CPP 21: Polymer Physics II

Time: Wednesday 9:30–12:30   Location: ZEU 114

CPP 21.1 Wed 9:30 ZEU 114

Structure analysis with micrometer spatial resolution in polymer fibers — •Norbert Stribeck[1], Ulrich Nöchel[1], and Armando Almendárez Camarillo[2] — [1]Universität Hamburg, Institut TMC, 20146 Hamburg, Germany — [2]Instituto Tecnológico de Celaya, 38010 Celaya Gto., Mexico

The investigation of structure gradients in fibers, cylindrical rods or pipes by the X-ray microbeam scanning technique is put on its theoretical fundament. It is shown that the observed smeared structure information is readily reconstructed by the inverse Abel transform, for which fast and low-noise algorithms are available [1]. As a result, the scattering patterns emanating from the series of volume elements on the fiber radius are obtained (X-ray scattering-fiber computer-tomography, XSF-CT). Perfect reconstruction is achieved when the structure in every voxel shows fiber symmetry (local fiber symmetry, LFS). Violation of LFS results in characteristic reconstruction errors [2]. These can be interpreted in terms of two elementary deviating topologies (tangential grain, radial grain). Application to nanostructure analysis of polymer fibers is demonstrated.

[1] Stribeck *et al.* Macromol. Chem. Phys. (2008) 209(19), 1976-1982
[2] Stribeck *et al.* Macromolecules (2008) 41(20), 7637-7647

CPP 21.2 Wed 9:45 ZEU 114

Investigation of changes in crystalline structure during deformation of semi-crystalline polymers by synchrotron radiation — •Konrad Schneider and Andreas Schöne — Leibniz Institut für Polymerforschung Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany

During deformation of semi-crystalline polymers very complex structural changes appear. To distinguish certain processes simultaneous WAXS and SAXS was measured during deformation. The characteristical changes will be presented and discussed in detail. First changes in the crystalline phase appears far before reaching the yielding point. This correlates with the onset of irreversible deformation. In the yielding region radical changes on long- as well as short scale range appear.

CPP 21.3 Wed 10:00 ZEU 114

Molecular weight dependence of the crystalline-amorphous superstructure of semi-crystalline polymers — •Albrecht Petzold and Thomas Thurn-Albrecht — Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany

During crystallization polymers form a crystalline-amorphous superstructure consisting of lamellar crystals with a typical thickness of about 10 nm. This non-equilibrium structure is often explained by the kinetics of crystallization during which the crystals which form fastest, are selected. The thickness d_a of the amorphous layers separating adjacent crystals is in most cases not considered. To find out which parameters and physical processes determine d_a, we undertook a systematic study of the corresponding structural parameters by small angle x-ray scattering using a series of polyethyleneoxide (PEO) with different molecular weight as a model system. We show that for this system the thickness of the amorphous layers is a well defined equilibrium quantity which depends only on molecular weight and temperature, and not on the conditions of crystallization, while the thickness of the crystalline layers is strongly influenced by the kinetics of crystallization and lamellar thickening and in general is much less uniform. The fact that d_a increasing with molecular weight indicates that the semi-crystalline morphology is related to structure of the chains in the amorphous melt before crystallization.

CPP 21.4 Wed 10:15 ZEU 114

Studying Radical Polymerization by Single Molecule Spectroscopy — •Dominik Wöll[1], Frans de Schryver[2], Klaus Müllen[3], and Johan Hofkens[2] — [1]Zukunftskolleg/Fachbereich Chemie, Universität Konstanz, Universitätsstraße 10, 78457 Konstanz, Germany — [2]Laboratory for Photochemistry and Spectroscopy, Celestijnenlaan 200 F, Katholieke Universiteit Leuven, 3001 Heverlee, Belgium — [3]Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55128 Mainz, Germany

The possibility to observe single molecules, first realized about 20 years ago, has opened up a fascinating field of research. Even though polymers are popular systems for single molecule spectroscopy studies, the process of radical polymerization has so far not been studied at the single molecule level.

