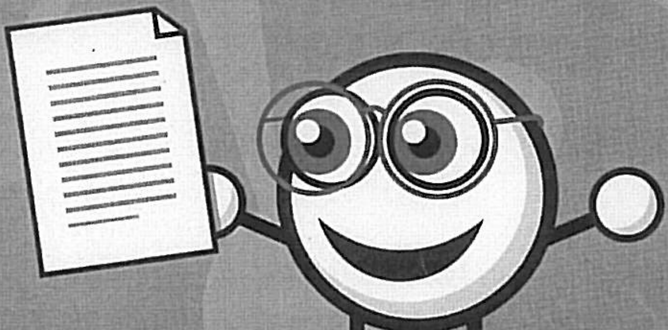
# epf'09

european
polymer congress
graz, austria

12.-17.7.2009
messe congress graz

# book of abstracts

## and basic information about the congress



Graz University of Technology
Institute for Chemistry and
Technology of Materials

| | | |
|---|---|---|
| OC6-15 | Hydrodynamic analysis of well-defined flexible linear macromolecules of low molar mass<br>Georges Pavlov, Diego Amorós, Christina Ott, Inna I. Zaitseva, Jose Garcia de la Torre, Ulrich S. Schubert | 52 |
| OC6-16 | Advanced thermal analysis solutions - HyperDSC, UV-DSC, UV-DMA, and Raman-DSC measurements to characterize polymeric materials<br>Iris Platthaus, Svenja Goth | 52 |
| OC6-17 | FTIR-ATR monitoring and SEC/RI/MALLS characterization of ATRP synthesized hyperbranched polyacrylates<br>Miguel Goncalves, Mário Rui Costa, Rolando Dias | 52 |

## Session 6A

Monday, July 13, 14:30 - 15:30, LH 4: Lecture Hall 4

| | | |
|---|---|---|
| OC6-3 | Polymerization Methods to obtain Amino-Functionalized Biocides<br>Elisabeth Kreutzwiesner, Frank Wiesbrock, Christian Slugovc, Franz Stelzer | 53 |
| OC6-4 | Microwave-assisted nitroxide-mediated polymerization in aqueous solution: effectiveness of the irradiation mode<br>Julien RIGOLINI, Laurent BILLON, Bruno GRASSL | 53 |
| OC6-5 | Microwave-assisted synthesis of ionic liquids - on the importance of internal temperature monitoring in microwave chemistry<br>David Obermayer, Bernhard Gutmann, C. Oliver Kappe | 53 |

## Session 6A-KL

Monday, July 13, 15:30 - 16:00, LH 4: Lecture Hall 4

| | | |
|---|---|---|
| KL6-2 | Microwave-assisted reactions: A powerful synthetic approach for polymerizations<br>Ulrich S. Schubert | 53 |

## Session 6A

Monday, July 13, 16:30 - 18:30, LH 6: Lecture Hall 6

| | | |
|---|---|---|
| OC6-6 | Power of Ion Mobility combined with High Resolution Mass Spectrometry for the Analysis of Complex Polymer Samples<br>Matthew Kennedy, Diana Uria, J Kirkpatrick | 54 |
| OC6-7 | Controlling the Critical Behavior of Paranematic to Nematic Transition in Liquid Single-Crystal Elastomers<br>Andrija Lebar, George Cordoyiannis, Zdravko Kutnjak, Brigita Rozic, Bostjan Zalar, Slobodan Zumer, Felicitas Brömmel, Simon Krause, Heino Finkelmann | 54 |
| OC6-8 | Dielectric spectroscopy of ultrathin polymer layers: from supported to freely-standing films<br>Simone Napolitano, Cinzia Rotella, Michael Wübbenhorst | 54 |
| OC6-9 | Rheology and GPC/SECComparing the Potential of two powerful Techniques in Polymer Analysis<br>Gerhard Heinzmann | 54 |
| OC6-10 | Gas analysis during polydimethylsiloxane ageing<br>MADELEINE PERDRILLAT Claire, De Sainte Claire Pascal, Delor-Jestin Florence | 55 |
| OC6-11 | Dynamic light scattering on highly swollen poly(acrylic acid) networks<br>Franziska Krahl, Volodymyr Boyko, Karl-Friedrich Arndt | 55 |

## Session 6B-KL

Monday, July 13, 16:30 - 17:30, LH 4: Lecture Hall 4

| | | |
|---|---|---|
| KL6-3 | Successive Synthesis of Well-Defined Miktoarm Star-Branched Polymers by Iterative Methodology Using Living Anionic Polymerization<br>Akira Hirao | 55 |
| KL6-4 | Effect of segregation strength and molecular architecture on the crystallization of single or double crystalline diblock copolymers and miktoarm star copolymers<br>Alejandro J. Müller | 55 |

