, modern Raman devices are fit for industrial real-time field use and thus of increasing interest for process control.

When setting up a Raman-based sensor, quantification is a first practical key problem. Direct evaluation of band intensities yields satisfying results only under rare, fortunate circumstances. An approach to improve reliability is to use a relative evaluation, preferably against another spectral feature. A second task is to correlate the spectral data to values of actual relevance for the process to be controlled. While fairly straightforward when dealing with concentrations, things are way more complex when monitoring e.g. polymerisation or crosslinking reactions, which are inherently difficult to calibrate and frequently non-linear over time.

For a successful in-line deployment of Raman process analysers, issues like wavelength stability and temperature effects of both the samples and the ambience need to be addressed alongside with the engineering effort of the process integration. To minimise measurement times and optimise analytical sensitivity it is preferable to customise the spectrometer to the problem. Alternatively to a precise equipment thermo-control, adaptive data evaluation procedures can take care of temperature drifts. These topics, together with some challenges in the seamless process integration of Raman probes, will be discussed for practical examples, including an in-line process control device for the degree of E/VA crosslinking inside assembled photovoltaics modules.



In-line Raman process analyser for measuring the degree of encapsulant crosslinking in industrial photovoltaics manufacturing

IL7

DIFFUSION NMR IN POLYMER SYSTEMS

Monika Schönhoff
University of Münster, Institute of Physical Chemistry, Münster, Germany

schonhoff@wwu.de

Pulsed field gradient (PFG)-NMR methods are a valuable tool for elucidating the structure of heterogeneous materials, such as porous polymer systems, colloidal carrier particles or vesicles. In particular the possibility of varying the observation time allows probing molecular displacements over different time and length scales. As a consequence, the information obtained is not only of structural nature, but allows the analysis of exchange processes of various kind. After an overview of PFG NMR applications in this area, this lecture will turn to polymer electrolyte systems, where the strength of PFG-NMR lies in multinuclear experiments to gain a complete picture of ionic transport.

In the search for advanced electrolytes in Li ion batteries, ternary polymer gel electrolytes consisting of ionic liquid, polymer and Li salt are suitable materials to yield a compromise between sufficient conductivity and mechanical stability. Here, multinuclear PFG-NMR of 7Li, 19F (anions) and 1H (cations) serves to analyze the transport processes as influenced by complex mutual interactions of the constituents. For example, in systems based on the poly(ionic liquid) PDADMATFSI a detailed comparison of relative diffusivities of anions and Li showed that charged chains are superior polymeric constituents in ternary gels in terms of their ability to enhance Li+ conduction. Transport numbers calculated from PFG-NMR diffusion coefficients thus serve to yield materials optimized for transport of specific ions.

IL8

VIBRATIONAL SPECTROSCOPY WITH HANDHELD INSTRUMENTS: INSTRUMENTATION, APPLICATIONS AND FUTURE ASPECTS

Heinz W. Siesler
University of Duisburg-Essen, Department of Physical Chemistry, Essen, Germany

hw.siesler@uni-due.de

Fourty years ago Raman and FT-IR spectrometers occupied a separate room and NIR spectrometers were just about to quit the phase as add-ons to UV-VIS or IR spectrometers and appear as stand-alone instruments. The following four decades were characterized by a multiplicity of exciting hard- and software developments for vibrational spectroscopy but apart from opening the lab to the process by the introduction of light-fiber optics, special probes and chemometric evaluation routines the techniques remained a domain for scientists. In contrast, the recent development of miniaturized, handheld instruments has not only led to a further extension of the range of applications by on-site and in-the-field measurements but also shows promise that these instruments may in the future be used by non-traditional user environments.

The reduction in size, however, must not lead to compromises in measurement performance and precision and the handheld instrumentation will only have a real impact on quality and process control if Raman, IR and NIR spectra of comparable quality to laboratory spectrometers can be obtained.

The presentation will provide an overview on the building principles and performance parameters of state-of-the-art handheld systems, discuss the pros and cons of the different techniques and will highlight the advantages of on-site measurements by means of selected application examples.

Finally, the transfer of spectra that have been measured on a laboratory FT-NIR spectrometer to the format of a handheld instrument by measuring only a few samples with both spectrometer types will be shortly demonstrated. Thus, despite the extreme differences in spectral range and resolution, data sets which have been collected and calibrations which have been developed thereof, respectively, over a long period on a laboratory instrument can be conveniently transferred to a handheld system without the requirement for elaborate complete rescanning and recalibration of spectra.

Handheld near-infrared spectrometer for on-site and in-the-field measurements

Abstracts of the contributed lectures

CL1

RAMAN SPECTROSCOPY INVESTIGATION OF ORIENTATION AND DISENTANGLEMENT IN SINGLE ELECTROSPUN FIBERS

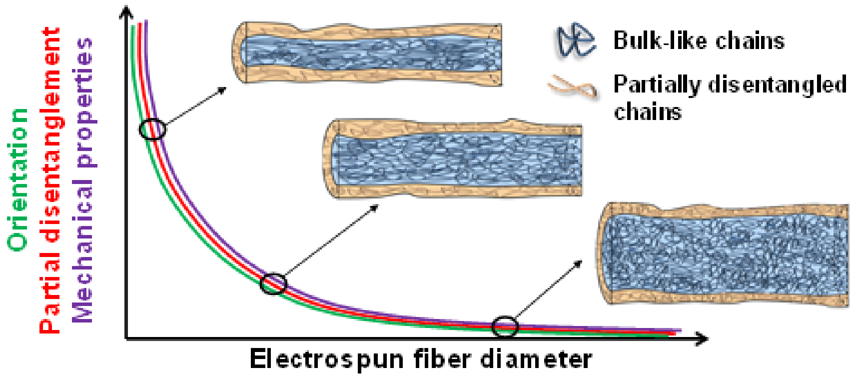
Marie Richard-Lacroix, *Christian Pellerin*
University of Montreal, Canada

marie.richard-lacroix@umontreal.ca

Electrospinning is a widely used technique to produce nano- to microscale continuous fibers by applying a high voltage on semi-diluted polymer solutions. Electrospun fibers are known to exhibit unusual and tunable properties in part because they are often frozen in out-of-equilibrium states due to the fast solvent evaporation and high elongational forces during the process. Their molecular orientation and the level of entanglement of the chains are critical (although challenging) parameters to characterize because they allow improving and tuning many properties. While molecular orientation is currently the subject of intensive study, the others are more challenging to probe experimentally.

Here, we report the first experimental demonstration for partial disentanglement in continuous polystyrene electrospun fibers on the basis of measurements by infrared spectroscopy on bundles of fibers and by polarized Raman spectroscopy on single fibers due to the appearance of bands associated with a conformation made possible by a level of entanglement that is lower than in the bulk. Results highlight that the capacity of the fibers to remain partially disentangled is directly related to the volatility of the solvent and to the time allowed for fiber collection.[1] We also show our capability to localize disentanglement-related Raman bands in individual fibers in the shell of the fibers and to quantitatively correlate their intensity with the fiber diameter. We show the exceptional level of orientation reached by the smallest fibers and the high correlation between the orientation of the chains, their disentanglement and the improvement of the modulus as a function of the diameter.[2] Combining these results allows us to draw a statistically meaningful picture of the chain organization polystyrene PS electrospun fibers.

[1] M. Richard-Lacroix, C. Pellerin. Macromolecules 2015, 48, 37.
[2] M. Richard-Lacroix, C. Pellerin. Macromolecules 2015, 48, 4511.



CL2

DEPTH PROFILING OF SYNTHETIC POLYMERS OF INTEREST FOR CULTURAL HERITAGE WITH ATR–FTIR SPECTROSCOPIC IMAGING

Alessandra Vichi, *Sergei G. Kazarian*
Imperial College London, Department of Chemical Engineering, London, United Kingdom

s.kazarian@imperial.ac.uk

Synthetic polymers, present as original material constituting the object or introduced during conservation treatments, can be easily found in museum collections. It has been observed that degradation phenomena can severely affect these materials up to the point the preservation of the artefacts becomes a challenge [1]. Attenuated Total Reflection (ATR)–FTIR spectroscopy is an excellent technique to analyse polymers and phenomena affecting their stability in a non–destructive way. Furthermore, when coupled with a Focal Plane Array (FPA) detector, FTIR spectroscopy allows obtaining chemical images of the distribution of the compounds detected.

We apply new approaches in micro and macro ATR–FTIR spectroscopic imaging to study polymers of interest for cultural heritage. We can control the angle of incidence (θi) with which the IR light hits the sample at the interface with the ATR crystal by placing apertures in the optical path. When the θi is modified, the depth of penetration of the evanescent wave into the sample is consistently changed (Fig. 1). Thus, depth profiling in ATR–FTIR imaging becomes possible and images revealing the composition of the sample at different depths can be collected.

With this novel method developed in our group [2], we demonstrated that by adding apertures in an IR microscope it is possible to discriminate stacked layers of polymers with sub–micrometres spatial resolution along the z–axis [3]. Moreover, when controlling the angle of incidence, anomalous dispersion causing shift of strong bands in ATR can also be reduced.

Our approach allows synthetic polymers to be probed at different depths, which would help to establish strategies for their conservation.

[1] B. Keneghan et al. Plastics: Looking at the Future and Learning from the Past, Archetype Pub, 2008.
[2] T. Frosch, K. L. A. Chan, H. C. Wong, J. T. Cabral, S. G. Kazarian. Langmuir 26, 2010, 19027.
[3] T. P. Wrobel, A. Vichi, M. Baranska, S. G. Kazarian. Appl. Spectrosc. 69, 2015, 1170.

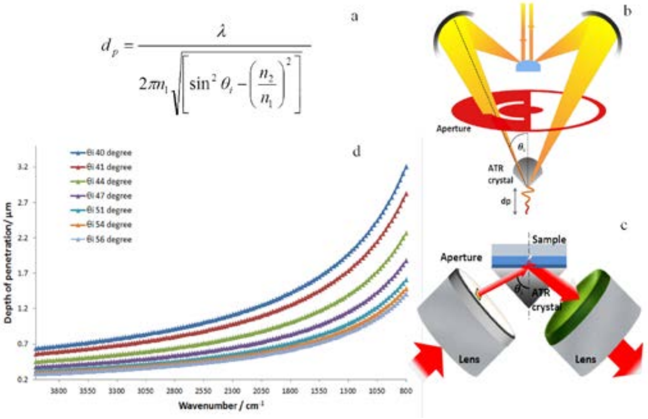


Fig. 1: a) Harrick's equation linking depth of penetration (dp) to wavelength (λ), the indexes of refraction of the ATR crystal (n1), the sample (n2) and the angle of incidence (θi). b) Schematic showing the use of aperture in the micro ATR set–up. c) Schematic showing the use of aperture in the macro ATR set–up. d) Simulated values of dp plotted against wavenumber for the macro set-up.

CL3

AMIDE–WATER HYDROGEN-BOND INTERACTIONS IN POLYMER BRUSHES AT THE SOLID–LIQUID INTERFACE

Andreas Furchner[1]*, Annika Kroning*[1]*, Sebastian Rauch*[2]*, Karsten Hinrichs*[1]
1) Leibniz-Institut für Analytische Wissenschaften – ISAS – e. V., Berlin, Germany
2) Leibniz Institute of Polymer Research Dresden, Germany

andreas.furchner@isas.de

Hydrogen-bond interactions play a crucial role in defining the structural and functional properties of organic molecules and surfaces, such as the formation of secondary structures in polymers and proteins. Of particular interest is the understanding of interactions in thin films at the solid–liquid interface, from which many applications follow. Examples are tissue characterization, structure analysis of protein films, and thin films for sensing applications.

One class of functional surfaces are polymer brushes that react upon external stimuli, such as temperature or pH variations, by changes in their structural and/or chemical properties. A prominent temperature-responsive polymer is poly(N-isopropylacrylamide) [PNIPAAm], which is widely used for physicochemical and bioapplications like controlled drug release. PNIPAAm's switching behavior between a swollen and collapsed state is thought to be mediated by changes in hydrogen-bond interactions between the polymer's amide groups and water.

Our aim is to investigate to what extent amide–amide interactions are involved in the brush's LCST transition, and whether this transition really renders the brushes either hydrophlic or hydrophobic. To achieve this aim, we employ infrared-spectroscopic ellipsometry (IR-SE), a power chemical analysis technique that enables us to probe the vibrational bands of ultra-thin films in-situ at the solid–liquid interface. Hydrogen-bond interactions distinctly impact these bands, particularly the amide bands. From their analysis, we identify various polymer–polymer and polymer–water interactions. We quantify them making use of rigorous optical modeling of IR-SE spectra. The modeling is based on a physical and chemical description of the hydrated brushes. We simultaneously determine the brushes' water content, thickness, and different interactions. We find that only a small fraction of amide groups transitions from interacting with water to interacting with other amide groups.

CL4

SPECTROSCOPIC CHARACTERIZATION OF « POLYDOPMAINE » FORMATION IN SOLUTION AND ON SURFACES AS A FUNCTION OF THE USED OXIDANT: TOWARDS A STRUCTURE-PROPERTY RELATIONSHIP.

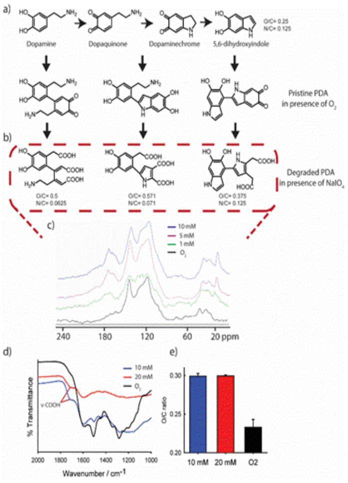
F. Ponzio[1]*, J. Barthès*[2]*, P. Bertani*[3]*, M. Michel*[4]*, M. d'Ischia*[5]*, Vincent Ball*[1]

[1)] *Université de Strasbourg, Institut National de la Santé et de la Recherche Médicale, Strasbourg, France*
[2)] *Protip SAS, Strasbourg, France*
[3)] *Université de Strasbourg, Centre National de la Recherche Scientifique, Strasbourg, France*
[4)] *Luxembourg Institute of Technology, Hautcharage, Luxembourg*
[5)] *University of Naples Federico II, Department of Chemical Sciences, Naples, Italy*

vball@unistra.fr

Efficient surface functionalization with polydopamine films (PDA) can be easily achieved on virtually any object via single immersion in slightly basic dopamine solutions allowing to overcome a major challenge in surface science [1]. In such conditions, however, poor homogeneity, low thickness and long time of reaction are usually the major limitations. Herein, we report a rational entry to the control of PDA deposition via chemical oxidation under slightly acidic conditions (pH 5.0) ensuring inhibition of uncontrolled autoxidation processes, to gain insight about the reaction mechanism and the impact of oxidation conditions on PDA structure [2]. Comparative chemical and spectroscopic (13C NMR, UV vis and FTIR spectroscopy) analysis of dopamine oxidation with three different oxidants (ammonium peroxodisulfate (AP), sodium periodate (SP)and copper sulfate, CS) revealed significant differences in the reaction course and allowed selection of periodate for the fast and homogeneous deposition of PDA films with thickness never reported before (more than 100 nm in 1h). Notably, PDA coatings with unprecedented superhydrophilic/superoleophobic properties were obtained in a one step reaction under conditions of high periodate concentration, due to degradation of quinone units to yield carboxyl functions [3]. Moreover these films still present biocompatibility and metal cation reduction properties. Overall, these results provide a novel rational methodology to tailor PDA coatings for technological applications based on periodate control over dopamine polymerization and post-synthetic functional group modification.

[1] H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith. Science 318 (2007) 426-430.
[2] M. D'Ischia, A. Napolitano, V. Ball, C.-T. Chen, M. J. Buehler. Acc. Chem. Res. 47 (2014) 3541-3550.
[3] F. Ponzio, J. Barthès, J. Bour, M. Michel, Ph. Bertani, J. Hemmerlé, M. d'Ischia, V. Ball. Chem. Mater. In revision (2016).



a)Monomer precursors, main types of oligomer components in PDA-O2 and b)in SP-degraded PDA, accounting for increased O/C ratios and decreased N/C ratios. c) 13C-CP MAS NMR spectra of solid PDA-O2 and PDA-SP 1, 5, and 10 mM. d) FTIR spectra of PDA-SP and PDA-O2 in the presence of SP and in the presence of O2. e) O/C atomic ratios obtained from XPS spectra of PDA-SP-10, 20mM and PDA-O2.

CL5

IONIZATION OF NON-POLAR POLYIZOBUTYLENE DERIVATIVES BY DART AND ESI ION SOURCES

Tibor Nagy[1]*, Lajos Nagy*[1]*, Ákos Kuki*[1]*, Borbála Antal*[1]*, György Deák*[1]*, Mihály Purgel*[2]*,*
Mijid Narmandakh[3]*, Béla Iván*[3]*, Miklós Zsuga*[1]*, Sándor Kéki*[1]

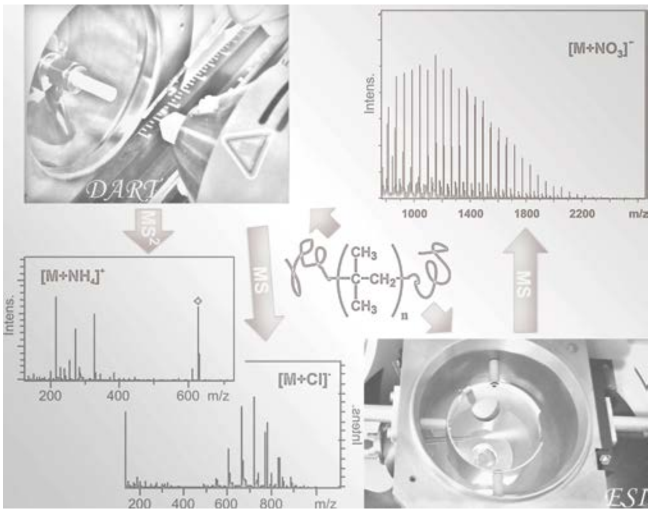
[1)] *University of Debrecen, Department of Applied Chemistry, Debrecen, Hungary*
[2)] *University of Debrecen, MTA-DE Homogeneous Catalysis and Reaction Mechanisms Research Group, Department of Physical Chemistry, Debrecen, Hungary*
[3)] *Hungarian Academy of Sciences, Research Center for Natural Sciences, Institute of Materials and Environmental Chemistry, Budapest, Hungary*

nagy.tibor@science.unideb.hu

The low molecular weight polyisobutylenes are of great interest due to their special applications. The end groups have great influence on the physical and chemical properties. Therefore, the characterization of the end groups and the initiator moiety is important. The DART (Direct Analysis in Real Time) and ESI (electrospray ionization) ionsources were applied for the identification of polyisobutylene derivatives with different end groups and in presence and absence of aromatic initiator moiety.

The DART does not require any sample preparation, thus it offers a fast characterization method. The DART-MS is capable of working in positive and negative ion modes also. Negative ion mode can be applied for the ionization of the intact oligomer by the formation of the [M+Cl]- adducts. In contrary, in positive ion mode considerable fragmentation processes can occur which indicates that tandem mass spectrometric measurement can be carried out for structural information.

It was proven that the formation of negatively charged stable adducts ([M+C_l]- and [M+NO_3]-) are possible under electrospray conditions. To obtain the adduct ions a solvent mixture with polar and non-polar solvents are required for the ionization and the solvation of the polyisobutylene derivatives. The acetone/dichlocomethane solvent mixture proved to be an appropriate solvent for all type of polyisobutylene derivatives. Further quantumchemical calculations and tandem mass spectrometric measurements were carried out in order to study the structures and the stability of the generated adducts.



DART and ESI ion sources are capable of ionizing non-polar polyisobutylene derivatives

CL6

SOLID-STATE NMR IN HYBRID MATERIALS

Ulrich Scheler
Leibniz Institute of Polymer Research Dresden, Germany

scheler@ipfdd.de

Solid-state NMR is a well-established method for the characterization of structure and dynamics in systems of low or local order. However because of its low sensitivity it usually is not considered as a method for the characterization of interfaces. Selective excitation at the interface in organic- inorganic hybrids is achieved either by heteronuclear trans-interface magnetization transfer by cross polarization or by selective excitation of the protons in the inorganic phase and subsequent spin diffusion into the organic matrix. As an example the OH signal of hydroxyapatite is selected by a chemical-shift selective T2 filter. Heteronuclear transfer works if there are two sensitive nuclei like 1H and 19F as demonstrated in Nafion membranes with polyelectrolyte multilayers. With short-range transfer only a small sub-ensemble is excited and further transfer steps to establish a gradient suffer from small sensitivity.

Polyelectrolyte multilayers produced by the layer- by- layer technique on hydroxyapatite nanoparticles provide a molecular ruler to convert spin diffusion into a length scale. In particular the aromatic signal from poly(styrenesulfonate) is used as a target signal to be distinguished from the other polymer signals at fast MAS, so that the buildup of this signal is monitored as a function of layer position. At fast MAS spin diffusion is readily described by a stretched exponential.

Application to biomimetic hydroxyapatite nanoparticles formed in collagen yields the expected signal buildup of the collagen matrix and unexpectedly a significant fraction of the water at a larger distance from the surface of the particles.