We investigated how the molecular motion of single fluorescent probes changes during the synthesis of polystyrene, polystyrene networks and polymethylmethacrylate by bulk radical polymerization. As probes, we have chosen perylene diimide derivatives of different sizes and functionalities. The translational motion over the entire conversion range from free diffusion to immobilization of the dyes could be followed by a combination of fluorescence correlation spectroscopy and wide-field microscopy. In contrast to ensemble measurements, the evolution of heterogeneities could be strikingly visualized by SMS. Such heterogeneities not only influence the progress of polymerization but also the properties of the synthesized polymer and are especially pronounced during the formation of networks.

CPP 21.5 Wed 10:30 ZEU 114

Polymer melt dynamics studied by Nuclear Magnetic Resonance — Patrick Hübsch[1], •Fabian Vaca Chavez[1], Wolfgang Binder[2], Ronald Zirbs[2], and Kay Saalwächter[1] — [1]Institute of Physics - Faculty of Natural Sciences II, Martin-Luther-University Halle-Wittenberg, Betty-Heimann-Str. 7, 06120, Haale, Germany — [2]Macromolecular Chemistry Group, Institute of Chemistry, Heinrich Damerow Strasse 4, 06120, Halle, Germany

Proton Multiple-Quantum (MQ) NMR is a powerful technique to investigate polymer dynamics due to its sensitivity to molecular motions on very different timescales [1]. In this work, we apply MQ NMR to linear poly(cis-1,4-isoprene) and poly(isobutylene) of different molecular weight above the glass transition over suitable ranges of temperature, in order to establish the dynamic regimes predicted by the tube model, and, for the first time, to extract actual time scale information. This directly complements many neutron scattering studies, which are restricted to the sub-μs-timescale. Measurements on PIB-grafted silica particles with different molecular weights and different chain densities on the surface of the particle are also shown. The data is analyzed by establishing scaling laws which can be directly associated with different dynamic regimes predicted by the tube/reptation model [2]. Full analytical analyses based on a correlation function which explicitly includes segmental, Rouse, and reptation dynamics are discussed.

[1] K. Saalwächter, Prog. NMR Spect., **2007**, 51, 1-35. [2] R. Graf, A. Heuer, H.W. Spiess, Phys. Rev. Lett., **1998**, 80, 5738-5741.

15 min. break

CPP 21.6 Wed 11:00 ZEU 114

Dielectric and electric relaxations at nanometric length scales — •Friedrich Kremer[1], Anatoli Serghei[1,2], Martin Tress[1], Joshua Rume Sangoro[1], and Ciprian Iacob[1] — [1]Institute for Experimental Physics I, University of Leipzig, Germany — [2]Department of Polymer Science and Engineering, University of Massachusetts Amherst, Amherst, MA 01003, USA

Dielectric spectroscopy benefits from the extraordinary advantage that its sensitivity increases with decreasing thickness of a sample capacitor. This enables one for instance to carry out broadband spectroscopic measurements on quasi isolated polymer coils in nano structured capacitor arrangements, having thicknesses as small as 100 nm. It is demonstrated that for polymers like polyvinyl pyridin (P2VP) or polyvinylacetate (PVAC) the dynamic glass transition can be measured for (averaged) sample thickness as small as $\sim$ 2 nm in a wide spectral range (10^{-2} Hz $- 10^6$ Hz) and at temperatures between 150 K to 350 K. No shift of the mean relaxation rate and no broadening of the relaxation time distribution function are found compared to the bulk liquid.

Electrode polarization is an ubiquitous phenomenon taking place at the interface between a metal and an ionic conductor. A quantitative theory will be presented, which enables one to deduce from its characteristic frequency, temperature and concentration dependencies – by use of a novel formula – the bulk conductivity of the ionic liquid under study. It is shown that the electrical relaxation processes take place within a nanometric layer at the (ionic conductor/metal) interface which can be analysed in detail.