## Session 6B

Monday, July 13, 17:30 - 18:30, :

| | | |
|---|---|---|
| OC6-18 | hydrodynamic and conformational properties of star-shape macromolecules<br>Alexander Filippov | 56 |
| OC6-19 | Shielding Effects in Reactions between Star-Branched Polymers<br>Markus Gerd Fröhlich, Gerhard Zifferer | 56 |

## OC6-14

# SAXS, viscometry and DLS studies of branched copolymers: unimolecular micelles and microgels

Daniel Gromadzki[a,b], Sergey Filippov[a], Miloš Netopilík[a], Ričardas Makuška[b], Alexander Jigounov[a] Josef Pleštil[a], Jiri Horský[a], Petr Štěpánek[a]

[a]*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic*
[b]*Department of Polymer Chemistry, Vilnius University, Naugarduko 24, LT-03225, Vilnius, Lithuania*

email: sfill225@mail.ru

We report on solution properties of loosely grafted copolymers composed of polystyrene (PS) backbone (degree of polymerization of PS backbone, $N_b = 95$) and variable length of poly(*tert*-butyl methacrylate) P(*t*BuMA) side chains (degree of polymerization of side chains, $N_{sc} = 14-222$) at fixed number of grafting sites *n* = 11 and polydispersity index ($M_w/M_n$) ranging from 1.05 to 2.63. Synthesis of these graft copolymers[1] is based on a novel synthetic route involving two independent controlled/"living" polymerization mechanisms, namely nitroxide-mediated radical polymerization (NMP) for the synthesis of the backbone and photoinduced "grafting from" *iniferter* process for building of P(*t*BuMA) branches. The viscosity-related contraction factors $g' < 1$ confirmed high degree of branching of the studied graft copolymers. Dilute solutions of graft copolymers in non-selective solvent (THF), examined by dynamic light scattering (DLS), small-angle X-ray scattering (SAXS) and viscometry, revealed a transition from linear coil conformation through wormlike-star to a microgel architecture under increasing number of monomeric units in side chains ($N_{sc}$)[2]. These data were further supported by the structure factors $R_g/R_h$ and $R_\eta/R_h$ obtained by independent measurements and extrapolated to infinite dilution. Persistence ngths of the samples exhibiting comb-like topology were larger compared to linear polystyrene backbone and P(*t*BuMA) side chains in THF suggesting stiffening of the main chain with increasing size of the attached side chains. Unimolecular micelles were detected by DLS and SAXS in solvent selective for grafts in *tert*-amyl alcohol.

---

[1] Gromadzki, D.; Makuška, R.; Netopilík, M.; Holler, P.; Lokaj, J.; Janata, M.; Štěpánek, P. Eur Polym J 2008;44:59-71.

[2] Gromadzki,D.; Filippov, S.; Netopilik,M.; Makuška, R.; Jigounov, A.; Pleštil, J.; Horský, J.; Štěpánek, P.; Eur. Polym. J.; accepted for publication in 2009

Acknowledgements: Support within Marie Curie RTN SOCON is gratefully acknowledged (DG).

---

## OC6-15

# Hydrodynamic analysis of well-defined flexible linear macromolecules of low molar mass

Georges M. Pavlov,[a, b, d] Diego Amorós,[c] Christina Ott,[a] Inna I. Zaitseva,[b] Jose Garcia de la Torre,[c] and Ulrich S. Schubert[a, d]

[a] Laboratory of Macromolecular Chemistry and Nanoscience,
Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, Netherlands;
E-mail: g.m.pavlov@tue.nl; u.s.schubert@tue.nl; http://www.schubert-group.com
[b] Departments of Physics, St. Petersburg University,
Ulianovskaya Str. 1, 198504 St. Petersburg, Russia
[c] Departamento de Quimica Fisica, Universidad de Murcia, 30071, Murcia, Spain
[d] Laboratory of Organic and Macromolecular Chemistry,
Friedrich-Schiller-University Jena, Humboldtstr. 10, 07743 Jena, Germany