To overcome the limitations from the low sensitivity dynamic nuclear polarization (DNP) is applied, which utilizes the high sensitivity in EPR, which can be transferred to NMR. The application of spin-labelled polyelectrolytes enables site-selective investigations

CL7

DYNAMICS OF POLYETHERCARBONATE POLYOLS IN COMPARISON TO POLYETHER POLYOLS

M. Pohl, E. Danieli, M. Leven, W. Leitner, B. Blümich, Thomas E. Müller
RWTH Aachen University, Institut für Technische und Makromolekulare Chemie, Aachen, Germany

thomas.mueller@tum.de

Polyurethanes are binary systems of a polyol and an isocyanate component, which, in a chemical reaction, form linear chains or a three-dimensional network, depending on the terminal functionality of the building blocks. Low viscosities of the polyol component are essential to avoid mass transport limitations during polyurethane formation and to achieve a uniform and well-defined product.

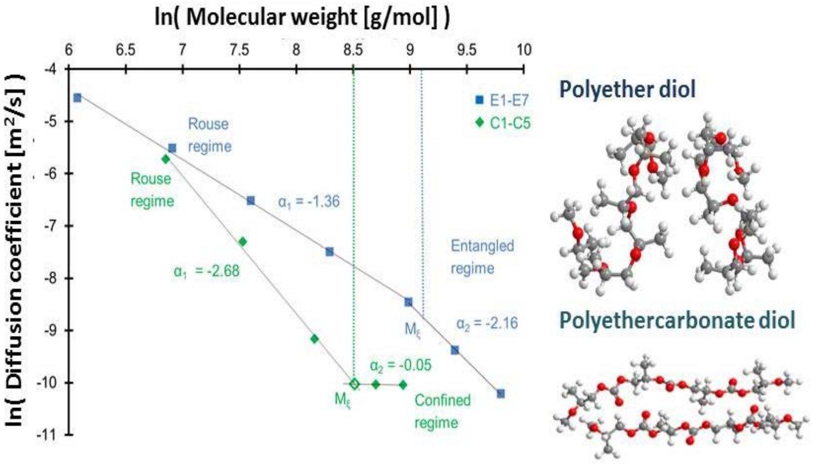
Conventional polyols are mostly epoxide homopolymers. To increase sustainability, CO_2 has been introduced as ubiquitous and renewable comonomer to attain CO_2-based polyols with more beneficial eco-balance. However, the incorporation of CO_2 leads to substantial increase in viscosity as the amount of CO_2 incorporated into the polymer chain increases.

To obtain a basic understanding of the dynamic behavior of polyols in melt we investigated the self-diffusion coefficient of oligomeric CO_2/propylene oxide copolymers (polyethercarbonate diols) in comparison to the corresponding propylene oxide homopolymers (polyether diols) using a single-sided NMR sensor (NMR-MOUSE).

- For polyethercarbonate diols with molecular weight below 4000 g/mol, the self-diffusion coefficient (DNMR) was linearly correlated with the molecular weight. At higher molecular weights, the time dependence of the diffusion coefficients revealed sub-diffusive motion and strong topological constraints, resulting in distinct sub-diffusive or confined diffusion, similar to diffusion of molecules through porous media.

- For polyether diols, the self-diffusion coefficients (DNMR) revealed the anticipated transition from free diffusion (Rouse regime) to reptation motion.

Thus, polyethercarbonate diols exhibit a time-dependent diffusion coefficient similar to sub-diffusion in porous media. Conventional polyether diols are subject to fewer topological constraints in the dynamic range and show classic diffusiveness. Understanding the molecular motion enables tuning the viscosity of polyols by varying the molecular architecture.



Double logarithmic plot of diffusion coefficient D(NMR) vs molecular weight for polyethercarbonate diols (green, lower curve) and polyetherdiols (blue, upper curve).

CL8

SEGMENTAL DYNAMICS OF POLY(ACRYLIC ACID) IN POLYELECTROLYTE COMPLEX COACERVATES STUDIED BY SPIN-LABEL EPR SPECTROSCOPY

Uwe Lappan, Brigitte Wiesner, Ulrich Scheler
Leibniz Institute of Polymer Research Dresden, Germany

lappan@ipfdd.de

The complex coacervation of oppositely charged polyelectrolytes has been studied by EPR spectroscopy. The spin-label technique employs stable radicals which are covalently linked to macromolecules. Rotational dynamics of such spin labels on time scales between 10 ps and 1 µs can be characterized by CW EPR spectroscopy, simulating the line shape. The dynamics of the spin labels is influenced by the restricted motion of the side group bearing the label and local polymer backbone motions at the point of the covalent attachment of the label.

Recently, we have studied the complex coacervation of oppositely charged polyelectrolytes in dependence on mixing ratio [1], pH and temperature [2] using spin-labeled poly(ethylene-alt-maleic acid) as reporter molecule. The study has shown that, if the polyacid is the excess component, the spectrum of a slow-motion component is superimposed by the spectrum of a fast-motion component. This indicates that the spin labels are located both in the core and in the shell of the PEC particles. In the opposite case, if the polycation is in excess, the spectra are dominated by a slow-motion component indicating that nearly all spin labels are located in the core. The diffusion coefficient characterizing the rotational motions of the polyacid backbone is significantly smaller at low degree of dissociation than at high degree of dissociation.

Here we present the application of spin-labeled poly(acrylic acid) to study the complex co-acervation with the strong polycation poly(diallyldimethylammonium chloride) in dependence on pH and temperature. It was found, that the segmental mobility of the polyanion is nearly constant in the range of pH 10 to 5, but decreases dramatically for pH values lower than 5.

[1] U. Lappan, B. Wiesner, U. Scheler. Macromol. Chem. Phys. 215 (2014) 1030-1035.
[2] U. Lappan, B. Wiesner, U. Scheler. Macromolecules 48 (2015) 3577-3581.

CL9

IR NANOPOLARIMETRY ON BIAXIALLY ANISOTROPIC SUPRAMOLECULAR STRUCTURES

Timur Shaykhutdinov, S. Pop, A. Furchner, K. Hinrichs
Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Berlin, Germany

timur.shaykhutdinov@isas.de

Understanding hierarchical self-assembly of low-dimensional supramolecular systems is of fundamental importance for applications in the field of polymer science, biotechnology, and bioengineering. For nanostructured material characterization, progress in the field of nanometrology is required, where it has become necessary to transform measurement concepts from micro- to nanoscale. Here we present a novel measurement method that combines resonance-enhanced AFM-IR, a high-sensitivity nanospectroscopic technique in the fingerprint region, with tunable polarized IR laser sources. This non-destructive label-free concept reinvents classical far-field IR polarimetry at the nanoscale which allows seeing intermolecular coupling interactions and hierarchical supramolecular ordering in nanostructured morphology by changing the polarization direction of the laser source.

Here we apply IR nanopolarimetric imaging for characterization of aggregation mechanisms of thin porphyrin films not accessible by conventional far-field IR microscopic techniques. As chlorophyll and heme, porphyrins serve as key components in a variety of biological systems. Their capability to self-organize over a wide range of length scales spanning from a few nanometers up to hundreds of micrometers highlights the importance of porphyrin-based compounds as highly versatile building blocks for synthesis of tailored multifunctional surfaces and biomimetic materials. Porphyrin aggregates come in a variety of shapes showing both diffusion- and attachment-limited aggregation patterns. We provide IR nanospectroscopic evidence that the morphology of porphyrin aggregates is dictated by stacking interactions and supramolecular orientation (Fig. 1). The nanospectroscopic analysis is supported by numerical calculations.

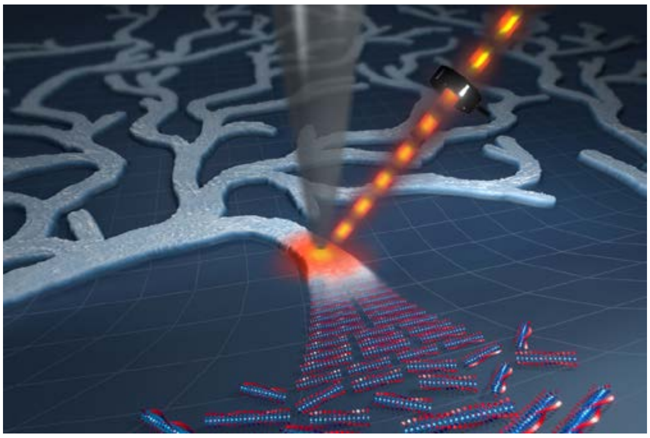


Fig. 1: Schematic representation of the IR nanopolarimetric setup for characterization of hierarchical self-assembly of ZnTPP (zinc tetraphenylporphyrin) aggregates.

CL10

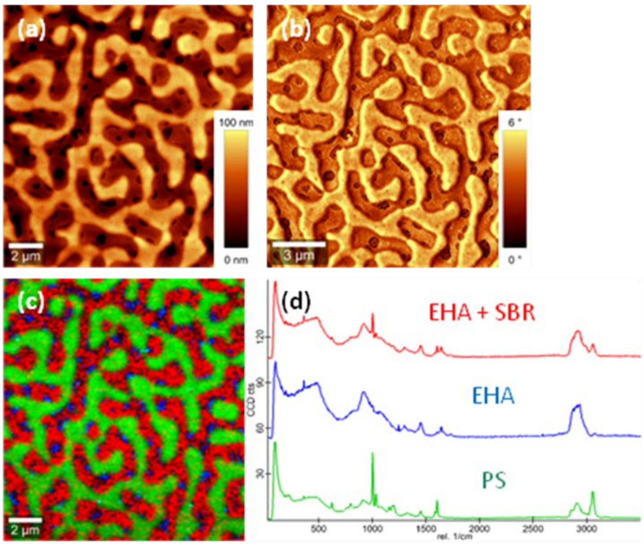
THE POWER OF CONFOCAL RAMAN-AFM IMAGING IN POLYMER RESEARCH

Ute Schmidt, Thomas Dieing, Joachim Keonen
WITec GmbH, Ulm, Germany

ute.schmidt@witec.de

Polymers play an essential role in modern materials science. Due to the wide variety of mechanical and chemical properties of polymers, they are used in almost every field of application and are still a dynamic area in the development of new materials with demanding requirements. For many of these developments knowledge about the morphology and chemical composition of heterogeneous polymeric materials on a sub-micrometer scale is crucial. The combination of a confocal Raman microscope with an AFM provides the ability to unequivocally determine the chemical composition of a material together with the morphology and phase separations in thin polymeric films. By acquiring Raman spectra at every image pixel, the high spatial and topographic resolution obtained with an AFM can be directly linked to the chemical information provided by confocal Raman spectroscopy. In polymer science Raman spectra provide quantitative information about various features such as: chemical nature (structural units, type and degree of branching, end groups, additives), conformational order (physical arrangement of the polymer chain), state of the order (crystalline, mesomorphous, and amorphous phases), orientation (type and degree of polymer chain and side group alignment in anisotropic materials).

The aim of this presentation is to present results obtained with a confocal Raman-AFM from a three component polymer blend consisting of PS:EHA:SBR in the blending ratio 1:1:1. Figure 1 shows the high resolution topographic (a) and viscoelastic properties (b). The structures visible however are not present in the ratio of the blending. The Raman image (c) and the corresponding spectra (d) reveal an overlay of the EHA and SBR phase. Further information regarding substrate wetting and phase formation which could be derived by combining the results of both techniques will be presented.



Confocal Raman-AFM images of a three component polymer blend PS:EHA:SBR (1:1:1): AFM topography (a), AFM phase (b), color coded Raman image (c) and corresponding spectra (d).

CL11

NANO-FTIR – QUANTITATIVE INFRARED IMAGING AND SPECTROSCOPY AT 10NM SPATIAL RESOLUTION

Andreas J. Huber
neaspec GmbH, Planegg, Germany

andreas.huber@neaspec.com

Scattering-type Scanning Near-field Optical Microscopy (s-SNOM) allows to overcome the diffraction limit of conventional light microscopy or spectroscopy enabling optical measurements at a spatial resolution of 10nm, not only at VIS frequencies but also in the IR or THz spectral range.

s-SNOM [1] employs an externally-illuminated sharp metallic AFM tip to create a nanoscale hot-spot at its apex. The optical tip-sample near-field interaction is determined by the local dielectric properties (refractive index) of the sample and detection of the elastically tip-scattered light yields nanoscale resolved near-field images simultaneous to topography.

Development of a dedicated Fourier-transform detection module for analyzing light scattered from the tip which is illuminated by a mid-IR broadband laser source enables IR spectroscopy of complex polymer nanostructures [2]. Applications presented (Fig.1) demonstrate analysis of egineered polymer nanostructures and interfaces, characterization of embedded structural phases in biominerals (bone) [3], or organic semiconductors [4] and other functional semiconductor nanostructures. Detailed near-field signal analysis enables quantitative measurements of dielectric values for polymers [5] or determination of free carrier concentration and mobility in low-dimensional structures [6,7], A modular system design enables straight forward integration of synchrotron-based broadband IR light sources or to realize pump-probe near-field measurements [8].

[1] F. Keilmann, R. Hillenbrand. Phil. Trans. R. Soc. Lond. A 362, 787 (2004).
[2] F. Huth, et al. Nano Lett. 12, 3973 (2012).
[3] S. Amarie, et al. Beilstein J. of Nanotech. 3, 312 (2012).
[4] C. Westermeier, et al. Nature Comm. 5, 4102 (2014).
[5] A. A. Govyadinov, et al. J. Phys. Chem. Lett. 4, 1526 (2013).
[6] J. M. Stiegler, et al. Nature Comm. 3, 1131 (2012).
[7] Z. Fei, et al. Nature Nanotech. 8, 821 (2013).
[8] M. Eisele, et al. Nature Phot. 8, 841 (2014).

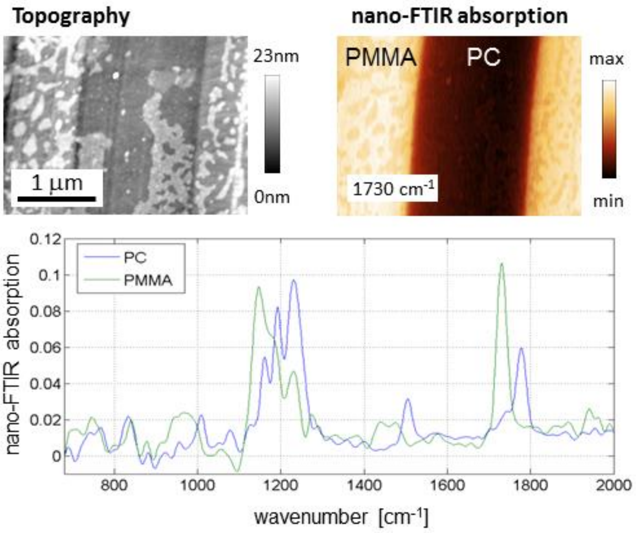


Fig. 1: (Top) Simultaneous topographic and material-selective near-field imaging of a PMMA-PC polymer hetero-structure. (Bottom) nano-FTIR near-field spectroscopic measurement close to the material interface exhibit similar spectral signatures of nanoscale PMMA and PC structures as conventional IR spectroscopic measurements allowing unambiguous identification of materials.

CL12

NOVEL MICRO-STRUCTURED SILICON SINGLE REFLECTION ELEMENTS: THEIR DESIGN, FABRICATION AND APPLICATION FOR IN SITU ATR-FTIR INVESTIGATIONS OF THE INFLUENCE OF AMMONIA ON THE STRUCTURE OF PEDOT/PSS COMPOSITE LAYERS

Ulrich Künzelmann, *Johann Wolfgang Bartha*
Technische Universität Dresden, Institut für Halbleiter- und Mikrosystemtechnik, Dresden, Germany

ulrich.kuenzelmann@tu-dresden.de

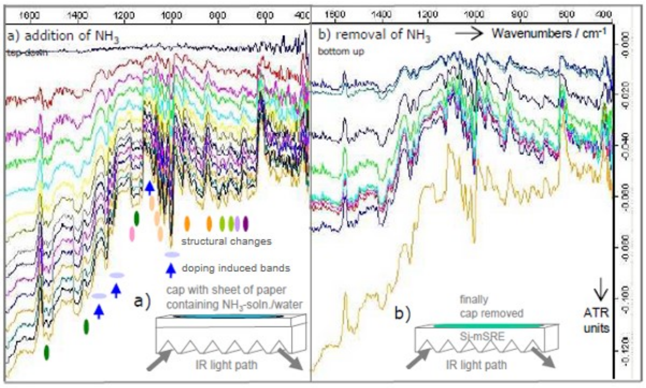
In situ FTIR spectroscopy in attenuated total reflection (ATR) geometry [1] always applies multi/single reflection elements mostly with long internal light paths, limited spectral ranges and transmittance. Novel micro-structured silicon single reflection elements (Si mSRE) as developed at the IHM overcome these drawbacks [2]. They are fabricated by anisotropic etch of double side polished Si(100) wafers with <110> directed line-space-structured SiO_2 hard masks at one side. The formed by Si(111) facets v-grooves provide coupling in and out of the IR radiation always with total reflection at the opposite flat Si(100) surface and 10-30 % total transmittance over the entire IR range.

Poly(3,4-ethylenedioxythiophene)/poly(styrenesulphonic acid) -PEDOT/PSS composite layers are e.g. applied as anodes in polymer light-emitting diodes [3] and for gas sensing elements [4]. Bar-like PEDOT/PSS particles are embedded in a PSS-rich surface layer. The oxidised PEDOT backbone with conjugating double bonds forms radical cations and dislocated charges provide intrinsic electrical conductivity. The charge is balanced by the counter ions in the surrounding PSS chains.

Ammonia disturbs the equilibrium by ionic interactions with the PSS. So the mobility of the charges in the PEDOT counterpart drops increasing the resistivity mainly monitored by spin coated with PEDOT/PSS interdigital comb structures.

In the ATR/FTIR experiment, structural changes of PEDOT/PSS layers at the totally reflecting mSRE face are found in dependence of the ammonia uptake (cf. figure); it is slightly influenced by the humidity. The spectra reveal the disappearance of typical doping-induced bands and structural changes as assigned in literature [1].

[1] C. Kvarnstrom et al. Electrochimica Acta 44 (1999) 2739-2750.
[2] H. Schumacher et al. Applied Spectroscopy 64, No.9 (2010) 1022-1027.
[3] M. M. de Kok et al. Phys. Stat. Sol. (a) 201, No.6 (2004) 1342-1359.
[4] Y. Seekaew et al. Organic Electronics 15 (2014) 2971-2981.



Initially the totally reflecting face of the mSRE is covered with the PEDOT/PSS layer followed by recording the reference spectrum. Then a closed cap with a sheet of paper wetted with a 25 % ammonia solution at the top of it is placed onto the mSRE a) providing an ammonia and water saturated atmosphere while FTIR spectra are recorded. After removing the cap b) the initial state is nearly restored.

CL13

CHEMICALLY SENSITIVE SEC DETECTION WITH FTIR AND QCL-IR SPECTROSCOPY

Sascha Morlock[1]*, Jennifer Kübel*[1]*, Timo F. Beskers*[2]*, Thorsten Hofe*[2]*, Manfred Wilhelm*[1]
1) *Karlsruhe Institute of Technology, Institute for Chemical Technology and Polymer Chemistry, Karlsruhe, Germany*
2) *PSS Polymer Standards Service GmbH, Mainz, Germany*

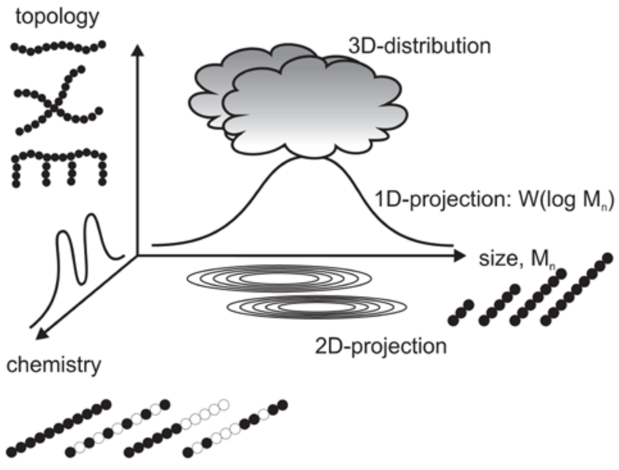
manfred.wilhelm@kit.edu

Polymers have three important molecular characteristics: the molecular weight distribution (MWD), the chemical composition and the topology. Those are of general interest, because they also influence the material properties. The MWD is usually determined using size exclusion chromatography (SEC). SEC detectors commonly in use do not provide any information about the chemistry or topology. This information is therefore normally gained separately using spectroscopic methods (generally IR and NMR). Especially when analyzing modern, complex materials, the correlated measurement of size, chemical properties and topology is of special interest.

Coupling spectroscopy with SEC seems a promising approach to gain this correlated information. An inherent problem to this pairing is the normally very high solvent signals, which arise from the low sample concentration necessary for SEC separation. Several approaches, mostly with highly complex or expensive equipment have been reported in literature and reviewed in [1]. FTIR is universally applicable to all polymers and is comparably cheap. Therefore it has the potential to be used as standard chemically sensitive SEC detector, which enables routine measurements of the molecular weight dependent chemical composition.

For the SEC-FTIR coupling we optimized a standard research FTIR spectrometer to gain best sensitivity and constructed specialized flow cells for the SEC coupling. To subtract the solvent signals the method is based on a newly developed mathematical solvent suppression routine. Additionally the general setup and the column dimensions were optimized.[2,3] For an even higher sensitivity stronger infrared light sources are needed. We present results from an IR spectrometer with a tunable Quantum Cascade Laser (QCL) light source, which has a higher light intensity, but a limited bandwidth.