CPP 21.7   Wed 11:15   ZEU 114

Heterogeneous Dynamics of Polymer PMA close to Glass Transition Temperature — •SUBHASIS ADHIKARI, MARKUS SELMKE, and FRANK CICHOS — Molecular Nano-photonics,Institute of Experimental Physics I,University of Leipzig,04103 Leipzig, Germany

In the study of glassy polymer systems there has been a long debate about the nature of heterogeneity of the material. There exist mainly two pictures of spatial and dynamic heterogeneities, where on one side the dynamical properties of change with the spatial position in the sample and on the other side with time at the same position of the sample. Recent experiments on single dye molecules in glassy glycerol suggest mainly a spatial heterogeneity, where each molecule shows a different dynamics. In this presentation we present recent results on this issue in long chain polymeric systems.We have analyzed the rotational diffusion dynamics of PDI dye molecule in high molecular weight glassy polymer PMA at both the ensemble and single molecule level close to Tg.Ensemble measurements have been done to compare with the single molecule measurement.From our single molecule measurements we obtain a broad distribution of rotational relaxation times of different individual molecules at a given temperature which indicates that the dynamics in some regions is orders of magnitude faster than the dynamics in other regions only a few nanometres away.Again this distribution becomes broader when temperature decreases to Tg.The rotationalcorrelation function of a single molecule is however well fitted by a stretched exponential decay. This nonexponential behavior gives a clear evidence of existence of dynamical heterogeneity.

CPP 21.8   Wed 11:30   ZEU 114

The glass transition in blends of molecular glasses — •ROMAN UEBERSCHAER, EVGENY TATAROV, THOMAS FUHRMANN-LIEKER, and JOSEF SALBECK — Universität Kassel, Heinrich-Plett-Straße 40, D-34132 Kassel, Germany

Blends of molecular glasses and their properties are of great interest for applications in optoelectronics. In this contribution we present results of differential-calorimetric measurements on binary blends of spiro-compounds. Spiro-compounds are low-molecular organic glass formers with glass transition temperatures well above 100 °C. The investigation was focused on the composition dependence of the glass transition temperature for two prototype blend systems. One system consists of two components that are miscible over the whole composition range. Applying the Fox law that approximates the inverse glass temperature as the sum of the inverse glass temperatures of the two compatible components weighted by their mass fractions, we found that a modified version of the Fox law where the weighting is related to the mole fraction predicts the glass transition temperature of the blend more accurately. This result might be useful for approximating the phase compositions of partially miscible blends from the corresponding glass transition temperatures. We discuss this issue with respect to the second system that exhibits a broad miscibility gap despite the high entropy of mixing that is expected for low-molecular substances.

CPP 21.9   Wed 11:45   ZEU 114

On the glassy state of multiphase and pure polymer materials — •STEPHAN ALEXANDER BAEURLE — Institute of Physical and Theoretical Chemistry, Regensburg University, D-93053 Regensburg, Germany

In this presentation we introduce a new glass theory and investigate its suitability for describing the mechanical response of thermoplastic elastomers composed of styrenic-block copolymers. The investigated materials are composed of glassy domains of polystyrene, which physically link soft rubbery chain segments made of either polybutadiene or polyisoprene. We demonstrate that the crossover in the shift factors, observed experimentally to change from Williams-Landel-Ferry to Arrhenius behavior passing through a characteristic crossover temperature T^* from below, coincides with the crossover from power-law to stretched-exponential behavior of the stress relaxation found in recent tensile experiments. Moreover, we show that the characteristic crossover temperature T^* is identical with the underlying true equilibrium second-order phase transition temperature T_2 of the polystyrene crosslinks, predicted by the thermodynamic theory of Gibbs and Di Marzio for pure glassy polystyrene in the infinite-time limit. By combining the recently introduced theory of Di Marzio and Yang with the significant-structure theory of Eyring and Ree, we develop a new glass theory, which is capable of explaining the mechanical response of multiphase as well as pure glassy materials. Moreover, we show a clear evidence for the existence of T_2 postulated in 1950s for pure glasses and hotly debated since then.