Samples of poly(styrene-diphenylethylene) copolymers of narrow molar mass distribution[1] were studied by molecular hydrodynamic methods. The interference optics of the Beckman XLI analytical ultracentrifuge for the study of the velocity sedimentation of the samples was used. The all translation friction values as well as the intrinsic viscosity were measured in toluene. The sedimentation data were treated with the Sedfit program which numerically solves the Lamm equation.[2] The Sedfit program can determine both the velocity sedimentation coefficient and the frictional ratio. The latter parameter is unambiguously related to the translational diffusion coefficient. The adequacy of its determination by the Sedfit program was checked by an independent experimental determination of the translational diffusion coefficient. As a consequence, velocity sedimentation experiments evaluated by use of the Sedfit program may be considered as a self-sufficient method for the determination of molecular characteristics of linear polymers with narrow molar mass distribution. The recently developed Multi-HYDFIT program[3] performing a joint analysis of different transport properties of multiple samples allows the adequate estimation of conformational characteristics of short flexible chains without volume effects. This work also provides an adequate test of the ability of the recently developed Multi-HYDFIT program for the joint analysis of different transport properties of multiple samples, coupled to the MC simulation results for the wormlike chains that improve the classical Yamakawa-Fujii theory.[4] This first and successful application to the global-fit methodology to short, synthetic oligomers reveals its interest beyond the typical biopolymer systems to which it had been applied previously.[3]

[1] Ott C., Pavlov G. M., Guerrero-Sanchez C., Schubert U. S. *J. Polym. Sci. Polym. Chem.* (submitted)

[2] Schuck P. *Biophysical J.* **2000**, *78*, 1606.

[3] Ortega A., Garcia de la Torre J. *Biomacromolecules* **2007**, 8, 2464.

[4] Yamakawa H., Fujii M. *Macromolecules* **1973**, *6*, 407; **1974**, *7*, 128.

---

## OC6-16

# Advanced thermal analysis solutions – HyperDSC, UV-DSC, UV-DMA, and Raman-DSC measurements to characterize polymeric materials

Iris Platthaus,[a] Svenja Goth,[a]

[a] PerkinElmer (LAS) Germany GmbH, Ferdinand-Porsche Ring-17, D-63110 Rodgau, Germany

email: iris.platthaus@perkinelmer.com

HyperDSCTM is a new DSC technique with fast scanning rates up to 750 °C/min which produces vastly increased sensitivity and permits analysis of materials without change due to annealing or re-crystallization phenomena. UV light sources coupled with power compensating differential scanning calorimetry (UV-DSC) and dynamic mechanical analysis (UV-DMA) have opened up new avenues for accurately characterizing isothermal photo-curing including gelation point, vitrifacation point, and cure kinetics. The examination of amorphous, melt, and semi-crystalline polymers is also presented which reveals a cutting edge hyphenated technique to better understand multiphase polymer materials.

---

## OC6-17

# FTIR-ATR monitoring and SEC/RI/MALLS characterization of ATRP synthesized hyperbranched polyacrylates

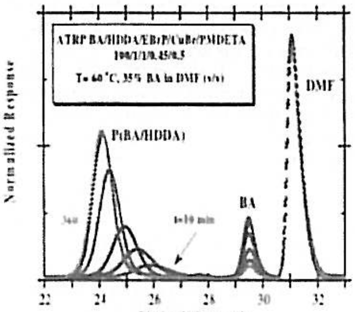
Miguel Gonçalves,[a] Mário Rui Costa,[b] Rolando Dias [a*]

[a] LSRE-Instituto Politécnico de Bragança, Quinta de Santa Apolónia, 5300 Bragança, Portugal;

[b] LSRE-Faculdade de Engenharia da Universidade do Porto, Rua Roberto Frias s/n, Porto, 4200-465, Portugal

email: rdias@ipb.pt

In the last few years, controlled radical polymerization (CRP) techniques have been explored to produced hyperbranched polymers with improved homogeneity as compared to those obtained by conventional free radical polymerization (FRP). This work reports the synthesis at 1 L scale of hyperbranched polyacrylates based upon acrylate/diacrylate monomers such as *n*-butyl acrylate (BA)/1,6-Hexanediol diacrylate (HDDA) and using atom transfer radical polymerization (ATRP).1 A FTIR-ATR immersion probe was used to monitor the polymerization reaction. The dynamics of the build-up of polymer structure was studied by off-line analysis of samples at different reaction times by size exclusion chromatography (SEC) with detection of refractive index (RI) and multi-angle laser light scattering (MALLS) signals, leading to molecular weight distribution and *z*-average radius of gyration. Kinetic measurements and observed parameters of the molecular architecture are compared with theoretical predictions2 which can be used to design new synthesis strategies to improve the homogeneity of hyperbranched polymers. Another goal of this study was elucidating the impact on polymerization of secondary reactions such as intramolecular cyclizations.



[1] Gao, H., Li, W., Matyjaszewski, K., *Macromolecules*, **2008**, *41*, 2335.

[2] Costa, M.R.P.F.N., Dias, R.C.S., *Polymer*, **2007**, *48*, 1785.