[1] Polym. Chem. 4 (2013) 2628-2650.
[2] Macromol. Rapid Commun. 33 (2012) 1747-1752.
[3] Polym. Chem. 6 (2015) 128-142.



The figure shows the three important molecular characteristics of polymers: the molecular weight distribution, the chemical composition and the topology. Here, the polymeric material is symbolized by a 3-D “cloud”. The molecular weight axis is determined by the SEC measurement. FTIR enables a simultaneous access to the chemical composition. Finally, QCL-IR offers a chance to characterize topology.

CL14

CHEMICAL IMAGING OF FILLED POLYMERS WITH WAVELENGTH DISPERSIVE SPECTROMETERS

Severine Bellayer, M. Jimenez, B. Gardelle, A. Beaugendre, M. Casetta, J. Bouquerel, S. Duquesne, S. Bourbigot
Ecole Nationale Supérieure de Chimie de Lille, UMET/ISP/R2FIRE, Villeneuve d'Ascq, France

severine.bellayer@ensc-lille.fr

Electron probe microanalyzer (EPMA) is a device often used in geology or in glass and steel industries. However, it is barely known or used in the polymer field. Like scanning electron microscopes (SEM), EPMA works by bombarding a micro-volume of a sample with a focused electron beam; however, the X-ray photons emitted are not collected with energy dispersive spectrometers (EDS), but with wavelength dispersive spectrometers (WDS). The use of EPMA usually results from the need to overcome the problem encountered with EDS, that is to say, low spectral resolution, low detection resolution, or background artifacts. In this presentation, we will investigate the use of EPMA for polymer microanalyses and compare it with a SEM equipped with EDS. To show the unique potential of this technique, various samples will be studied: a fire protective epoxy-based coating submitted to aging in salted water (Figure 1), the distribution of organometallic catalysts into a thermal insulating silicone polymer, or the pattern of stratification of fluoropaints. Compared to EDS, WDS allowed to quickly obtain X-ray imaging of the migration of trace elements such as chloride and catalysts into a polymer and mapping fluor element at a good resolution, as well as allowed the interpretation of a mechanism of action [1], which was impossible using only EDS because of its too low detection resolution.

[1] S. Bellayer, M. Jimenez, B. Gardelle, G. Delaplace, J. Bouquerel, S. Duquesne, S. Bourbigot. Polym. Adv. Technol. 26, 8, 2015, 1020–1026.

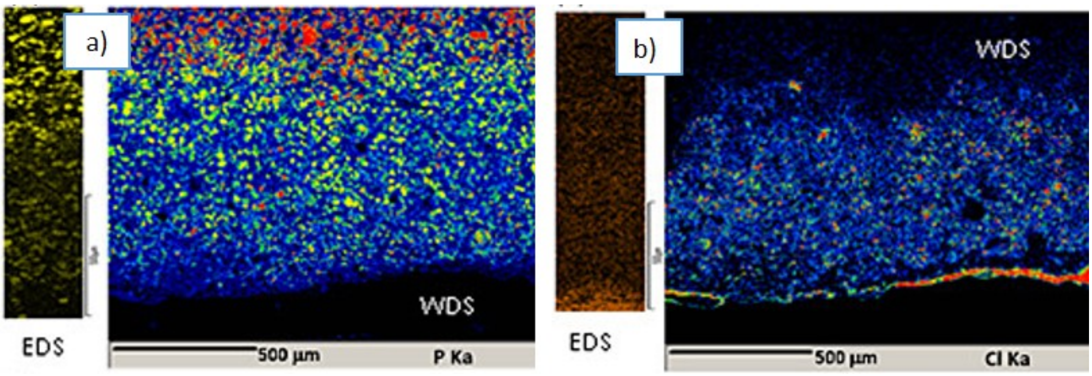


Fig. 1: EPMA (on the right) and corresponding EDS (on the left) X-ray mappings of (a) phosphorus, (b) chloride of the cross section of the epoxy-based intumescent coating after immersion in salt water.

CL15

FLUORESCENCE SPECTROSCOPY AND IMAGING ON AGED POLYMERIC PV ENCAPSULANTES

Gabriele C. Eder[1], *Yuliya Voronko*[1], *Bernhard Kubitschek*[2], *Karl Knoebl*[3]
[1)] *OFI, Austrian Research Institute for Chemistry and Technology, Vienna, Austria*
[2)] *AIT, Austrian Institute of Technology GmbH, Energy Department, Vienna, Austria*
[3)] *University of Applied Sciences, FH Technikum Wien, Vienna, Austria*

gabriele.eder@ofi.at

UV-Fluorescence measurements have recently been proven to be a quite selective tool to detect degradation effects of polymeric encapsulates within photovoltaic (PV) modules. UV- Fluorescence effects can best be detected in dark environment using for excitation an UV-light source (LEDs or lasers) and as detection tool either (i) the eye or a photographic camera (image creating method) or (ii) an probe connected to an UV/VIS spectrometer via an optical fibre (visualising the downshift of the reflected light). The method can be applied completely non-destructive to PV-modules mounted outside in the field or indoors in the laboratory.

In the original state directly after production, the polymeric encapsulant (mostly ethylene-vinyl acetate, EVA) of the PV modules does not show any fluorescence effects. However, with increasing lifetime and in dependence on the climatic stress factors at the installation site, increasing fluorescence showing specific patterns can be observed. It has to be noted that the fluorescence spectra obtained for the naturally and/or artificially aged modules depend

(i) on the composition of the PV-module; in particular if gas tight (glass, backsheets with Al-barrier layers) or breathable (polymeric backsheets) are used

(ii) the type of EVA used – especially on the additive mixture and peroxidic curing system used

(iii) on the stress factors (temperature, humidity, irradiation, ….) applied at the installation site or in the climatic chamber in accelerated ageing tests

As many of the thereby visualized effects cannot be unequivocally linked to clear causes/failures yet, the work presented focusses on the chemical and physical explanation/clarification of the depicted artefacts through combination with other image based methods (EL and Pulse-Phase thermography) and chemical analysis (IR Spectra, DSC und TD/GC-MS) of the same modules.

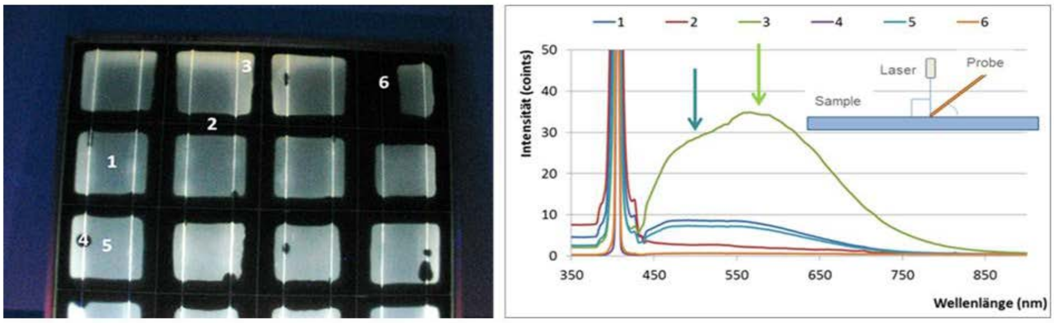


Figure left: Fluorescence image; right: Fluorescence spectra of the positions indicated in the image

CL16

IN-SITU RAMAN SPECTROSCOPY DURING ELECTROCHEMICAL OXIDATION OF ANILINE

Zuzana Moravkova, Alexey Popov
Leibniz Institute for Solid State and Materials Research, Dresden, Germany

zuzana.moravkova@pada.cz

Aniline oligomers, the first products in polyaniline (PANI) preparation, play an important role in the evolution of various morphologies of PANI. The molecular structure and adsorption/assembly properties of aniline oligomers are still under the discussion. Two types of aniline oligomers have been reported in the literature [1]:

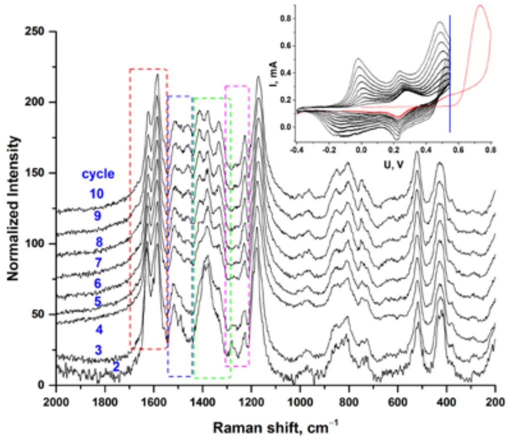
- Short oligomers of molecular structure different from PANI, supposedly containing N-substituted phenazinium structure and/or branched quinonoid structures [1]. They were observed at first stages of chemical oxidation of aniline, especially at higher pH. Such oligomers are not expected during the electrochemical oxidation of aniline in acidic media [2].

- Linear oligomeric structures were observed to grow from the former during the chemical oxidation of aniline and are accepted as the only intermediates in the electrochemical oxidation of aniline. Even though they have the basic structure of PANI-chain, but the distribution of charges on the short chain segments is different (Figure).

To observe the intermediates of aniline oxidation, in-situ studies are necessary, but electrochemical experiments are so far limited to UV-Visible spectroscopy. Resonance and surface enhanced Raman spectroscopy and spectroelectrochemistry are good methods of studying thin films in their natural environment [3].
In this work, the electrochemical oxidation of aniline have been studied in-situ on platinum and roughened gold electrode. The first products of electrochemical oxidation of aniline are directly observed by Raman spectroscopy and SERS, and presented in the context of chemically prepared aniline oligomers.

Acknowledgement: The stay of Zuzana Moravkova at IFW Dresden is supported by DAAD via Leibniz fellowship.

[1] J. Stejskal, M. Trchova. Polym. Int. 2012, 61, 240.
[2] E. Dmitrieva, L. Dunsch. J. Phys. Chem. B 2011, 115, 6401.
[3] M. Trchova, Z. Moravkova, J. Dybal, J. Stejskal. ACS Appl. Mater. Interfaces. 2014, 6, 942.



Raman spectra measured at potential 0.55 V vs. Ag/AgCl on platinum electrode at different cycles of potentiodynamic oxidation of aniline. Spectral ranges connected with ring-stretching modes, N-H bending modes, stretching modes of charged and uncharged –N- are marked with red, blue, green and pink rectangle, respectively. Inset: Cyclovoltagram of the polyaniline film growth on platinum electrode.

CL17

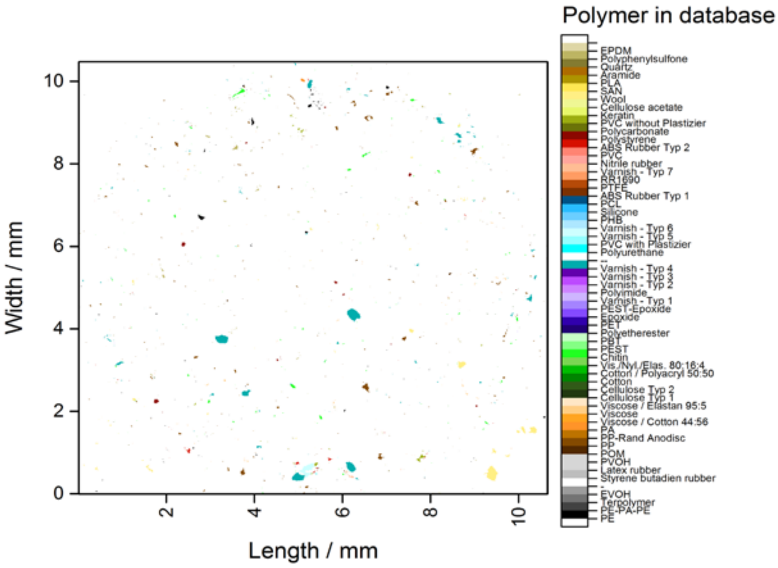
AUTOMATED ANALYSIS OF µFTIR IMAGING DATA FOR MICROPLASTIC SAMPLES

Sebastian Primpke[1]*, Claudia Lorenz*[1]*, Richard Rascher-Friesenhausen*[2,3]*, Gunnar Gerdts*[1]
[1)] *Alfred-Wegener-Institute Helmholtz Centre for Polar and Marine Research, Helgoland, Germany*
[2)] *Hochschule Bremerhaven, Studiengang Medizintechnik, Bremerhaven, Germany*
[3)] *Fraunhofer MEVIS, Institute for Medical Image Computing, Bremen, Germany*

sebastian.primpke@awi.de

The pollution of the oceans with plastic particles smaller than 5 mm, called microplastics is moving into the focus of science and governments. To determine the amount of microplastics several steps are necessary, starting with the sampling, work up and finally analysis. Each step has its own challenges due to small size of the particles.[1] For analysis the imaging with µFTIR microscopy is a powerful tool allowing the analysis of complete filters. Systematic screening for optimal conditions and filter materials have already been performed.[2] While the measurement is performed mostly by the spectrometer, the data interpretation process is highly time consuming as it has to be made by hand on the basis of false color images. To overcome the manual part we developed a novel approach based on the Bruker OPUS© Software to decrease the high time demand for the analysis of microplastics. With this approach it was possible to analyze measurement files from focal plane array (FPA) FTIR mapping containing up to 1.8 million single spectra. These spectra were compared with a database of different synthetic and natural polymers by various methods. By benchmark tests their performance was monitored with the focus on accuracy and data quality. After optimization high quality data was generated which allowed image analysis. Based on these results an approach for image analysis was developed, giving information for the particle size distribution for each polymer type as well as their distribution on the filter. It was possible to collect all data with relative ease even for complex sample matrices. This approach has significantly decreased the time demand for the interpretation of FTIR-imaging data and increased the generated data quality.

[1] M. Bergmann, L. Gutow, M. Klages. Marine Anthropogenic Litter, Springer, Cham Heidelberg New York Dordrecht London, 2015.
[2] M. G. J. Löder, M. Kuczera, S. Mintenig, C. Lorenz, G. Gerdts. Environ. Chem. 2015, 12, 563-581.



Result of the automated filter analysis for a sediment sample showing microplastic particles in combination with particles of natural origin. The particles are labeled with different colors representing the found database hit. The gained data is suitable for image analysis yielding particle size and distribution.

CL18

INVESTIGATION OF MICROPLASTICS IN MARINE SAMPLES BY FTIR AND RAMAN MICROSPECTROSCOPY

Andrea Käppler[1], Dieter Fischer[1], Julia Muche[1], Klaus-Jochen Eichhorn[1], Christian Laforsch[2], Sonja Oberbeckmann[3], M. Labrenz[3]
1) Leibniz Institute of Polymer Research Dresden, Germany
2) University Bayreuth, Animal Ecology I, Bayreuth, Germany
3) Leibniz-Institut für Ostseeforschung Warnemünde, Germany

fisch@ipfdd.de

Several million tons of plastic debris enter the oceans every year caused by industry, inappropriate disposal of waste, waste from fishing activities and waste from ships. Macro plastic parts in the ocean are degraded to secondary microplastics (MP), mostly in the range from 1 µm to 5 mm. Primary MP on the other hand, are microbeads in cosmetic products, cleaning agents and industrial incorrect disposed raw materials. The impacts of MP on marine ecosystems can cause many problems for animals, birds and humans, like the absorption of toxic contaminants by MP, the potential association of MP with pathogenic microorganism, the mistake with food and that MP itself can contain toxic additives.

We show the first results, achieved with samples collected from different sites in the Baltic Sea and adjacent river systems, gathered from the water surface, from the water column and from sea sediments and beaches to get knowledge of the composition, size and distribution of MP in the oceans.

After preparation we get cleaned samples on a silicon filter [1]. On this filter we identify MP by FTIR and Raman microspectroscopy. All particles > 500 µm are separately measured. The particles < 500 µm remain on the filter and will be measured individual and by imaging. Afterwards we identify the polymer and the particle size and distribution.

The most identified plastic types are PE, PP, PS, PVC, PC and polyester. An example for a Raman image is shown in Fig. 1.

We compared Raman imaging and single point measurements and additionally FTIR and Raman Imaging. These and further topics, like the comparison of different sampling sites will be discussed in the talk. It can be summarized that Raman microspectroscopy is an outstanding method to detect MP in aquatic systems down to 1 µm. Detailed results are described in [1, 2].

[1] A. Käppler, D. Fischer, K.-J. Eichhorn et. al. Anal. Bioanal. Chem. 2015; 407: 6791.
[2] D. Fischer, A. Käppler, K.-J. Eichhorn. American Laboratory 2015; 47: 32.

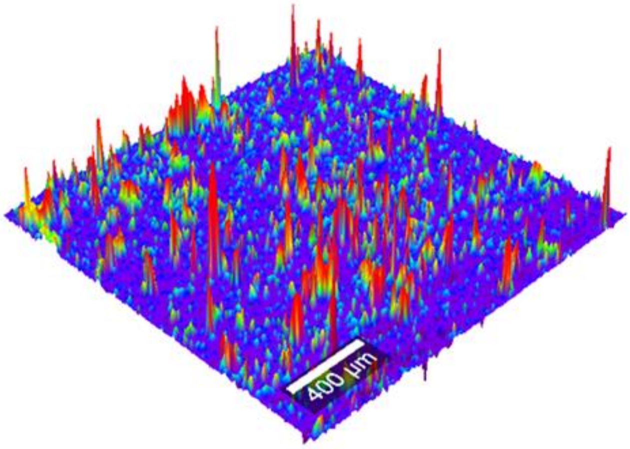


Fig. 1: 3D Raman Image (z-axis: intensity of the CH range 2800-3000cm-1) of a sample from a setting sediment sampler at the island Gotland, Baltic Sea

CL19

PYROLYSIS GAS CHROMATOGRAPHY MASS SPECTROMETRY (PY-GCMS) FOR SIMULTANEOUS TRACE ANALYSIS OF NINE COMMON PLASTICS IN ENVIRONMENTAL SAMPLES

Marten Fischer, Barbara M. Scholz-Böttcher
Carl von Ossietzky University of Oldenburg, Institute for Chemistry and Biology of the Marine Environment, Oldenburg, Germany

bsb@icbm.de

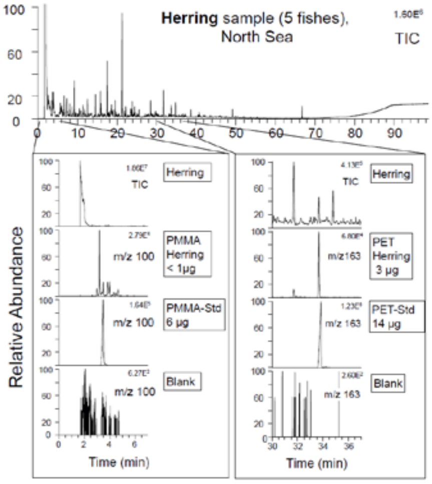
There is a raising concern about plastic debris in the marine environment. The proportion of micro plastic (MP) is expected to increase steadily due to ongoing fragmentation processes. Sources, distribution and accumulation behavior of small MP (< 1mm) is comparably poorly understood due to restricted availability of data (e.g. Cózar et al. 2014, PNAS 111, 10239-10244).

Identification and quantification of MP in the water column, sediment and biota is time consuming and leaks of standardization. Exclusively microscopically recognition and counting forfeit reliability below 100 µm particle size. Combined microscopic and spectroscopic FTIR- and RAMAN-techniques are the most established in MP analysis. Counting their size related abundances concurrently MP particles are identified via their polymer specific spectra.

Pyrolysis gas chromatography mass spectrometry (Py-GCMS) is frequently used for identification and rarely for quantification of single plastics in natural samples. Comparably fast, quantitative chemical and weight related data complementary to number and size related records are generated.

Our study applies Py-GCMS combined with thermochemolysis for simultaneous analysis of nine majority plastics (PE, PP, PET, PS, PVC, PC, PA, PMMA, PUR. Selected fragment ions of specific pyrolysis products enable a sensitive polymer specific identification and quantification on µg trace level and even below. Prior to Py-GCMS environmental samples need a multistep enzymatic, oxidative treatment and occasionally pre- or pursued density separation in order to reduce accompanying organic as well as inorganic matrix compounds and achieve substantial MP-concentrations.

The quality and potential of this method will be shown concerning reproducibility, recovery, reliability and possible interferences with common occasionally remaining matrix particles like wood, chitin and cellulose fibers. The application of Py-GCMS to environmental samples will be shown on selected fish samples.



Total ion chromatogram (TIC) of a processed herring sample (juveniles, 5 stomachs pooled) with amplified sections of indicator ion chromatograms for PMMA and PET opposed to respective traces from standards (Std) and procedural blank.

CL20

MICROPLASTIC ANALYSIS BELOW 100 µM: RAMAN MICROSPECTROMETRY TO CORRECT VISUAL COUNTINGS

Robin Lenz[1], *Kristina Enders*[1], *Colin Stedmon*[1], *David Mackenzie*[2], *Torkel Gissel Nielsen*[1]
[1)] *Technical University of Denmark, National Aquatic Institute, Copenhagen, Denmark*
[2)] *Technical University of Denmark, Department of Micro- and Nanotechnology, Kgs. Lyngby, Denmark*

roble@aqua.dtu.dk, kren@aqua.dtu.dk

Many studies on microplastic as environmental pollutants exclude items < 300 µm. This allows for a sufficiently accurate analysis using simple and inexpensive methods, i.e. visual microscopy. However, knowledge about occurrence, physical and chemical properties and distribution of microplastics in the lower µm size range are of special interest for two major reasons. These particles are in the food size range of many planktonic key species at the bottom of marine foodwebs. Secondly, more detailed studies on small-sized microplastics (potentially including nanoplastics) are needed to better understand the underlying fragmentation and inter-compartmental exchange dynamics, thus the cycling of marine plastic litter from sources to sinks.