CPP 21.10   Wed 12:00   ZEU 114

Build-up and relaxation of stresses in a glass-forming soft-sphere mixture — •JOCHEN ZAUSCH[1] and JÜRGEN HORBACH[2] — [1]Inst. f. Physik, Universität Mainz, Staudinger Weg 7, 55099 Mainz — [2]Inst. f. Materialphysik im Weltraum, DLR, Linder Höhe, 51147 Köln

Glass-forming liquids under shear often exhibit the effect of shear thinning, i.e. the decrease of viscosity η upon increasing shear rate $\dot{\gamma}$ if $\dot{\gamma} \gtrsim 1/\tau$ (with τ the relaxation time). The viscosity is related to the shear stress $\sigma = \dot{\gamma}\eta$ that is built up due to the external shear field. Employing extensive non-equilibrium Molecular Dynamics computer simulations of a glass-forming binary Yukawa mixture we aim at understanding the transition from a quiescent state to steady shear. To this end, we monitor the stress as a function of the strain $\dot{\gamma}t$ after a suddenly commencing or terminating shear flow.

After switching on the shear field, the stress σ shows an overshoot at a strain $\dot{\gamma}t \approx 0.1$ that marks the transition from elastic to plastic deformation. The stress increase is closely related to the development of structural anisotropies, which we quantify by a projection of the pair correlation function onto a spherical harmonic of degree 2. After switching off the external drive in the elastic regime, stresses decay to zero on the time scale τ, whereas a switch-off in the plastic regime leads to the much faster decay on time scale $1/\dot{\gamma}$. We attribute this behaviour to the different distributions of local shear stresses in these regimes. Our results are corroborated by confocal microscopy experiments of colloidal systems and by a theoretical approach in the framework of mode-coupling theory (J. Phys.: Condens. Matter **20**, 404210 (2008)).

CPP 21.11   Wed 12:15   ZEU 114

Microrheology with Fluorescence Correlation Spectroscopy — •SILKE RATHGEBER[1,2], HANS-JOSEF BEAUVISAGE[1], HUBERT CHEVREAU[1,3], NORBERT WILLENBACHER[4], and CLAUDE OELSCHLAEGER[4] — [1]Max Planck-Institute for Polymer Research, 55128 Mainz, Germany. — [2]Johannes Gutenberg-University Mainz, 55099 Mainz, Germany. — [3]Ecole Polytechnique Universitaire de Lille, 59655 Villeuneuve D`Ascq Cedex, France. — [4]Technical University Karlsruhe, 76131 Karlsruhe, Germany.

We show that fluorescence correlation spectroscopy (FCS) can be applied to passive microrheological (MR) experiments. We performed measurements on a high molecular weight poly(ethylene oxide)-water solution in order to allow direct comparison of the results to the measurements of Weitz and Mason using diffusing wave spectroscopy (DWS) and quasielastic light scattering (QELS). We derived the bulk rheological shear moduli covering more than five decades in frequency ($\omega \leq 10^{-1}$ rad/s to $\omega \geq 10^4$ rad/s). The MR results are compared to those obtained with bulk rheological methods on the same samples using a rotational rheometer as well as a piezo driven squeeze flow apparatus. Good agreement between MR results probing the local rheological response and those obtained from the bulk methods are found. MR with FCS covers a similar ω range as QELS and DWS together with some limitations to higher ω due to the lower spatial resolution of FCS compared to DWS. However, the small sample sizes ($10\ \mu$ L) and small tracer concentrations (nM) involved in FCS make this method a powerful tool in particular for biological and medical applications.