In a pilot study 2014/15 [1,2], we applied a newly designed in-line filtration device aboard the Danish research vessel DANA, where subsurface samples were taken along a transect from the North Sea across the Atlantic to the Sargasso Sea region. The analysis of filtered microplastic particles was done by single spot measurement Raman microscopy, where we could show an accuracy increase in the size range < 100 µm, compared to criteria-based visual microscopy. The spectroscopic analysis was conducted using an own library of material reference data, which also included spectra of "natural", i.e. weathered post-consumer plastic polymers. We further demonstrated how Raman can be used to reveal information on degradation processes of microplastics from the marine environment by measuring artificially UV-aged plastic polymers.

Although we found a range of signal confounding factors in Raman microplastic analysis, such as strong spectral influence and fluorescence of additives, degradation and residual organic matrices, we argue that Raman is a valuable technique for identification and characterisation of small microplastics, if available methods are developed and adapted especially for microplastic analysis purposes.

[1] R. Lenz, K. Enders, C. Stedmon, D. Mackenzie, T. Nielsen. MarPolBul 100 2015 (1) 82–91.
[2] K .Enders, R, Lenz, C. Stedmon, T. Nielsen. MarPolBul 100 2015 (1) 70–81.

CL21

NMR AND FTIR STUDY OF THERMORESPONSIVE BLOCK COPOLYMERS IN AQUEOUS SOLUTION

Jiri Spevacek, Rafal Konefal, Jiri Dybal
Academy of Sciences of the Czech Republic, Institute of Macromolecular Chemistry, Prague 6, Czech Republic

spevacek@imc.cas.cz

It is well known that poly(N-isopropylacrylamide) (PNIPAm) and other thermoresponsive polymers show in aqueous solutions a lower critical solution temperature (LCST). They are soluble at lower temperatures but heating above the LCST results in phase separation which makes solutions milk-white turbid. On the molecular level, both phase separation in solutions and similar volume phase transition in hydrogels are assumed to be a macroscopic manifestation of a coil-globule transition followed by further aggregation. Their thermosensitivity makes these polymer systems interesting for miscellaneous biomedical and technological applications.

Using NMR and FTIR spectroscopies we studied D2O solutions of block copolymers poly(ethylene oxide) (PEO)-PNIPAm; these copolymers are soluble in water at room temperature but at elevated temperatures they form micelles [1]. Both linear PEO-b-PNIPAm and Y-shape PEG-b-(PNIPAm)2 copolymers with various length of PNIPAm block were studied. Formation of micellar structures results in a marked broadening of 1H NMR signals for a major part of PNIPAm segments. The fraction of PNIPAm units with significantly reduced mobility (units in micellar core) then can be determined from reduced integrated intensities in high-resolution NMR spectra. We have found that presence of the PEO block and copolymer architecture significantly affect phase transition and structures of PNIPAm component, as well as behavior of water molecules. From ATR FTIR spectra combined with quantum-chemical calculations it follows that at temperatures above the transition the degree of dehydration of PNIPAm segments (C=O groups) is higher in block copolymers in comparison with suspension of the neat PNIPAm. 2D NOESY NMR spectra revealed certain conformation changes already in the pre-transition region.

Acknowledgment: Support by the Czech Science Foundation (project 15-13853S) is gratefully acknowledged.

[1] W. Zhang, L. Shi, K. Wu, Y. An. Macromolecules 2005, 38, 5743-5747.

CL22

INITIAL STAGES OF COIL-TO-GLOBULE TRANSITIONS OF STIMULI-RESPONSIVE POLYMERS IN WATER

Marcin Pastorczak[1]*, M. Nejbauer*[1]*, P. Skibinski*[1,2]*, Cz. Radzewicz*[1]
[1] *University of Warsaw, Faculty of Physics, Institute of Experimental Physics, Warsaw, Poland*
[2] *Polish Academy of Sciences, Institute of Physical Chemistry, Warsaw, Poland*

marcin.pastorczak@fuw.edu.pl

Stimuli-responsive polymers are materials whose solubility, diffusivity and chain conformation may be abruptly changed after even tiny modification of external conditions such as temperature or pH [1]. Most often their stimuli-responsiveness is connected with changes of equilibrium between hydrophilic polymer-water and hydrophobic polymer-polymer interactions which leads to the conformational transition of a polymer chain. Although, the transition itself is rather a slow process of a timescale of microseconds, the changes of polymer-water interactions should happen in a ultrafast timescale.

In this work we study initial (sub-nanosecond) stages of conformational transition in the temperature responsive poly(vinyl methyl ether) and in the pH-responsive poly(methacrylic acid). In order to follow kinetics of the early stages of coil-to-globule transitions in these systems we applied the temperature-jump and pH-jump methods in femtosecond pump-probe infrared and femtosecond stimulated Raman spectroscopies. As a trigger of a pH-jump transition we use 1450 nm pump pulse which excites overtone of the stretching vibration of water, the subsequent relaxation of which leads to the homogeneous thermalization of the sample. As a trigger of the pH-jump we use the photoacid piranine whose pKa decreases from 6 to 0 upon electronic excitation to S1 state.[2] In the aqueous solution of poly(methacrylic acid) it leads to dissociation of piranine into its photobase and a proton and transfer of the latter to carboxylate group of poly(methacrylic acid). The data analysis is focused on the region of polymer C-H stretching modes which is known to reflect well both hydrophilic and hydrophobic interactions in water/polymer systems.[3]

This research has been financed by Polish National Science Centre (NCN) - „Fuga” grant No. DEC-2013/08/S/ST4/00556.

[1] S. Dai et al. Soft Matter, 2008, 4, 435.
[2] B. J. Siwick et al. JACS, 2007, 129, 13412.
[3] Y. Maeda, Langmuir, 2001, 17, 1737.

CL23

NEW PROCESS SPECTROSCOPIC APPROACHES FOR THE COIL-TO-GLOBULE / GLOBULE-TO-COIL TRANSFORMATION IN A CONCENTRATED PNIPAM SUSPENSION

Peter Werner, Roland Hass, Oliver Reich
University of Potsdam, Institute of Chemistry, Physical Chemistry-innoFSPEC, Potsdam, Germany

pwerner@uni-potsdam.de

As a typical member of smart polymers, Poly(N-isopropylacrylamide) (PNIPAM) is one of the most investigated polymers within recent decades. The thermo-sensitive behaviour of PNIPAM has great potential for several physical and biological applications like drug delivery systems, protein separation, biosensors or catalyst carrier. PNIPAM exhibits a reversible coil-to-globule transition induced by a temperature change around the lower critical solution temperature (LCST). Because of the high potential for diverse applications it is of high interest to understand the complete mechanism behind this transition effect.

In order to detect new details behind the transition process of thermo sensitive polymers in concentrated suspensions, inline process analytical technologies (PAT) are required. With the help of PAT dynamic changes during the coil-to-globule transition are detectable.

In this contribution a new PAT for a highly concentrated PNIPAM particle suspension is presented. Photon Density Wave (PDW) spectroscopy is a method to characterize independently the absorption and scattering properties of highly turbid liquid suspensions. With the use of this PAT in an automated reactor the coil-to-globule and globule-to-coil transition of PNIPAM as a function of different heating and cooling rates has been investigated. PDW spectroscopy displays a direct correlation between the heating and cooling rates and the broadening of the hysteresis, i.e. the LCST is dependent of the heating and cooling rates. In addition, an inverse hysteresis is observed by PDW spectroscopy for the PNIPAM transition process.

CL24

LOW-FREQUENCY RAMAN SPECTRA OF PROPYLENE COPOLYMERS AND POLYMORPHS OF POLYPROPYLENE

Elena A. Sagitova[1], *P. Donfack*[2], *G. Yu. Nikolaeva*[1], *K. A. Prokhorov*[1], *P. P. Pashinin*[1],
P. M. Nedorezova[3], *A. N. Klyamkina*[3], *A. Materny*[2]
[1)] *Russian Academy of Sciences, Prokhorov General Physics Institute, Moscow, Russia*
[2)] *Jacobs University Bremen, Department of Physics and Earth Sciences, Bremen, Germany*
[3)] *Russian Academy of Sciences, Semenov Institute of Chemical Physics, Moscow, Russia*

sagitova@kapella.gpi.ru

Raman spectroscopy is a well-known powerful and nondestructive technique, which allows analyzing the structure of polymers in any state from a nascent form through a tailor-made product. Especially, the Raman spectra of polypropylene provide insights about the chemical and phase compositions, the contents of different configurational and conformational states, and the degree of macromolecular orientation. While the spectral range 600-3100 cm^{-1} is often used to characterize the polypropylene structure, the also structurally informative lower wavenumber range 0-600 cm^{-1} is however less studied, in part due to the relatively more demanding low-frequency Raman measurements.

In our work, we have studied low-frequency Raman spectra of random copolymers of propylene with olefins and different polypropylene polymorphs (isotactic α- and γ-phase, syndiotactic, and smectic polypropylene). Here we discuss the evolution of the Raman bands in the region 25-600 cm^{-1} as a function of the changes in the phase composition, polypropylene crystallinity degree and the content of the incorporated monomers (1-butene and 1-octene). We show that the Raman mode at 105 cm^{-1} in the spectra of the α- and γ-phase polypropylene shifts to 97 cm^{-1} upon decrease of polypropylene crystallinity. We observed two lines at 97 and 105 cm^{-1} in the Raman spectra of propylene/1-butene copolymer, if 1-butene content exceeds 20 mol.%. Thus, we found out additional structure-sensitive features in low-frequency Raman spectra of the polypropylene and propylene copolymers.

This work is supported by the Russian Foundation for Basic Research (16-02-00808-a).

CL25

FTIR SPECTROSCOPIC AND RAMAN IMAGING INVESTIGATIONS OF CELLULOSE GRAFT COPOLYMERS

Enrico Pigorsch, M. Zahel, St. Möckel, T. Arndt
Papiertechnische Stiftung, Heidenau, Germany

enrico.pigorsch@ptspaper.de

Cellulose fiber based materials have gained increasing interest as an environment-friendly resource that is as well as biodegradable and renewable and abundant and relatively inexpensive. These materials are already today not only used for packaging but also for composite applications in light weight constructions and others.

Recently, several studies have been undertaken to extend the possible applications of cellulosic material by modifying the surface of cellulose fibers to improve their interfacial adhesion and to give them new thermoplastic properties [1].

Ways of chemical modification of cellulose fibers are to bind small organic molecules or to graft polymer chains onto its surface via the three available hydroxyl groups in the ß-(1-4)-D-glucose units [1,2]. In this way, the main architecture and the inherent properties of the core cellulose fibers remain preserved and a shell of thermoplastic cellulose derivates is composed in order to change the interfiber properties.

The presentation gives results of FTIR spectroscopic and Raman imaging investigations on several differently modified cellulose material (e.g. poly(-caprolactone) grafted) which were performed to verify the successful modification and to analyse differences in the distribution of the modifications as well as between different cellulose fibers and on the surface of single fibers.

The analysis of the Raman imaging measurements showed, in general, a relatively homogeneous distribution of grafted polymer on one fiber but significant differences between different fibers which vary with different reaction times and conditions. Further studies will be aimed to correlate the distribution of fiber modifications with the mechanical and thermoplastic properties of paper sheets made from grafted cellulose fibers.

[1] S. Kalia, M.W. Sabaa (Eds.). Polysaccharide Based Graft Copolymers, Springer Heidelberg 2013
[2] D. Roy, M. Semsarilar, J. T. Guthrie, S. Perrier. Chem. Soc. Rev. 38 (2009) 2046–2064

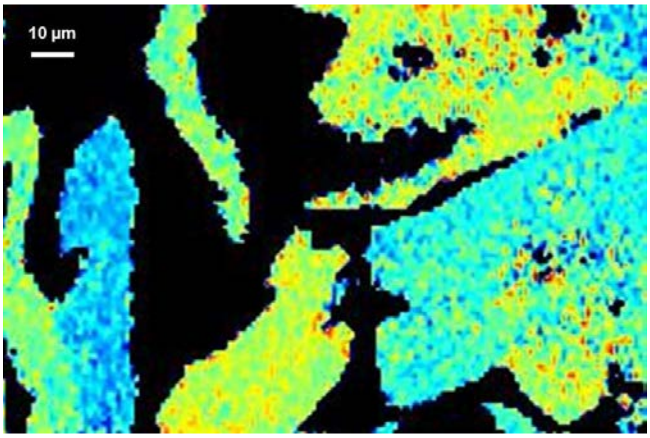


Fig. 1: Raman image of cellulose fibers grafted with poly(ε-caprolactone). The different grey shades show different contents of grafted polymer on the fiber surfaces using the band area of the carbonyl band at 1728 cm-1 from the spectra normalized at the cellulose band at 1126 cm-1.

CL26

MONITORING THE CURE PROCESS OF THIN FILMS POLYMERS FOR MICROELECTRONIC PACKAGING APPLICATIONS BY RAPID SCAN IN-SITU FT-IR SPECTROSCOPY

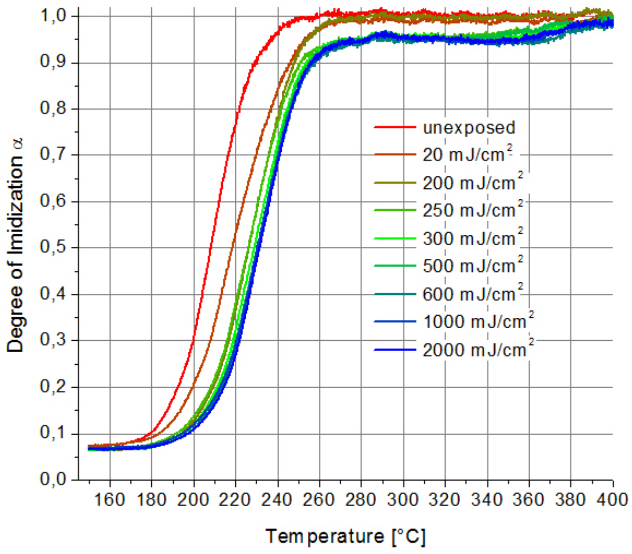
Frank Windrich[1,3]*, Mikhail Malanin*[2]*, Klaus-Jochen Eichhorn*[2]*, Brigitte Voit*[2,3]
[1] *Fraunhofer IZM, Center "All Silicon System Integration Dresden", Dresden, Germany*
[2] *Leibniz Institute of Polymer Research Dresden, Germany*
[3] *Technische Universität Dresden, Organic Chemistry of Polymers, Dresden, Germany*

frank.windrich@assid.izm.fraunhofer.de

Rapid scan in-situ FT-IR spectroscopy was used to characterize the cure process in thin films of two low-temperature cure polymer materials. First, the imidization reaction of an ester-type photosensitive polyimide was investigated in the temperature range of 50 – 450°C by temperature dependent rapid scan in-situ FT-IR spectroscopy. The influence of the UV crosslinkable methacrylic functional group in the polymer sidechain on the imidization reaction was studied. The completion of the imidization is in the range of 250°C for non-crosslinked precursor films. Depending on the amount of crosslinking the full conversion temperature is shown to be shifted to higher values. Above a certain threshold the degree of imidization is limited to ≈95%. The reaction continues with further increase in temperature (see Fig. 1). The imidization reaction in general is characterized by a chemically-controlled and a diffusion controlled region with significant different reaction rates.

Second, the thermosetting process of a low-k polymer dielectric based on divinyl siloxane bis-benzocyclobutene (DVS bis-BCB) was studied. Due to the chemical nature of the DVS bis-BCB resin a highly crosslinked network is formed during the cure process. The network formation has a high impact on the molecular mobility of the reacting groups, leading to a significant change in the reaction rate. Especially above 80% degree of cure at temperatures below 210°C a significant reduction of the reaction rate was measured. This is caused by a diffusion limited process in the thin DVS bis-BCB polymer film. Above 230°C the reaction is more chemically controlled, which yields rather fast a nearly full converted polymer film.

Based on the experimental data a cure model has been developed, which takes into account the conversion dependent diffusion contribution. The model is suitable to characterize the cure process of both low-temperature cure polymer thin films.



Influence of the UV exposure dose on the degree of imidization for an ester-type photosensitive polyimide, measured with rapid scan FT-IR spectroscopy at 5 K/min heating rate

Abstracts of the posters

P1

SYNTHESIS AND CHARACTERIZATION OF POLYMERIC IONIC LIQUIDS BY AB STEP GROWTH POLYMERIZATION

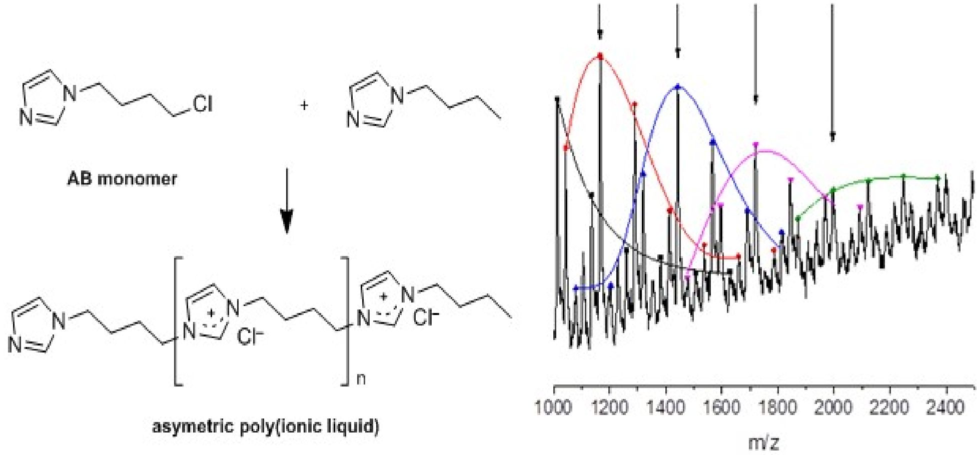
Marcus Suckow[1,2], *Manta Roy*[3], *Karin Sahre*[1], *Liane Häußler*[1], *Nikhil Singha*[3], *Brigitte Voit*[1,2], *Frank Böhme*[1]

[1] *Leibniz Institute of Polymer Research Dresden, Germany*
[2] *Technische Universität Dresden, Organische Chemie der Polymere, Dresden, Germany*
[3] *Indian Institute of Technology, Rubber Technology Centre, Kharagpur, India*

Boehme@ipfdd.de

Poly(ionic liquid)s with alkyl imidazolium moieties in the main chain were synthesized by step growth addition polymerization of the AB monomers 1-(4-chlorobutyl)-1H-imidazole (1), 1-(6-chlorohexyl)-1H-imidazole (2), and 1-(6-bromohexyl)-1H-imidazole (3) in the melt. The molar masses of the polymers were controlled by adding 1-butyl-1H-imidazole as monofunctional chain stopper. The bromine containing monomer 3 polymerized spontaneously at room temperature whereas the chlorine containing monomers 1 and 2 were sufficiently stable up to 40 °C. This could be evidenced by DSC measurements which showed a broad exothermal peak above 40 °C caused by the polymerization. MALDI-TOF investigations proved that exchange reactions which might disturb the expected directional chain topology (AB-AB-AB…) did not occur. This is an important precondition for the intended grafting reactions of the AB monomers on halide containing polymers without any danger of gelation. Additionally, the results of the MALDI-TOF investigations indicated partial complexation of the polymer with the matrix and structural rearrangements during the measurements.

The MALDI-TOF spectrum shown in the figure exhibits distinct peak groups which were attributed to complexes of the polymer with 2,5-dihydroxybenzoic acid which was used as matrix. The average peak distance within the groups corresponds to the expected molar mass of one repetition unit of the polymer but without chlorine as counterion (123.1 Da). This unexpected result indicates that the ionic imidazolium moieties were converted into neutral moieties during the measurements.



MALDI-TOF spectrum of a poly(ionic liquid) with asymmetric chain structure based on the AB monomer 1. The arrows mark peak groups of different polymer/matrix complexes.

P2

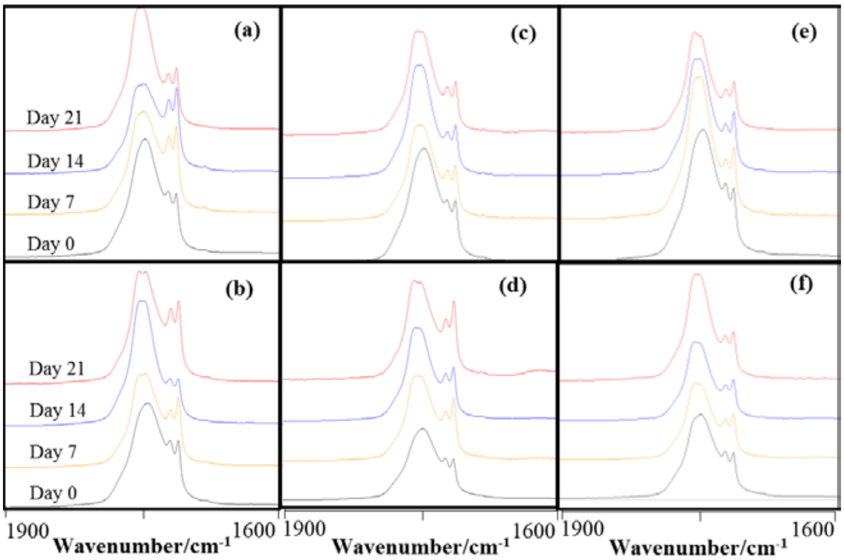
HYDROLYTIC DEGRADATION OF BIODEGRADABLE FILMS BASED ON POLY(LACTIC ACID)/POLY(BUTYLENE SUCCINATE)/FATTY ACID BLENDS

Natthakan Ratsameetammajak[1], *Robert Molloy*[2], *Dieter Baurecht*[3], *Runglawan Somsunan*[1]
1) *Chiang Mai University, Faculty of Science, Department of Chemistry, Chiang Mai, Thailand*
2) *Chiang Mai University, Faculty of Science, Material Science Research Center, Chiang Mai, Thailand*
3) *University of Vienna, Faculty of Chemistry, Department of Physical Chemistry, Vienna, Austria*

r.somsunan@gmail.com

Nowadays, plastics are widely used in many applications, especially for food packaging. However, their slow degradation rates have become a major environmental concern. Therefore, it is necessary to reduce packaging use or replace them with biodegradable plastics that can degrade in a short period of time under certain and specific conditions. In this study, biodegradable films based on poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) blends were produced containing different contents (0, 2 and 4%wt) of fatty acids (lauric acid (LA), palmitic acid (PA) and stearic acid (SA)). The effect of types and amounts of fatty acids on accelerated hydrolytic degradation behavior of the prepared biodegradable plastic films was undertaken in distilled water at 50°C for 3 weeks. The property changes of the films were reported in terms of their weight loss, molecular weight, structures, and fracture surfaces. These were monitored by weight loss measurement, dilute-solution viscometry, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM), respectively. The results show that the films with the fatty acid show higher hydrolysis degradation rates as compared to the films without fatty acid. It was also found that the hydrocarbon chain length affected directly the rate of hydrolysis degradation.

Research reported in this publication was supported by the ASEAN-European Academic University Network (ASEA-UNINET).



ATR-FTIR spectra of films based on PLA and PBS blends containing (a) 2% of LA, (b) 4% of LA, (c) 2% of PA, (d) 4% of PA, (e) 2% of SA, and (f) 4% of SA before and after hydrolytic degradation in distilled water at 50°C.

P3

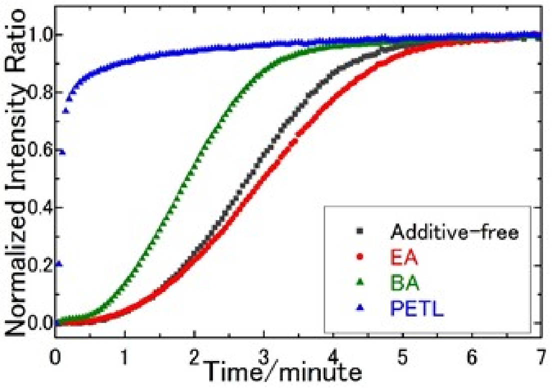
EFFECT OF ADDITIVES ON THE CRYSTALLIZATION BEHAVIOR OF POLY(HYDROXYBUTYRATE-CO-HYDROXYHEXANOATE)

Shuhei Suzuki[1], *Hitoshi Sashiwa*[2], *Harumi Sato*[1]
[1] *Kobe University, Graduate School of Human Development and Environment, Kobe, Japan*
[2] *KANEKA CO., Settsu Osaka, Japan*

166d407d@stu.kobe-u.ac.jp

Poly(hydroxybutyrate-co-hydroxyhexanoate) (P(HB-co-HHx)) is a promising biodegradable copolymer of the polyhydroxyalkanoate family (PHA). P(HB-co-HHx) has an excellent flexibility, because the second monomer prevent for crystallization of PHB and crystallinity of this polymer can be controlled by changing the percentage of HHx. However, there is still a need to improve the crystallization rate. To overcome this point, we have used three types of additives (pentaerythritol ; PETL, behenamide ; BA, and erucamide ; EA). We have investigated the effect of additives on the crystallization behavior of P(HB-co-HHx) by using infrared spectroscopy .

We focused on specific bands of P(HB-co-HHx) and additives in the 3700cm^{-1} ~ 3050cm^{-1} region of IR spectra. A band at 3435cm^{-1} is assigned to the crystal mode of 2ν C=O stretching and a band at 3457cm^{-1} is assigned to the amorphous mode of it. Figure 1 shows the normalized intensity ratio of the band at 3435 and 3457 cm^{-1} for P(HB-co-HHx) and P(HB-co-HHx) containing nucleating agent (PETL, BA, and EA) during isothermal crystallization. The crystallization rate of P(HB-co-HHx) with (PETL) which has four hydroxy groups is faster than that of other films during isothermal crystallization.process. It is very likely that intermolecular interaction between P(HB-co-HHx) and PETL promotes crystallization of P(HB-co-HHx).



Crystallization rate of four kinds of samples during isothermal crystallization process.

P4

NMR STUDIES TO PROBE THE INTERACTION BETWEEN THERMORESPONSIVE POLYMERS AND MODEL DRUGS

Frank Termühlen, Monika Schönhoff
University of Münster, Institute of Physical Chemistry, Münster, Germany

term.frank@wwu.de

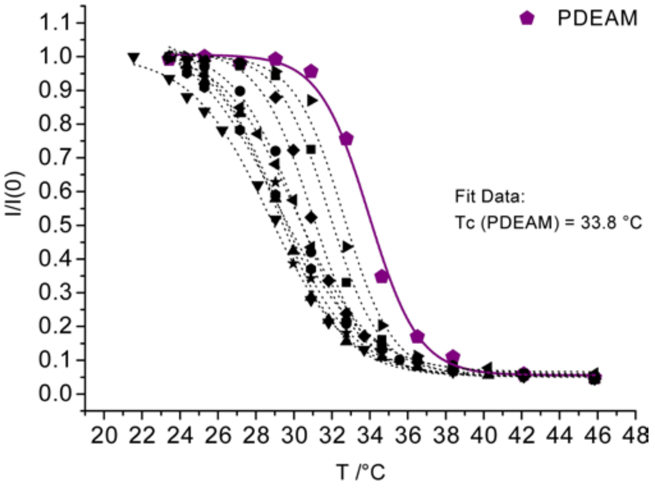
Current research in the field of pharmaceutical technology focuses strongly on the process of controlled drug delivery. In this context thermoresponsive polymers, showing a so called lower critical solution temperature, are of great interest. Polymers exhibiting such a behavior are soluble in water but become insoluble above the LCST. Of special interest in current research is Poly(N-isopropylacrylamide) (PNIPAM) and its derivatives. We have previously studied the interaction of small aromatic model molecules with PNIPAM and their influence on the transition behavior of the polymer using temperature dependent relaxation studies and one-pulse acquisition.[1]

We now turn towards Poly(N,N-diethylacrylamide), which behaves very much alike PNIPAM and even shows the same LCST in pure solutions.

In a comparative study we examine the influence of small aromatic molecules on the LCST behavior of both polymers. Specifically we focus on the influence of substitution patterns on the LCST by comparing ortho, meta and para substitution patterns of Dihydroxybenzene and Hydroxybenzaldehyde on both PNIPAM and PDEAM. We combine data from NMR and DSC experiments, compare homopolymers and gels. We find that the depression of the transition temperature follows the trend ortho < para ~ meta for PNIPAM and PDEAM.

Additional focus has been placed on temperature dependent spin-spin relaxation measurements to study the incorporation of the cosolutes into the polymer matrix.

[1] C. Hofmann, M. Schönhoff. Colloid Polym. Sci. 2012, 290, 689-698.



Integral of the liquid state proton signal of PDEAM in dependence on temperature. Purple points: pure PDEAM. Black points: Different additives.

P5

PHASE SEPARATION BEHAVIOUR OF POLY(ETHYLENE GLYCOL) AND POLY(PROPYLENE GLYCOL) STUDIED BY ATR-FTIR SPECTROSCOPY

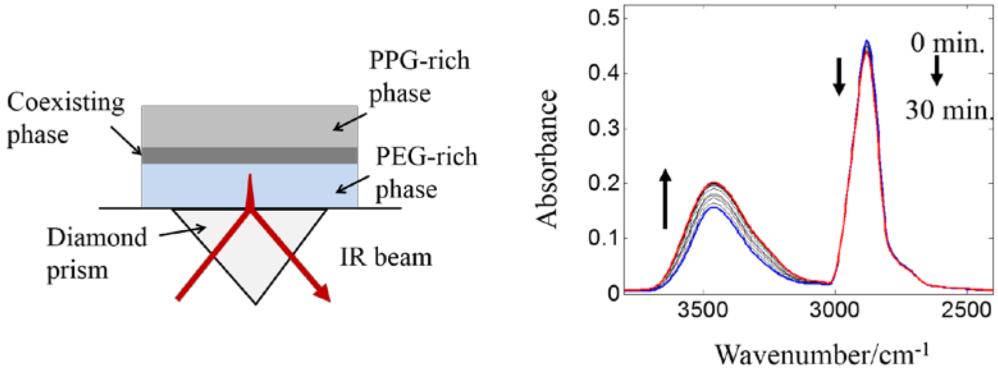
Hideyuki Shinzawa, Junji Mizukado, Sergei G. Kazarian
National Institute of Advanced Industrial Technology and Science, Japan
Imperial College London, Department of Chemical Engineering, London, United Kingdom

h-shinzawa@aist.go.jp

Phase separation behaviour of binary mixture solution based on Poly(Ethylene Glycol) (PEG) and Poly(Propylene Glycol) (PPG) was demonstrated by Fourier Transform Infrared (FTIR) spectroscopy to reveal the development of transient molecular interaction between PEG and PPG.

Time-resolved spectra of the polymer mixture of PEG and PPG were collected as a function of time during the phase separation by in situ ATR-FTIR spectroscopy. The variations of spectral bands were readily observed during the emergence of the PEG-rich phase. For example, with the development of PEG-rich phase, the signal arising from the OH stretching mode of PPG band showed obvious decrease and this was then compensated by the increasing absorbance of the spectral band associated with that of PEG.

The ATR-FTIR spectra were subjected to two-dimensional (2D) correlation analysis to identify subtle but important variation of the absorbance of the spectral bands related to the v(OH) stretching modes. Cross peaks appearing in 2D IR correlation spectra suggested the presence of specific bands, showing delay in the increase in the absorbance of these spectral bands due to the intermolecular interactions between PEG and PPG. Consequently, it was confirmed that some parts of PEG and PEG molecules can develop H-bonded complex based on the interactions of terminal OH groups.



A schematic illustration of in-situ ATR-IR measurement of binary mixture of PEG and PPG undergoing phase separation (left). Time-dependent IR spectra of binary mixture of PEG and PPG collected during phase separation (right).

P6

POLARIZED ATR-IR SPECTROSCOPY INVESTIGATION OF SUPRAMOLECULAR COMPLEXES OF BLOCK COPOLYMERS INTO ULTRA-THIN FILMS

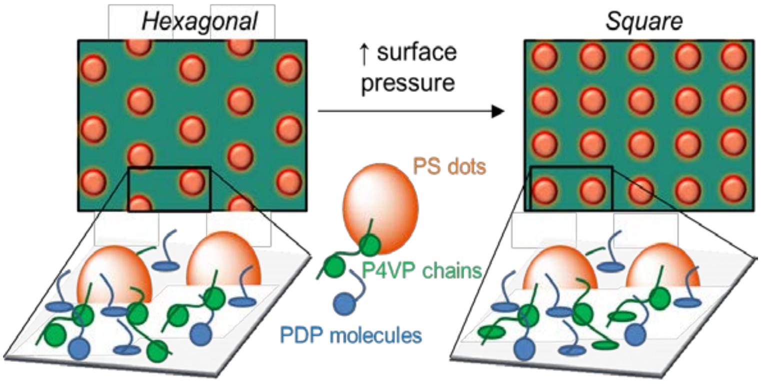
Marie Richard-Lacroix, Kateryna Borozenko, C. Geraldine Bazuin, Christian Pellerin
University of Montreal, Canada

marie.richard-lacroix@umontreal.ca

Langmuir-Blodgett (LB) deposition is efficient for producing ultrathin films of amphiphilic block copolymers with well defined nanostructures and long range order. Here, we investigate LB films of a polystyrene-b-poly(4-vinyl pyridine) (PS-P4VP) copolymer where the P4VP block is complexed with 3-n-pentadecylphenol (PDP) and in a composition where the “dot” morphology is observed.

AFM results highlight that the system undergoes an order-order transition, in which the dot array changes from having hexagonal-like order at surface pressures below the transition to having square-like order at surface pressures above the isotherm plateau associated with the transition. We used polarized infrared (IR) multi-reflection attenuated total reflection (ATR) spectroscopy to investigate specifically the orientation parameters (<P2>) for each of the system moieties, the level of complexation between the P4VP units and the phenol group of the PDP molecules, as well as the changes associated with the transition. Results surprisingly reveal that the alkyl chain of the PDP molecules are dominated by the gauche conformation, with a fairly high orientation perpendicular to the substrate. The main molecular changes associated with the macroscopic transition are an unexpected edge-on to isotropic reorganization of the P4VP pyridine rings and an increase of the level of P4VP complexation with PDP.

We propose a new mechanism that involves an entropically-driven transition from a 2D extended conformation to a 3D folding of the P4VP chains. We further show how it nicely bridges the molecular-level changes to the macroscopic hexagonal-to-square reorganization of the dots and extend the proposed model to pure PS-P4VP and to several other amphiphilic copolymers.



P7

POLYMERS AS TEMPLATES FOR AU AND AU@AG BIMETALLIC NANORODS: INVESTIGATION BY SURFACE ENHANCED RAMAN SPECTROSCOPY (SERS)

Dieter Fischer, *Rafael Contreras-Caceres, Claudine Dawson, Petra Uhlmann*
Leibniz Institute of Polymer Research Dresden, Germany

fisch@ipfdd.de

SERS is a powerful method to obtain Raman signals of low concentrations of molecules adsorbed on metallic surfaces. As surface we fabricated nanoassemblies composed by Au and core-shell Au@Ag bimetallic nanorods immobilized onto pH-responsive poly(2-vinylpyridine) (P2VP) polymer brushes. We proved the potential application of these nanostructures for the fabrication of pH nanosensors capable of detect changes in the pH of aqueous media. The SERS activity of the nanoassemblies was demonstrated using a dye molecule, rhodamine 6G (R6G), as model analyte. The remarkable SERS intensity of silver compared to gold was confirmed. In addition, the SERS signal intensity depended on both the concentration of particles deposited on the functionalized substrate and the thickness of the silver shell surrounding the gold nanorod (Fig. 1).

Enhancement factors on the order of 1011 for immobilized Au@Ag nanoparticles demonstrated the ability of this novel nanostructured system for applications in the detection of conventional SERS analytes and offer the possibility to fabricate stable macroscopic devices for SERS spectroscopy applications.

[1] R. Contreras-Caceres, D. Fischer et al. Chem. Mater. 25, 158-169, 2013.

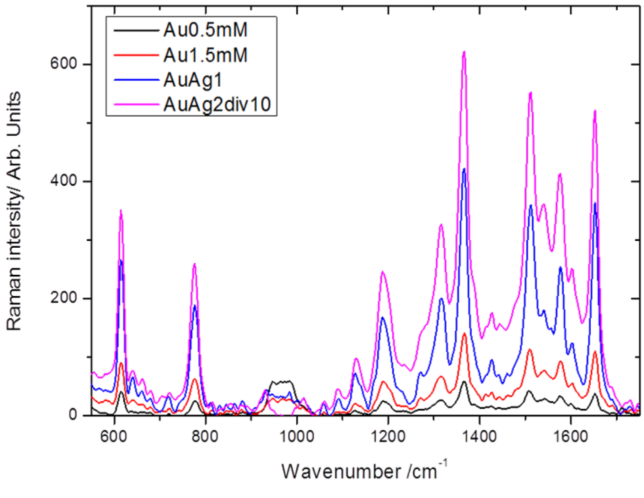


Fig. 1: Raman spectra of R6G (10-5 M) aqueous solution adsorbed on PV2P brushes with Au nanorods 0.5 mM and 1.5 mM, Au@Ag core-shell nanorods with thin Ag layer (AuAg1) and Au@Ag core-shell nanorods with thick Ag layer (AuAg2)

P8

TURBIDIMETRY AND FLUORESCENCE STUDY OF EFFECT OF HYALURONAN ADDITION TO CATIONIC MICELLAR SOLUTION

Tereza Pilgrová, Petra Holínková, Miloslav Pekař
Brno University of Technology, Faculty of Chemistry, Institute of Physical and Applied Chemistry, Brno, Czech Republic

xckrutisova@fch.vut.cz

Hyaluronan as negatively charged polyelectrolyte can interact with positively charged surfactant micelles via electrostatic interactions to form core-shell like aggregates. These self-assembly systems can solubilize hydrophobic active substances and therefore, they are potential carriers in drug delivery applications. This study deals with electrostatic association of cationic micelles of CTAB or Septonex with hyaluronan. The cationic micelle/hyaluronan complexes were studied using turbidimetry and fluorescence spectroscopy method. Turbidimetric titration was chosen as an indicator of the loss of transmitted light intensity due to the scattering effect of particles associated from hyaluronan and surfactant in it. Fluorescent probe pyrene was selected for spectroscopy experiments because of its unique sensitivity to polarity of the medium, so this fluorescence method was used as an indicator of presence of hydrophobic domains in the system. Effect of components concentration and molecular weight of hyaluronan were evaluated. Results of turbidimetry revealed that aggregates formation (turbidity increasing) depends especially on a charge ratio of surfactant molecules and hyaluronan carboxyl groups. It was found a difference in association of low molecular weight and high molecular weight of hyaluronan. Fluorescence results confirmed presence and stability of micellar aggregates in studied systems.

P9

FLUORESCENCE ANISOTROPY STUDY OF MICROSTRUCTURAL CHANGES OF HYALURONAN-CETYLTRIMETHYLAMMONIUM BROMIDE HYDROGEL

Petra Holínková, Filip Mravec, Miloslav Pekař
Brno University of Technology, Faculty of Chemistry, Institute of Physical and Applied Chemistry,
Brno, Czech Republic

xcucekajova@fch.vut.cz

This fluorescence study deals with the microstructural changes of physical hydrogel formed by mixing hyaluronan solution with oppositely-charged surfactant cetyltrimethylammonium bromide (CTAB), where micelles of CTAB form directly either physical crosslinks of the hyaluronan hydrogel network. Fluorescence measurements were carried out on this hyaluronan-based hydrogels containing two different fluorescence probes, hydrophobic perylene and hydrophilic one, rhodamine 6G. The excitation and emission spectra, fluorescence intensity, steady-state fluorescence anisotropy and lifetime of probes in the samples were measured. The fluorescence anisotropy values obtained in these experiments were used to estimate a microviscosity of the corresponding hydrogel regions during fortnight ageing. It is observed that the hydrophobic domains do not undergo significant structural changes. However, the microviscosity of hydrophilic parts gradually decreases, which indicates some structural changes in the nearby area of rhodamine molecules during ageing.

P10

FUNCTIONALIZATION OF SEIRA SUBSTRATES TOWARDS BIOSENSING

Felix Rösicke[1,2,3]*, Christoph Kratz*[2]*, Timur Shaykhutdinov*[1]*, Jörg Rappich*[1]*, Karsten Hinrichs*[2]

[1)] *Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Institut für Silizium-Photovoltaik, Berlin, Germany*
[2)] *Leibniz-Institut für Analytische Wissenschaften - ISAS - e.V., Berlin, Germany*
[3)] *Humboldt-Universität zu Berlin, School of Analytical Sciences Adlershof (SALSA), Berlin, Germany*

karsten.hinrichs@isas.de

In material and life science is a great interest in biosensing surfaces for a variety of bio-technical applications. There are several surface modification techniques providing the possibility to attach specific biomolecules to surfaces, in particular from respective diazonium compounds using different electrochemical techniques [1-2]. Following this route pre-functionalized graphene sheets were transferred to various substrates. For detection of small amounts of surface species we in particular investigated the functionalization of gold island films on silicon as Surface Enhanced Infrared Absorption (SEIRA) templates [3]. The surfaces were characterized by UV-VIS ellipsometry, Infrared Ellipsometry, Infrared Microscopy and Infrared-AFM. The enhancement of infrared vibrational bands of the molecule specific termination was observed.

[1] P. Kanyong, G. Sun, F. Rösicke, V. Syritski, U. Panne, K. Hinrichs, J. Rappich. Electrochem. Commun. 51, 103 (2015).
[2] X. Zhang, A. Tretjakov, M. Hovestaedt, G. Sun, V. Syritski, J. Reut, R. Volkmer, K. Hinrichs, J. Rappich. Acta Biomaterialia 9, 5838 (2013).
[3] C. Kratz, T. W. H. Oates, K. Hinrichs. Thin Solid Films (2016) in press.

P11

IN-SITU-ATR-FTIR SPECTROSCOPY AT POLYPEPTIDE AND POLYELECTROLYTE BASED COATINGS

Martin Müller, Birgit Urban, David Vehlow, Bernhard Torger, Mieke Luisa Möller
Leibniz Institute of Polymer Research Dresden, Germany

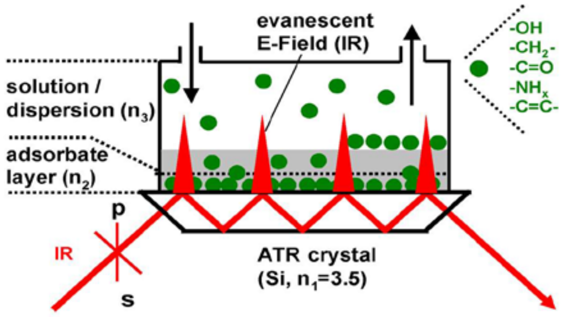
mamuller@ipfdd.de

in-situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy is a powerful tool to characterize polymer coatings at inorganic model substrates [1]. In this contribution we summarize various examples and analytical options of in-situ-ATR-FTIR spectroscopy for the characterization of polypeptide and polyelectrolyte based layers in the application field of life science.

At first the principle ATR-FTIR detection and technical measurement concept based on an ATR mirror attachment operated by the single-beam-sample-reference (SBSR) concept [2] housing a homebuilt thermostatable flow cell (IPF Dresden), which allows for appropriate background compensation and signal to noise ratio, are given. Secondly, exemplary results on polypeptide, polyelectrolyte and polyelectrolyte complex (polycation and polyanion) based coatings are given with respect to:

- Deposition and composition [2-5]
- Conformation and orientation [6-11]
- Interaction to particles [12], proteins [13-17] and drugs [18-20]

[1] Thin Solid Films 2014, 556, 1–8.
[2] Macromol. Rapid Commun. 1998 19 (7), 333.
[3] Macromol. Rapid Commun. 2001, 22 (6), 390-395.
[4] Adv. Biomaterials 2010, 12(12), 676-683.
[5] Polymers 2011, 3, 762-778.
[6] Thin Solid Films 1997, 310/1-2, 138-147.
[7] Biophys. Journal. 2000, 78(5), 2499-2510.
[8] Biomacromolecules 2001, 2(1), 262-269.
[9] J. Phys. Chem. 2003, 107 (32), 8189-8197.
[10] Spectrochim. Acta Part A: Molec. Biomolec. Spectrosc. 2010, 77, 709-716.
[11] Langmuir 2010, 26 (24), 18893–18901.
[12] Journal of European Ceramic Society 2011, 32, 363-370.
[13] Microchim. Acta 1997, 14, 671-674.
[14] Mat. Sci. & Engin. C 1999, 8-9, 167-173.
[15] Macromol. Rapid Commun. 1999, 20(12), 607-611.
[16] Biomacromolecules 2006, 7(4), 1285-1294.
[17] Z.Phys.Chem. 2007, 221, 127-138.
[18] J. Pharm. Biomed. Anal. 2012, 66, 183-190.
[19] Spectrochim. Acta Part A: Molec. Biomolec. Spectrosc. 2013, 104, 546-553.
[20] Biointerphases 2015, 10(1), 011001-011010.



Scheme of the in-situ ATR-FTIR setup including polarized light [1].

P12

POLYMER AND HYBRID PHOTONIC CRYSTALS

Giovanni Manfredi, Paola Lova, Chiara Bastianini, Paolo Giusto, Davide Comoretto
Università degli Studi di Genova, Dipartimento di Chimica e Chimica Industriale, Genova, Italy

giovanni_m_88@msn.com

Photonic crystals are interesting systems composed by materials having different refractive index and organized in a periodic structure with dimensionalities in the order of visible light wavelength. This arrangement creates a photonic band gap, i.e. an interval of wavelengths for which propagation of light is neglected inside the crystal thus creating strong reflections. These systems can be used in many applications [1] and can be obtained using different materials.

Polymers offer the possibility to obtain flexible, low cost multilayers and are also easy to process. The response to vapors of these systems embedding homopolymers or nano-composites is interesting and allows to obtain chromatic sensors [2]. Moreover, fluorescence enhancement effects or optical switching can also be addressed.[3,4] The use of metals and inorganic compounds inside photonic crystal is also a great deal giving the possibility to study plasmonic [5] . In this communication, we present recent results obtained creating polymer and hybrid photonic crystals. Systems comprising periodicities of 1, 2 or 3 dimensionalities are reported discussing both the growth techniques as well as their photonic applications.

[1] D. Comoretto. Springer International Publishing, 2015.
[2] P. Lova et al. ACS Photonics 2, 537-543, doi:10.1021/ph500461w (2015).
[3] R. J. Knarr III et al. Polymer 84, 383-390, doi:10.1016/j.polymer.2016.01.009 (2016).
[4] G. Canazza et al. Laser Phys Lett 11, doi:10.1088/1612-2011/11/3/035804 (2014).
[5] V. Robbiano et al. Advanced Optical Materials 1, 389-396, doi:10.1002/adom.201200060 (2013).

P13

FTIR DETECTION OF DRUG RELEASE FROM POLYELECTROLYTE COMPLEX COATINGS

David Vehlow, Birigt Urban, Mieke Luisa Möller, Bernhard Torger, Martin Müller
Leibniz Institut of Polymer Research Dresden, Germany

mamuller@ipfdd.de

Herein we report FTIR spectroscopic data on the loading and the release of drugs at coatings of polyelectrolyte (PEL) complexes (PEC) [1-4]. PEC coatings loaded by bone healing drugs like bisphosphonates are relevant for the functionalization of bone substitute materials (BSM) like solid implants (titanium based osteosynthetic plates) as well as bone defect fillers (calcium phosphate cements).

Drug loaded PEC coatings were prepared by solution complexation of biorelated polycations and polyanions and integration of drugs followed by casting the formed colloid dispersions onto model and BSM substrates. As model substrates IR transparent silicon and germanium internal reflection elements (IRE) were chosen to have analytical access by both in-situ ATR-FTIR and ex-situ transmission (TRANS) FTIR spectroscopy. In typical experiments, Ge IRE were coated by casting and drying 100 microliter of a drug/PEC NP dispersion and either dipped into aqueous release media (TRANS-FTIR) or immersed by release media in in-situ flow cells (ATR-FTIR) sealing the Ge IRE. Afterwards FTIR spectra in TRANS (dry state) or ATR mode (wet state) were subsequently recorded and the intensities of specific IR bands of the drug were plotted versus release time.

It was evidenced that PEC NP films were stable in contact to the release media by the constantness of related polymer bands with time. Retarded drug releases from PEC NP films up to several days in comparison to the pure drug films were obtained by the intensity decrease of related drug bands like the n(O-P-O) of bisphosphonates. The influence of preparation protocol, PEL topology and media parameters (pH, salt) is discussed.

[1] Biomed. Anal. 2012, 66, 183.
[2] Biointerphases 2013, 8, 25.
[3] Biointerphases 2015, 10(1), 011001.
[4] Nanomaterials 2016, 6, 53.

P14

CHARACTERIZATION OF THIN BIOINSPIRED POLYDOPAMINE FILMS BY IN-SITU-ATR-FTIR SPECTROSCOPY

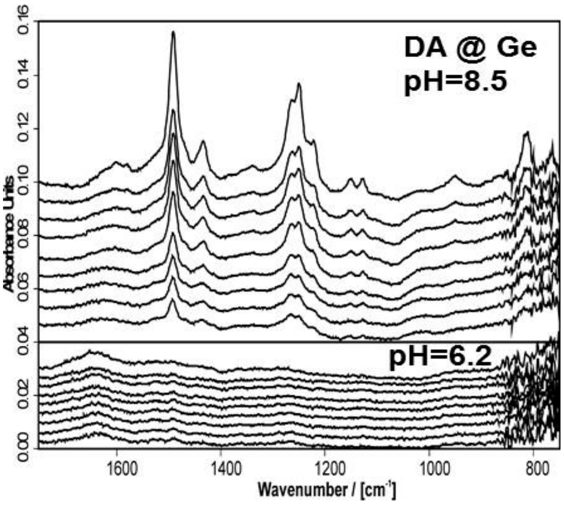
David Vehlow, Birgit Urban, Martin Müller
Leibniz Institute of Polymer Research Dresden, Germany
Technische Universität Dresden, Fachbereich Chemie, Dresden, Germany

mamuller@ipfdd.de

The reactive deposition of dopamine (DA) from weakly alkaline solutions forming adhesive films at various kinds of substrates was initially observed by Lee [1] and further studied by Ball [2]. This process is inspired by the adhesion of mussels via byssus threads, which contain proteins rich in the amino acid L-DOPA chemically related to DA. Still the complete sequence of reaction steps from DA to an adhesive material suggested to be "polydopamine" (PDA) and melanin-like is unresolved. Indole derivatives are claimed to be intermediates on the monomer level further polymerized to PDA.

Herein we present in-situ-ATR-FTIR data on the reactive deposition of DA and other catecholamines at germanium (Ge) and silicon (Si) model substrates [3] to further elucidate the deposition mechanism and final structure of the PDA material. A dedicated pseudo-double-beam ATR-FTIR attachment [4] housing a thermostatable flow cell allowing presence or absence of oxygen to a certain degree was used. DA solutions were contacted to Ge and Si internal reflection elements (IRE) and DA deposition was followed as a function of time or concentration. The formation of thin PDA films (SFM: 50 nm) at Ge could be rationalized via characteristic IR bands assigned to phenolic and aromatic groups. Their time courses were correlated revealing deposition rate constants of k = 0.013 min-1. Furthermore, inner surface sensitive ATR-FTIR and bulk phase sensitive transmission-FTIR were used to study the chemical compositions of PDA films, of PDA particles in the bulk phase above PDA films and of original melanin. Obviously, PDA films consist of both surface and bulk (particle) initiated PDA material, the latter of which is rather melanin-like. Finally, application oriented studies revealed sustained release of model drugs and low protein adsorption [5].

[1] Science 2007, 318, 426.
[2] Langmuir 2011, 27, 2819.
[3] Langmuir 2011, 27(20), 12499.
[4] Chimia 1992, 46, 200-214.
[5] Thin Solid Films 2014, 556, 1.



in-situ ATR-FTIR spectra on dopamine deposition kinetics at the Ge substrate.

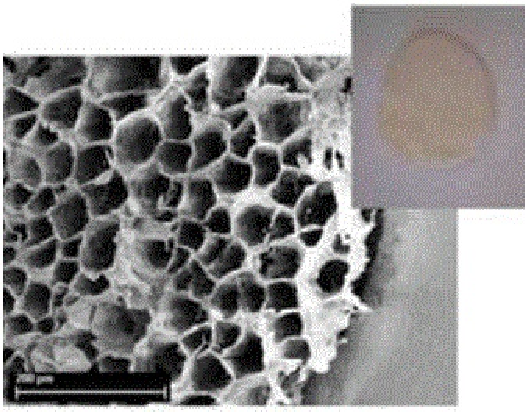
P15

NANOSTRUCTURED BIOCOMPOSITES BASED FLAX FIBERS

Rabiaa Hajji
University of Gabes, National Engineering School of Gabes, Tunisia

rabiaahajji15@gmail.com

The development of natural biopolymer materials is becoming increasingly important due to the decrease of petroleum resource and their use as a substitute for non-biodegradable petroleum based plastics [1]. Flax (Linum usitatissimum L.) is one of the most widely utilized lignocellulosic materials. Flax fibers are very promising because they show high mechanical strength, chemical stability, bio-degradability, non-toxicity and are composed mostly of cellulose (70%), hemicelluloses (15%), pectin (1-15%) and lignin (2-5%) [2]. In recent years, much attention has been focused on cellulose based cryogels. Transforming cellulose to cryogel-like materials enhances its properties and expands its use within the biomedical field and filtration and sorption processes. But yet, there is a lack of research efforts towards the direct use of raw lignocellulosic materials for cryogels preparation. Flax fibers cryogels have been successfully regenerated, for the first time, from 1-ethyl-3-methylimidazolium acetate (EMIMAc). The results show that the Flax fiber concentration in the EMIMAc solutions and the lyophilization process influence the cryogels properties (porosity, bulk density, crystallinity and BET surface area). A direct correlation between the crystallinity of cryogels and the concentration of flax fibers in the EMIMAc solutions, has been established by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) characterizations. Mechanisms of nanofibrils reorganization have been suggested so as to explain the variation of the porosity, the bulk density and mainly the crystallinity of the materials during the lyophilization process



Lightweight and highly porous cryogels with honeycomb-like structures

SEM show that the hierarchical structures,with pores of different sizes from micro to nanoscale, were affected by the Flax concentrations in EMIMAc. show at a low magnification that the cross-section of cryogels has micropores arranged in a honeycomb pattern.Indeed, from the pores shape,the formed ice rods were assumed to have had a polygonal cross-section.

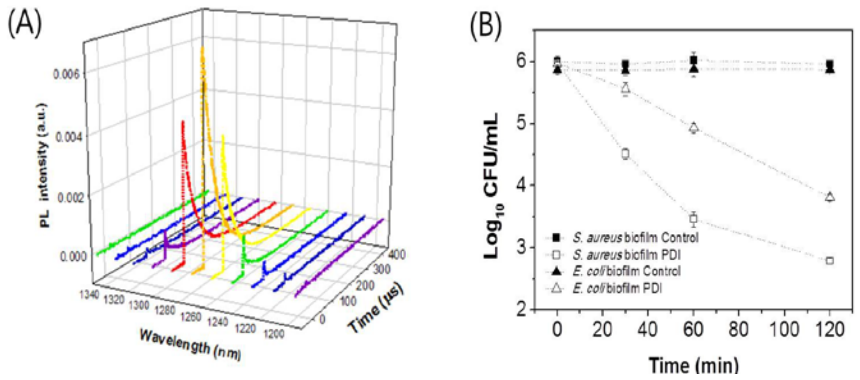
P16

SINGLET OXYGEN DYNAMICS AND BACTERICIDAL EFFECT OF PHOTOFUNCTIONAL POLYMER

Kang-Kyun Wang, *Yong-Rok Kim*
Yonsei University, Seoul, Korea

kara1905@yonsei.ac.kr

Reactive oxygen species (ROS) have been a leading subject in chemical, environmental, medical, and agricultural science since their unique physicochemical properties and highly reactive nature. ROS induce both positive and negative effects by the involvement with metabolism of cells and organs due to the highly active reactivity and selectivity. In a field of life science, there are many applications of ROS such as photodynamic cancer therapy, blood product decontamination, water disinfectant, plant development, plant immunity, and pest exterminations. The photophysical factors determining the efficiency of transient ROS generation has been investigated in terms of the molecular structures and electronic properties. In the presentation, the fabricated polymers are introduced along with singlet oxygen dynamics and their excellent photo-induced functionalities for the photodynamic inactivation of various bacteria.



(A) Time and wavelength-resolved singlet oxygen phosphorescence from photofunctional polymer (B) Survival curves of S. aureus (square symbol, dot line), and E. coli (triangle symbol, dot line) on the inner surface of photofunctional polymer tube after pre-incubation for 24 h: Control (w/o light), PDI (w/ light)

P17

APPROPRIATE OPERATING CONDITIONS OF CYCLONES FOR HDPE DRYING PROCESS

S. A. Razavi Alavi[1,2], *Ebrahim Nemati Lay*[1], *S. K. Afzali*[2]

[1)] *University of Kashan, Faculty of Engineering, Department of Chemical Engineering, Kashan, Iran*

[2)] *Research and Development/Jam Petrochemical Co. Asaluyeh, Bushehr, Iran*

enemati@kashanu.ac.ir

Optimizing operating conditions of cyclones in high density polyethylene (HDPE) drying process play an important role on quality of HDPE powders. In this research work, appropriate operating conditions of cyclones for HDPE drying process have been investigated for a wet feed of 56000 kg/hr containing 40000 kg/hr dry feed and 16000 kg/hr n-hexane in different grades of BL3, BL4 and EX5 in HDPE polymers. Pressure drops in both cyclones has direct effect on flow pattern of gas-particles flow as well as quality of particles collected at the bottom of the dryer. The optimum pressure drops have been achieved by controlling the quality of dried powders as 15 to 17 and 9 to 13 mbar for two-stage dryer respectively. Also by keeping temperature in range of 328.15 to 356.15 K in the bed, the dried product of HDPE powder was produced with humidity close to 0.1 % and the crystallinity about 62.26 % and proper particle size distribution.

P18

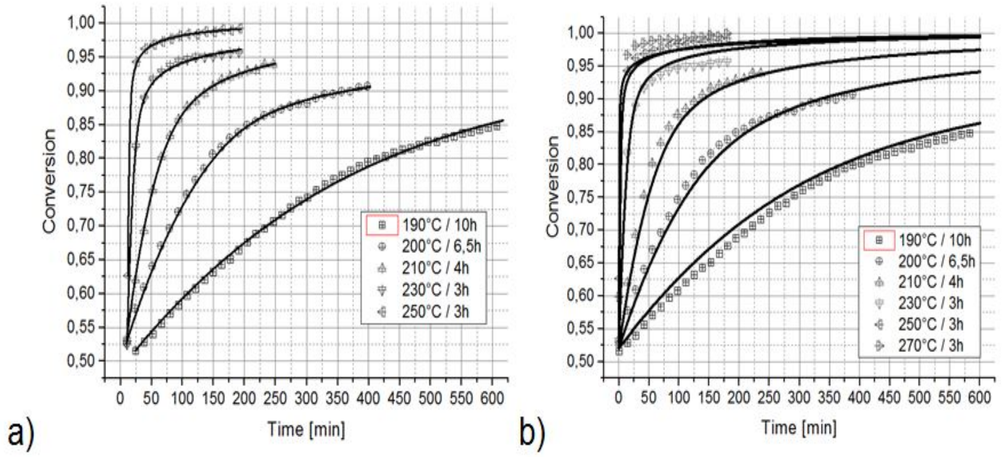
IN-SITU FT-IR STUDY OF THE REACTION KINETICS OF DIVINYL SILOXANE BIS-BENZOCYCLOBUTENE IN SOLID STATE AND MODELING OF THE POLYMERIZATION PROCESS

Frank Windrich[1,3], Mikhail Malanin[2], Klaus-Jochen Eichhorn[2], Brigitte Voit[2,3]
1) *Fraunhofer IZM, Center "All Silicon System Integration Dresden", Germany*
2) *Leibniz Institute of Polymer Research Dresden, Germany*
3) *Technische Universität Dresden, Organic Chemistry of Polymers, Dresden, Germany*

frank.windrich@assid.izm.fraunhofer.de

The polymerization process in solid state of divinyl siloxane bis-benzocyclobutene (DVS bis-BCB) was followed by in-situ Rapid Scan FT-IR spectroscopy at temperatures from 190-270°C, which exceeds the former in-situ FT-IR investigations [1]. A partially polymerized DVS bis-BCB resin available from Dow Chemical was used for this investigation (Cyclotene 3022-57). DVS bis-BCB has 4 reactive elements per monomer unit, which undergoes a [4+2] Diels-Alder cycloaddition to form a highly crosslinked network. The polymerization depends strongly on the molecular mobility of the reacting partners. With increasing polymerization degree the molecular mobility decreases due to network formation leading to a significant change in the reaction rate. A new cure model has been developed (results see Fig. 1), which takes into account the conversion dependent diffusion contribution using an apparent rate constant instead of using a step function [2].

[1] T. M. Stokich, W. M. Lee, R. A. Peters. MRS Proceedings 1991, 227, 103.
[2] M. Wöhrmann, M. Töpper, H. Walter, K.-D. Lang. IEEE 61st Electronic Components and Technology Conference 2011, 392.



Regression results (a) and modeled conversion (b) for the isotherm polymerization of DVS bis-BCB (crosses = measured data)

P19

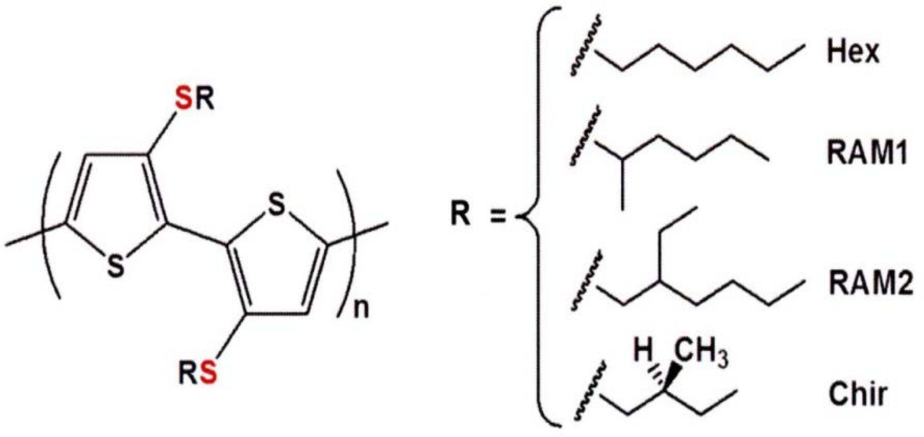
SULFUR-OVERRICH POLYTHIOPHENES FOR BHJ SOLAR CELLS

Elisabetta Salatelli, Francesca Di Maria, Massimiliano Lanzi, Martina Marinelli, Luca Zuppiroli
Università di Bologna, Dipartimento di Chimica Industriale "Toso Montanari", Bologna, Italy

elisabetta.salatelli@unibo.it

The increase in global demand for energy, coupled with the decrease of fossil fuel resources, has spurred a growing interest in politics, academia and industry towards renewable energies. Among these, a valid alternative is definitely represented by the production of electrical energy using photovoltaic devices, whose high production costs, purchase and installation, however, have limited diffusion and use. In recent years, it is therefore sought a solution to the problem finding in π conjugated polymers a promising alternative to silicon, as it is possible to realize devices on flexible substrates, on a large area and with low production costs. The polythiophene derivatives play a key role in this sector because, thanks to their excellent optical properties and charge transport, considerable conversion efficiencies in solar cells of the bulk heterojunction type (BHJ) can be achieved. To overcome the conversion efficiency obtained with conventional polymers, e. g. poly(3-hexylthiophene), it is necessary to design and synthesize new materials with specific characteristics such as low energy gap, high charge mobility, optimal location of frontier orbitals and finally good solubility.

In particular, new sulfur-overrich polythiophenes have been synthesized starting from bithiophene units of head-to-head regiochemistry functionalized in the 3-3’ positions with four different solubilizing thioalkyl chains, to study the effects on the optical and electrochemical properties as well as the morphology of the active layer when blended with the fullerene derivative PCBM. The newly synthesized polymers have been fully characterized by various analytical techniques, such as 1H-NMR, UV-vis and PL spectroscopy, gel permeation chromatography (GPC), thermal analyses (DSC, TGA), cyclic voltammetry (CV) and circular dichroism (CD). Their performances as the active layer in bulk heterojunction solar cells have been carefully examined.



Structure of synthesized polymers

P20

TEMPERATURE-DEPENDENT FT-IR AND RAMAN IMAGING SPECTROSCOPY INVESTIGATION OF PHASE SEPARATION IN THE POLYMER BLEND PHB/PLA

Dieter Fischer[1]*, Miriam Unger*[2]*, Harumi Sato*[3]*, Yukihiro Ozaki*[3]*, Heinz. W. Siesler*[4]
1) *Leibniz Institute of Polymer Research Dresden, Germany*
2) *Physical Electronics GmbH, Ismaning, Germany*
3) *Kwansei Gakuin University, School of Science & Technology, Sanda, Japan*
4) *University Duisburg-Essen, Department of Physical Chemistry, Essen, Germany*

fisch@ipfdd.de

FT-IR and Raman imaging are powerful methods for obtaining information on the miscibility and morphology of polymer blends. Both techniques offer the possibility to combine spectral and spatial information and deliver “chemical images”. Owing to the higher spatial resolution of 400 nm, Raman mapping holds considerable promise over FT-IR imaging (10 µm resolution) in the study of a system with domains on the submicrometer scale.

We study the structural changes of the phase separation of a poly(3-hydroxybutyrate) (PHB)/poly(L-lactic acid) (PLA) (50/50) blend between 25 °C and 175 °C.

From the FT-IR images it could be derived that even beyond the melting point of PLA (145 °C) the lateral position and the geometry of the PHB-rich and PLA-rich phases were retained up to 165 °C. Furthermore, the FT-IR images derived during and after the melting of PHB (174 °C) provided an insight into the homogenization process of the polymer melt.

The FT-IR interpreted domains are in the Raman images clusters of much smaller grains (Fig. 1). The Raman images revealed that domains of PHB in PLA coalesce to more distinct separated phases with increasing temperature up to 125 °C. Larger domains are observed above 125 °C up to the melting point of PHB at 174 °C. Both phases start to coalesce above 125 °C and coalesce more intense during melting.

Based on the imaging spectra below and above melting of both components the first overtones of the C=O absorption bands in the FT-IR spectra and two band pairs at 1730/1776 cm-1 and 843/878 cm-1 in the Raman spectra were used to calculate PHB/PLA and PLA/PHB ratio images [1].

The investigations on the phase separation in the blend PHB/PLA prove that FT-IR and Raman imaging in combination with variable-temperature measurements can provide new insights into structural phenomena of phase-separated polymer blends.

[1] M. Unger, H. Sato, Y. Ozaki, D. Fischer, H. W. Siesler. Appl. Spectroscopy 67 (2013) 141.

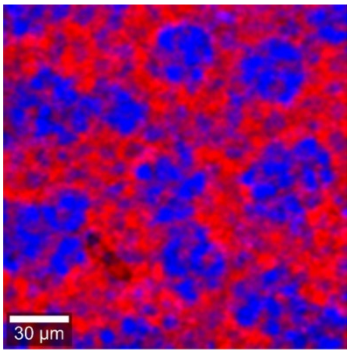


Fig. 1: Raman Image of the blend PHB (blue) / PLA (red) at 25 °C, PLA: 878 cm-1, PHB: 1730 cm-1

P21

RAMAN STRUCTURAL CHARACTERIZATION OF “NECK REGION” FOR FILMS OF SINGLE-CRYSTAL MATS OF ULTRAHIGH MOLECULAR WEIGHT LINEAR POLYETHYLENE

K. A. Prokhorov[1], *Elena A. Sagitova*[1], *G. Yu. Nikolaeva*[1], *P. P. Pashinin*[1], *S. N. Chvalun*[2]
(1) *Russian Academy of Sciences, Prokhorov General Physics Institute, Moscow, Russia*
(2) *Karpov Physico-Chemical Institute, Moscow, Russia*

sagitova@kapella.gpi.ru

The mechanical characteristics and gas permeability of polymers depend strongly on molecular orientation. For this reason, molecular orientation plays a key role in the determination of the physical properties of polymers.

Polyethylene films undergo stretching with the formation of the so-called neck (at the initial stage of deformation). Along the neck (10 - 100 µm in length) the spatial transition occurs from the isotropic to the ordered structure of the material, where the axes of majority of the macromolecules become oriented along the direction of deformation. Structural changes (namely, changes of macromolecular orientation, phase and conformational composition) in the necking region can be studied only with high spatial resolution.

In our contribution, we present a Raman spectroscopic study of the neck region for uniaxially-drawn films of solution-crystallized single-crystal mats of ultrahigh molecular weight linear polyethylene (UHMW PE).

We found out different deformation mechanisms of the single-crystal mat films and the film, prepared by the UHMW PE powder compression, that obviously could be explained by very different structure of the amorphous phase of these samples. In the films, produced by the powder compression, a large number of chain entanglements in the amorphous phase prevent the unfolding of chains during the uniaxial drawing and restrict the draw ratio. On the contrary, the amount of chain entanglements in the films of single crystal mats is relatively small, and, hence, the chain unfolding of the lamellar crystallites can easy occurs during deformation.

Comparison of molecular orientational order at high degree of deformation for polyethylene and composites with different fillers is carried out.

Program III.2 of the Russian Academy of Sciences "Fundamental optical spectroscopy and its applications".

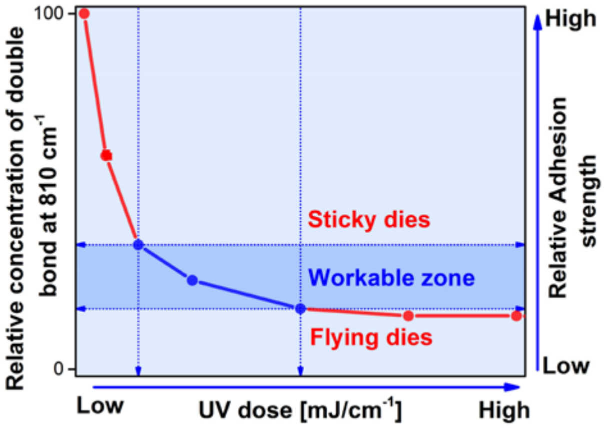
P22

ADHESION CONTROL IN SEMICONDUCTOR PROCESSING VIA FOURIER TRANSFORM INFRARED SPECTROSCOPY

Marko Omazic[1], *Gernot Oreski*[1], *Michael Pinczolits*[2], *Matko Erceg*[3], *Gerald Pinter*[4]
[1)] *Polymer Competence Center Leoben, Austria*
[2)] *Infineon Technologies AG, Villach, Austria*
[3)] *University of Split, Faculty of Chemistry and Technology, Split, Croatia*
[4)] *Montanuniversität Leoben, Institute of Material Science and Testing of Plastics, Leoben, Austria*

marko.omazic@pccl.at

Polymer film with an adhesive layer commonly known as a dicing tape is state of the art for semiconductor processing, providing mechanical protection and ensuring temporary bonding of semiconductors. At the first stage where the wafer is laminated and processed on the dicing tape, high adhesion is needed to enable optimum mechanical sawing results. Before pick-up, the adhesion strength is reduced by UV irradiation for an easy pick-up of separated semiconductor dies. During UV irradiation, the adhesive layer is cross-linked and the most prominent change in chemical structure can be attributed to the double bond of the acrylic adhesive [1]. Thus, the decrease of the double bond groups after UV irradiation can be correlated with decrease in adhesion strength [2]. Control of the adhesion strength on the interface semiconductor/dicing tape represents a crucial parameter for successful processing of semiconductor chips (Graph 1).
Infrared Spectroscopy (FTIR) allows us to get an insight in changes of the chemical structure of the surface adhesive layer before and after the UV exposure process. Therefore, FTIR was used as a method for characterization of the chemical structure of the adhesive, while peel test was used to characterize changes in physical-mechanical properties. Different dicing tapes were investigated.



Graph 1: The control of double bond conversion represents key technology for adhesion performance of dicing tapes and for quality control of the UV curing processes. Therefore, by controlling the double bond conversion - the degree of cross-linking, one can control the adhesion strength.

P23

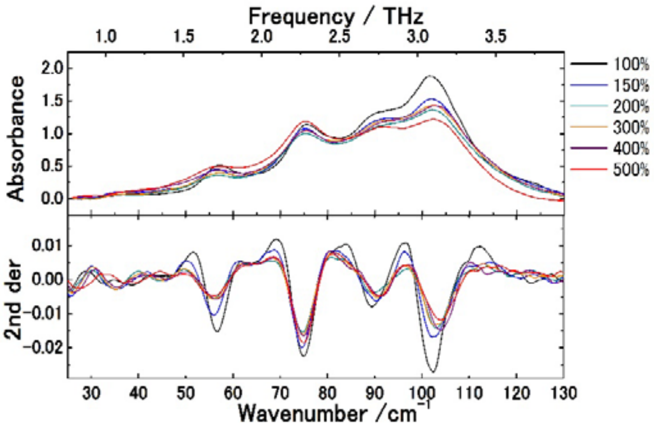
STRETCH-INDUCED CRYSTALLINE PHASE TRANSITION OF POLY(BUTYLENE SUCCINATE) BY TERAHERTZ SPECTROSCOPY

Seika Tatsuoka[1]*, Yukihiro Ozaki*[2]*, Hiromichi Hoshina*[3]*, Harumi Sato*[1]
[1] *Kobe University, Graduate School of Human Development and Environment, Kobe, Japan*
[2] *Kwansei Gakuin University, Graduate School of Science and Technology, Sanda, Japan*
[3] *RIKEN Sendai, Japan*

164d408d@stu.kobe-u.ac.jp

Poly(butylene succinate)(PBS) is a biodegradable synthetic polyester and used in a wide range because of its characteristic, soft and low flexural modulus. Another characteristic of PBS is that the polymer shows reversible crystal transition from α to β crystal form by stretching. The crystalline structure of PBS is usually α crystal (helical structure), but it changes to β crystal (zigzag structure) by drawing. Previous researches have revealed the stretch-induced crystalline phase transition of PBS by using Raman spectroscopy or X-ray diffraction. However the crystalline phase transition with its higher-order conformation during drawing has not reported yet. Therefore, we have investigated the crystalline phase transition in the low-frequency region by using terahertz spectroscopy. In order to get the spectra reflected to higher-order structure of crystal transition, we have investigated polarized THz spectra of PBS during stretching process.

We have observed four peaks in the 30-130 cm-1 region. The position of the peak observed around 100cm-1 shifted as raising the draw ratio of PBS film. While the peak shifts to higher wavenumber in the vertical polarization, it shifts to lower wavenumber side in the horizontal polarization. In consideration of the behavior of the peak around 100 cm^{-1}, we can infer that at least two peaks exist in this wavenumber region and the peak observed in the higher wavenumber is assigned to the β crystal structure.



Terahertz spectra with vertical and horizontal polarization of PBS film measured at room temperature.

P24

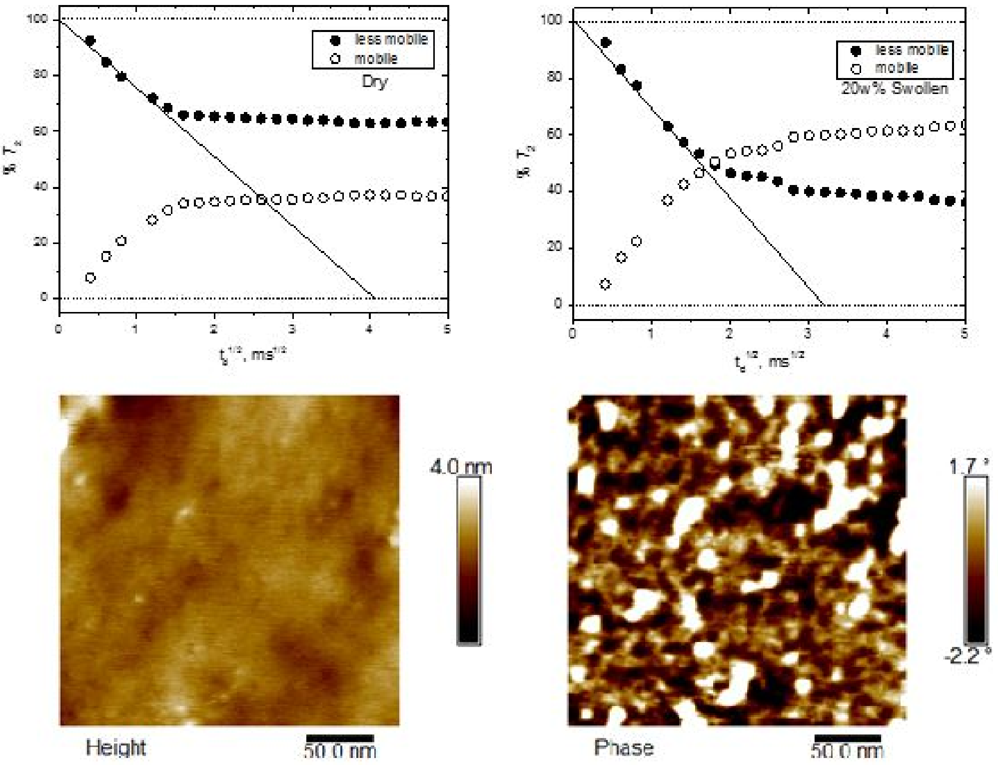
NANO-SCALE MORPHOLOGICAL ANALYSES OF PEG-BASED POLYACRYLATE GEL

Bing Wu[1,2,3], Mingwen Tian[3], Jianjun Xu[3], Junyu Li[3], Dermot Brougham[2], Victor M. Litvinov[3]
1) *Dublin City University, National Institute for Cellular Biotechnology, Dublin, Ireland*
2) *University College Dublin, School of Chemistry, Belfield, Dublin, Ireland*
3) *DSM Resolve, Geleen, Netherlands*

bing.wu2@mail.dcu.ie

Due to it biocompatibility, PEG-based polyacrylate material has been widely used in the field like biomedical coating and tissue engineering. On the other hand, UV-curing has been extensively implemented to produce these materials in large scale in industry partially because of its easy applicability. However, the rather uncontrollable radical polymerization often results in a heterogeneous product with complicated morphological property. These distributed microstructures traditionally are probed by atomic force microscopy (AFM), electron microscopy (EM) and X-ray and neutron diffraction. However, solid state NMR spin diffusion experiments opened up a new possibility in this area with its unique feature which does not require any sample preparation like staining.

In this study, we focused on using NMR to probe the ‘nanogel’ formation during the curing procedure. A series of PEG-based polyacrylate hydrogels with different curing degrees were synthesized via UV-initiated polymerization. As suggested by previous publications using AFM and SAXS analyses, a two–phase-system should be formed during the initial curing stage, and this two-phase system would gradually disappear when the curing reaction completed. By analyzing samples with different swollen degree, the ‘nanogel’ formation is discussed with the change in the domain size and the sample’s corresponding curing degree.



Top: Spin diffusion measurement of samples at dry and swollen condition, a clear change on domain size. Bottom: AFM picture of the samples surface, a clear phase separation.

P25

INVESTIGATION OF RUBBER NETWORK STRUCTURE BY USING LOW-FIELD NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Beatriz Basterra-Beroiz[1]*, R. Rommel*[1]*, F. Kayser*[1]*, S. Westermann*[1]*, J. L. Valentín*[2]*, G. Heinrich*[3,4]
1) Goodyear Innovation Center Luxembourg, Colmar-Berg, Luxembourg
2) Institute of Polymer Science and Technology (CSIC), Madrid, Spain
3) Leibniz Institute of Polymer Research Dresden, Germany
4) Technische Universität Dresden, Institut für Werkstoffwissenschaft, Dresden, Germany

beatriz_basterraberoiz@goodyear.com

Low-Field (LF) Nuclear Magnetic Resonance (NMR) spectroscopy is an essential tool for the analysis of molecular parameters in elastomeric materials [1], as it provides information of both structure and dynamics while being a non-destructive, fast and inexpensive technique.

In this work, a comparison between classical T1 and T2 relaxation experiments [2] and advanced Double-Quantum NMR measurements [3] is discussed for rubber compounds. The understanding of residual dipolar interactions considering different physical models is reviewed in order to quantify the average crosslink density and the related molecular mass between crosslinks. These results are compared to other experimental methods, such as stress-strain tests analyzed using the Tube Model of rubber elasticity [4] and equilibrium swelling measurements [5].

[1] K. Saalwächter. Rubber Chemistry and Technology: September 2012, Vol. 85, No. 3, pp. 350-386.
[2] V. M. Litvinov, P. P. De. Spectroscopy of Rubbers and Rubbery Materials. Rapra Technology Ltd, 2002.
[3] K. Saalwächter. Nuclear Magnetic Resonance Spectroscopy 51 (2007) 1-35.
[4] G. Heinrich, E. Straube, G. Helmis. Adv. Polym. Sci.,1988, 85, 33-87.
[5] J. L. Valentín, J. Carretero-González, I. Mora-Barrantes, W. Chassé, K. Saalwächter. Natural Rubber. Macromolecules 2008, 41, 4717-4729.

P26

NMR STUDY OF THERMORESPONSIVE POLYOXAZOLINE HOMOPOLYMERS AND COPOLYMERS IN AQUEOUS SOLUTION

Rafał Konefał, J. Spěváček, P. Černoch
Academy of Sciences of the Czech Republic, Institute of Macromolecular Chemistry, Prague 6, Czech Republic

konefal@imc.cas.cz

Thermoresponsive polymers are class of materials that respond to changes in temperature. Along with the changes at the macromolecular level dramatic phase or property changes occur. In last decades various thermoresponsive polymers and their derivatives, which exhibit a temperature-induced phase transition and form globules upon heating of their aqueous solutions, has attracted considerable attention [1].

The polyoxazolines (POx)s have been of great interest to researchers due to their versatility in the preparation of materials with tailor-made properties and, more recently, due to their excellent biocompatibility and tunable thermosensitive properties. It has been well established that in aqueous solution (POx)s exhibit interesting solution properties forming self-assembled structures.

We used NMR spectroscopy to study D2O solutions of thermoresponsive poly(2-ethyl-2-oxazoline) (PEtOx) homopolymers and random copolymers PEtOx-co-poly(2-methyl-2-oxazoline) (PMeOx) of various composition. Temperature dependences of integrated intensities in high-resolution 1H NMR spectra enabled us to determine the fraction p of polymer units with significantly reduced mobility. By series of NMR measurements we obtained temperature intervals of the phase transition for all studied samples and we found that temperature dependence of the p-fraction for PEtOx homopolymer shows a lower maximum value and broader transition width in comparison with frequently studied poly(N-isopropylacrylamide) (PNIPAm) (Fig. 1). For PEtOx-co-PMeOx copolymers the transitions are substantially broader and maximum values of the p-fraction significantly smaller in comparison with PEtOx homopolymer. To obtain information on behavior of water molecules during the phase transition we used measurements of spin-spin relaxation times T2.

Acknowledgements: Support by the Czech Science Foundation (project 15-13853S) is gratefully acknowledged.

[1] V. O. Aseyev, H. Tenhu, F. M. Winnik. Adv. Polym. Sci. 196, 1 (2006).

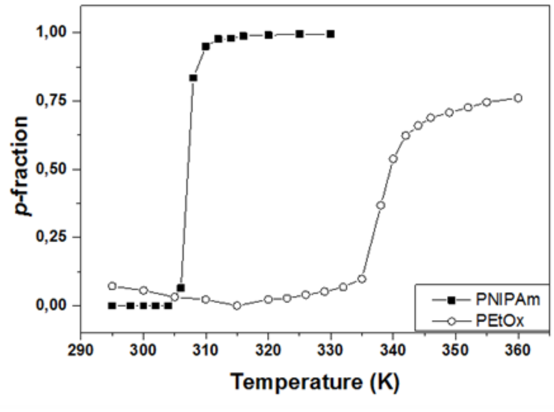


Fig. 1: Temperature dependences of the fraction p of polymer units with significantly reduced mobility for PEtOx (○) and PNIPAm (■) in D2O solutions (c = 5 wt%) during gradual heating.

P27

L-NMR USED FOR THE CHARACTERIZATION OF POLYMERS

Monique F. H. Ensinck, H. Linssen
DSM Resolve, Geleen, Netherlands

monique.ensinck@dsm.com

NMR has become synonymous with the elucidation of structures. It can be used not only for identifying small organic molecules but also for elucidating the polymer composition, sequence distribution and special orientation in combination with other techniques.

1D and 2D NMR is a powerful technique for quantification, information about the chemical composition, characterization of polymers, determination of the average molecular weight (on basis of endgroup analysis), the number of branches and the amount of additives in a polymer.

P28

FCS NANORHEOLOGY OF BIOPOLYMERIC HYDROGELS - A NOVEL APPROACH TO STUDY PASSIVE RHEOLOGY OF HYDROGELS

Jakub Mondek, Miloslav Pekař
Brno University of Technology, Faculty of Chemistry, Brno, Czech Republic

xcmondek@fch.vutbr.cz

Fluorescence correlation spectroscopy (FCS) represents one of the most sensitive fluorescence techniques due to single molecule detection. Microrheology serves as a tool to study viscoelastic properties of microenvironment of observed particles. Firstly, we used 100 nm and 30 nm latex particles to study mean square displacement (MSD) of these particles in Newtonian fluids to verify the use of this method in measurement of micro(nano)rheology. The comparison of MSD determined by FCS compares well with those determined by dynamic light scattering method (DLS), classical microrheology (MR) – in case of 100 nm particels or calculated theoretical MSD. FCS can be used to determine MSD in greater extent of time than both techniques and we can determine MSD in time range where MSD cannot be determined by MR or DLS. Most importantly, we were able to measure passive micro and nanorheology, i.e. MSD as function of time in hydrogels with no extra force from the outside. The movement of particles occurred only due to Brownian motion. Passive nanorheology could represent a great potential in research of viscoelastic properties of small volumes, e.g. very expensive samples or samples where the small focus (or no extra force) is needed. Cells could represent such an example.

P29

IDENTIFICATION OF MICROPLASTICS IN MARINE SAMPLES BY RAMAN MICROSPECTROSCOPY

Dieter Fischer[1]*, Andrea Käppler*[1,2]*, Julia Muche*[1]*, Sonja Oberbeckmann*[3]*, Matthias Labrenz*[3]*,*
Klaus-Jochen Eichhorn[1]*, Brigitte Voit*[1,2]
[1)] *Leibniz Institute of Polymer Research Dresden, Germany*
[2)] *Technische Universität Dresden, Organic Chemistry of Polymers, Dresden, Germany*
[3)] *Leibniz-Institut für Ostseeforschung Warnemünde, Rostock, Germany*

fisch@ipfdd.de

Microplastics (MP) are micro-sized particles of synthetic polymers in a size range from 5 mm down to 1 µm. They have been observed in marine ecosystems worldwide. Because of their small size MP can be mistaken for food and can be ingested by a variety of organisms. Not only MP themselves, but also embedded additives, adsorbed toxic contaminants or associated potentially pathogenic microorganisms pose a potential risk for the marine foodweb. In the first instance reliable data about the occurrence of MP in marine environments and valid analytical systems are necessary for a risk assessment.

We show the excellent possibilities of Raman Microspectroscopy to identify MP in marine samples distinctly on the basis of the chemical structure. At first the results of the manual step-by-step measurement of larger particles (5 – 0.5 mm) of Baltic Sea samples by Raman Spectroscopy will be shown. Secondly the automated Raman Imaging of marine MP samples (< 0.5 mm) will be presented. For this purpose the particles are extracted from the marine sample, chemically and enzymatically purified and finally filtered on a Si filter [1]. By Raman Imaging we get complete Raman spectra for each measurement "point" of a sample area. The space-resolved Raman Images are generated by choosing a characteristic spectral band range of the synthetic polymers. All particles with a high intensity in this spectral range are coloured, (Fig. 1).

The spectrum of each coloured particle is evaluated and, in case the particle is likely of synthetic nature, the polymer is identified using a spectra database. Furthermore the size of all identified MP can be obtained. Detailed results of our investigations are in [2]. In conclusion Raman Imaging is a good method to detect MP down to 1 µm.

[1] D. Fischer, A. Käppler, K.-J. Eichhorn. American Laboratory 47 (2015) 32.
[2] A. Käppler, F. Windrich, M. Löder, M. Malanin, D. Fischer, K.-J. Eichhorn, B. Voit. Anal. Bioanal. Chem. 407 (2015) 6791.

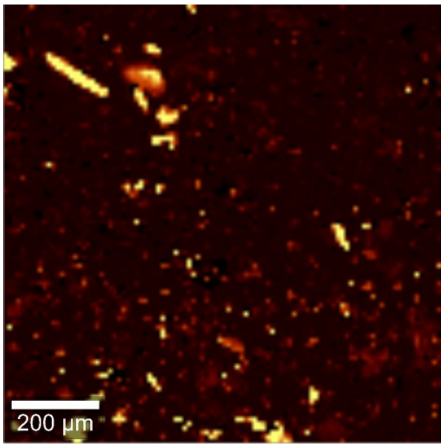


Fig. 1: Raman Image of a marine microplastic sample on a Si filter using the spectral range 2780 – 2980 cm^{-1}

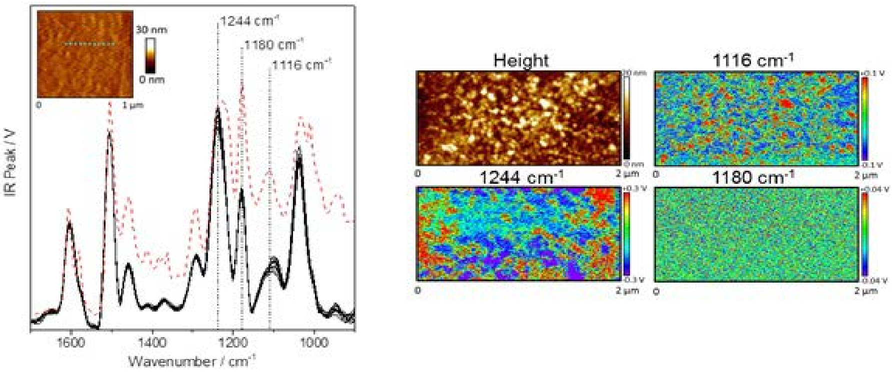
P30

MAPPING THE NANOSTRUCTURAL HETEROGENEITY OF NETWORK POLYMERS USING AFM-IR AND NANO-THERMAL ANALYSIS

Suzanne Morsch[1], *Simon Gibbon*[2], *Stuart Lyon*[1]
[1] *University of Manchester, School of Materials, Corrosion and Protection Centre, Manchester, United Kingdom*
[2] *AkzoNobel Supply Chain, Research & Development, Gateshead, United Kingdom*

suzanne.morsch@manchester.ac.uk

The nanostructure of network polymers is expected to dictate the ultimate physical properties of these materials (e.g., fracture toughness, and small molecule transport through them). Conventionally, internal topography has been characterized using microscopic techniques (AFM, SEM) in conjunction with bulk chemical analysis (vibrational spectroscopy and thermal analysis), so that chemical interpretation of the microscopic evidence has been ambiguous. In this work, we apply cutting edge scanning probe techniques, namely AFM-IR and nano-thermal analysis, to directly characterize the physicochemical heterogeneity within highly cross-linked epoxy-phenolic resins. Deflection of an AFM probe is used as a local sensor to detect photothermal expansion of ultrathin resin sections in response to infrared excitation, or to detect local melting transitions directly using a heated AFM probe. These ultra-high-resolution techniques are used to establish the nanoscale morphology, chemical heterogeneity and local thermal transitions for a series of epoxy-phenolic resin materials, where the effects of cure time, catalyst content and the addition of a monofunctional phenolic additive are examined. We demonstrate that a heterogeneous nanostructure develops within highly cross-linked networks.



Local AFM-IR spectra (alongside the bulk ATR FTIR spectrum, dashed red line); and AFM-IR infrared maps at wavelengths associated with the cross-linking reaction, for 100 nm thick epoxy-phenolic resin sections.

P31

CHARACTERIZATION OF POLY (ε-CAPROLACTONE) BY USING TERAHERTZ IMAGING

Chihiro Funaki[1]*, Takuya Toyouchi*[1]*, Hiromichi Hoshina*[2]*, Yukihiro Ozaki*[3]*, Harumi Sato*[1]
[1)] *Kobe University, Graduate School of Human Development and Environment, Kobe, Japan*
[2)] *RIKEN Sendai, Japan*
[3)] *Kwansei Gakuin University, Graduate School of Science and Technology, Sanda, Japan*

161d413d@stu.kobe-u.ac.jp

Poly (ε-caprolactone) (PCL) is one of biodegradable polyester with relatively low melting point(60 ℃) and flexibility. Terahertz (THz) spectroscopy is a powerful tool for monitoring the intermolecular interaction and higher order structure through the low-frequency vibrations exhibited by large molecules. Therefore, THz spectroscopy should help to understand how large molecules form higher order conformation. In addition, THz imaging makes it possible to measure structures in a sample without altering or destroying it in the process. In the present study, we have investigated the characterization of PCL by using THz imaging.

We measured the absorption peaks of PCL at room temperature during the drawing process in frequency range from 0.5 to 4.5 THz. In the THz spectra of crystalline PCL, two major peaks are found at 1.42 and 2.03 THz. [1] The peak at 2.03 THz was assigned to a vibration of zigzag structure along the fiber axis, and the peak at 1.42 THz was attributed to a vibration due to the intermolecular interaction between zigzag structures.

Figure 1 shows visual image and THz transmission image with the 1.42/2.03 THz peak intensity ratio. The intensity ratio indicates that molecular chain is oriented in a chain direction of stretching. Thus, the THz image was revealed the PCL molecular orientation was different by position during the drawing process.

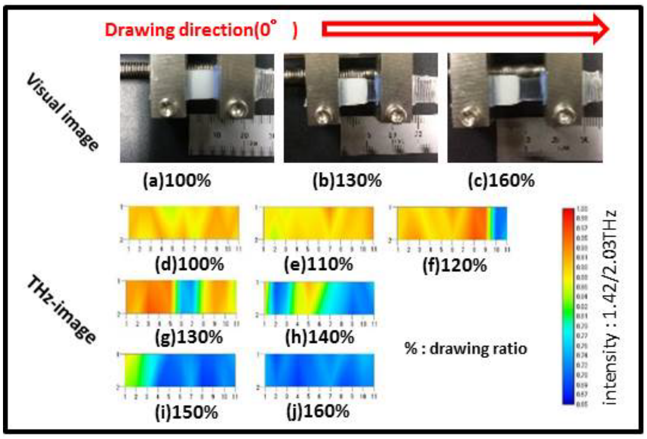


Fig. 1: Terahertz transmission image of PCL press film which produced by stretching. The angle between the stretched direction of the THz electric field was set to 0°(parallel).

P32

IR/NIR SPECTROSCOPIC BIREFRINGENCE IMAGING OF POLYMERIC SPHERULITE

Yuta Hikima, Ryoki Mitsui, Masahiro Ohshima
Kyoto University, Japan

hikima@cheme.kyoto-u.ac.jp

Infrared (IR) Spectroscopic imaging method using polarized lights is a promising technique to obtain simultaneously morphological information, chemical composition and molecular orientation in polymeric materials. However, the procedure was complicated because the calculation of degree of molecular orientation required measuring infrared spectra with at least two different polarization states. On the other hand, polarized optical microscopy (POM) is utilizing to observe the morphology of birefringent materials such as inorganic or polymeric crystals. In this method, the distribution of sample anisotropy can be detected from the intensity map of transmitted light through the sample placed between two polarizers. In this study, a polymer spherulitic crystal placed between two orthogonal polarizers was measured using IR/NIR spectroscopic imaging (wavenumber range was from 6500 to 650 cm-1) to confirm the feasibility of simultaneous imaging of sample anisotropy and chemical information. The background spectrum was measured with only a linear polarizer, and spectroscopic imaging was performed after inserting the sample and the other polarizer into the light path. The sample was polylactide (PLA) spherulite crystallized at 140oC. Transmitted light intensity thorough the PLA crystal was much higher than that through the amorphous region. The transmittance map at NIR region visualized clearly the morphology of polymer spherulite, and agreed well with the POM image. The typical IR/NIR absorption spectra of PLA was observed at the pixels inside the polymer crystal. Thus, it was succeeded that the chemical information and the sample anisotropy were simultaneously visualized using IR/NIR spectroscopic imaging method.

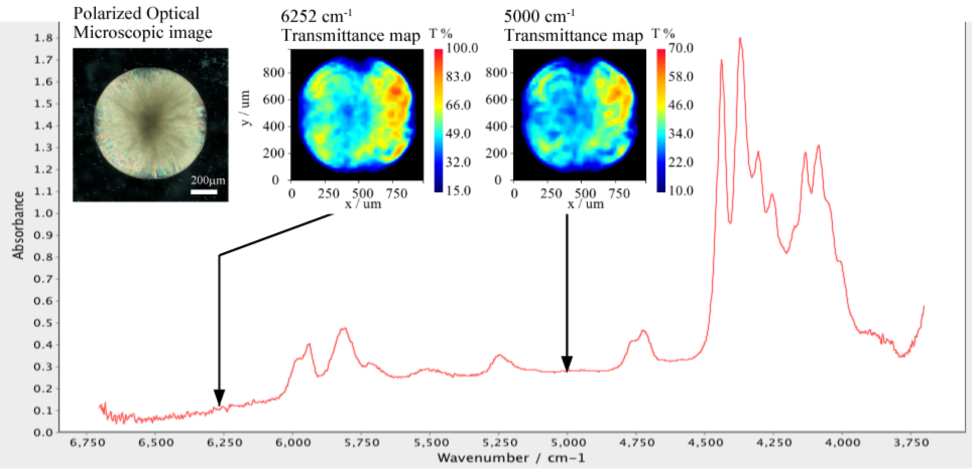


Figure shows the NIR spectrum of a polylactide spherulite placed between two orthogonal linear polarizers. Insets are (left) a polarized optical image and transmittance maps at (middle) 6252 cm^{-1} and (right) at 5000 cm^{-1} of the polylactide spherulite. The morphology of spherulite in the transmittance maps agreed well with that in the polarized optical image.

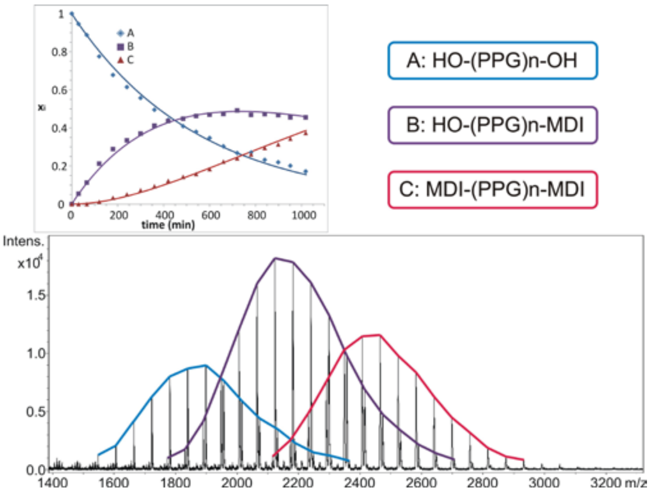
P33

MATRIX-ASSISTED LASER IONIZATION/DESORPTION MASS SPECTROMETRIC STUDY OF THE 4,4`-DIPHENYLMETHANE-DIISOCYANATE AND POLYOL UNCATALYZED REACTIONS

Borbála Antal[1], Tibor Nagy[1], Anita Dékány-Adamoczky[1], József Karger-Kocsis[2], Miklós Zsuga[1], Sándor Kéki[1]
[1] *University of Debrecen, Department of Applied Chemistry, Debrecen, Hungary*
[2] *Budapest University of Technology and Economics, Department of Polymer Engineering, Budapest, Hungary*

antal.borbala@science.unideb.hu

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was applied for the investigation of the reaction of the the 4,4`-diphenylmethane-diisocyanate (MDI) with polyols involving polypropylene glycol (PPG, Mn = 2000 g/mol), polytetrahydrofuran (PTHF, Mn = 1000 g/mol), poly(ε-caprolactone)-diol (PCLD, Mn = 2000 g/mol) and polypropylene glycol glycerol triether (PPG_GL, Mn = 1000 g/mol) without any catalyst. Samples were taken out from the reaction mixtures and quenched by methanol in order to study the kinetics of the reactions. The unreacted polyols and their end-capped derivatives appeared in the mass spectra and the corresponding intensity fractions were obtained. However, the intensity fractions might not correspond to the molar fractions. In order to convert the intensity fractions of the series into molar fractions the relative response factors were estimated applying internal standards in the MALDI samples. These molar fractions versus time plots were utilized to investigate the kinetics of the reactions. The pseudo rate constants were obtained by fitting first-order consecutive reaction equations to the measured data. The order of the pseudo rate constants proved to be the following: PCLD > PTHF > PPG ≈ PPG_GL. Furthermore, it was determined that the reactivity of the hydroxyl group of the polyols is independent from the other reacted hydroxyl group in case of the PCLD, PTHF and PPG. On the contrary, in the case of PPG_GL with MDI the reaction of the second hydroxyl group is faster which shows positive effect for the reaction.



MALDI-TOF MS proved to be an appropriate method for the investigation of the reaction of MDI with polyols

P34

EASY ACCESS TO THE CHARACTERISTIC RATIO OF POLYMERS USING ION-MOBILITY MASS SPECTROMETRY

Shinsuke Kokubo, *Philipp Vana*
Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Germany

shinsuke.kokubo@stud.uni-goettingen.de

For designing and synthesizing polymer, it is often essential to precisely evaluate the molecular weight and the conformation of the individual polymer chains. Within this context, ion-mobility mass spectrometry, IM-MS, attracts attention as a very powerful tool for obtaining these properties. In this study, we measured the contribution of each individual monomer unit to the increment of the collision cross sections, CCS_{eff}, of polymer and exploited this information for evaluating the stiffness, i.e., the characteristic ratio of the polymer.

IM-MS measurements were carried out with Synapt G2 HDMS (Waters). Polyethylene glycol, PEG (M_n ~ 400 and 1000) and polypropylene glycol, PPG (M_n ~ 425, 1000 and 2000) were dissolved in methanol and injected into an electron-spray ionization source, followed by separation according to ion mobility.

PEG and PPG were mainly observed as single sodium cation, Na^+, adducts in the mass spectrum. CCS_{eff}, of PEG and PPG were measured in dependence of the number of monomer units, n. CCS_{eff} were clearly proportional to n in the respective chains. This is analogous to the fact that polymer size is proportional to n. Based on this idea, we derived a globule model equation which connects CCS_{eff} with n (Figure 1).

The correlation factor of this equation contains the characteristic ratio, C_n, which can thus easily be extracted by plotting $5/18 \times CCS_{eff}$ vs $n^{2/3}$ (Figure 1).

The evaluation of the data yielded 3.96 and 5.76 for C_n of PEG and PPG, respectively. They showed very good agreement with the literature-known C_n of 3.6-5.7[1-3] and 4.9-6.2[5,6] for PEG and PPG, respectively.

The presented method is extremely quick and easy to perform and provides stunningly rapid access to the stiffness data of synthetic polymers.

[1] Polymer, 1967, 8, 397.
[2] J. Polym. Sci. Part A-2, 1969, 7, 575.
[3] J. Polym. Sci. Polym. Phys. Ed., 1978, 16, 501.
[4] Polymer Handbook 3rd ed., Wiley, New York, 1989.
[5] J. Polym. Sci. Part B, 1982, 20, 1585.
[6] Macromolecules, 1995, 28, 8629.

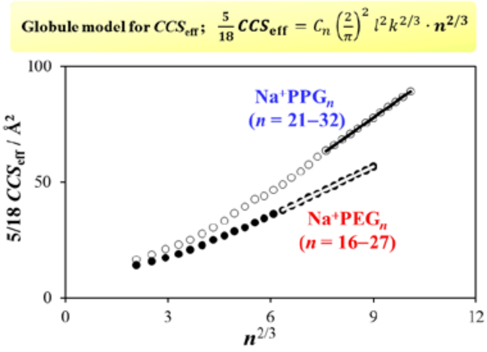


Fig. 1: Experimentally obtained 5/18xCCS_{eff} of Na^+PEG_n and Na^+PPG_n vs $n^{2/3}$. The white and black linear lines correspond to the linear fitting for Na^+PEG_n and Na^+PPG_n.

P35

XPS DEPTH PROFILING BY CLUSTER ION SOURCES FOR CHARACTERIZATION OF POLYMERS, ORGANIC AND COMPOSITE MATERIALS.

Andrey Lyapin, Stefanie Zauzig
Physical Electronics GmbH, Ismaning, Germany

alyapin@phi-europe.com

The objective of successful XPS sputter depth profiling is to accurately identify the layer thicknesses and chemical composition of materials within thin film structures. Cluster ion beam sputtering has been widely used in recent years with the intent to address this essential analytical goal for a broader range of materials, including organic materials. C60 cluster ion beam sputtering provided the first access to quantitative chemical state information below the surface for many polymers, organic and inorganic oxide materials [1, 2].

The recent introduction of argon gas cluster ion beam sputtering to the XPS community has further expanded the capability of successful depth profiling with an emphasis on preserving the chemical structure of challenging polymer and organic materials that exhibit rapid radiation induced damage due to the mobility and reactivity of free radicals that are formed during the sputtering process when other ion sources are used [3].

The purpose of this study is to present the benefits of using either C60 or argon gas cluster ion beam sputtering for XPS compositional depth profiling by characterizing several organic and inorganic thin film structures.

[1] T. Nobuta, T. Ogawa. J Mater Sci 2009 44 1800.
[2] Y. Yamamoto, K. Yamamoto. J. Non-Cryst.Solids 2010 356 14.
[3] T. Miyayama, N. Sanada, M. Suzuki, J. S. Hammond, S.-Q. D. Si, A. Takahara. J. Vac. Sci. Technol. A 2010 28 L1.