CPP 13: Focused Session: Confinement of Polymers in Nanoscopic Layers - How Much do Properties Change? I

Time: Tuesday 10:30–13:00 Location: ZEU 160

Invited Talk CPP 13.1 Tue 10:30 ZEU 160
Rheological Response of Ultrathin Polymer Films — •Gregory McKenna, Paul O'Connell, and Jinhua Wang — Texas Tech University, Lubbock, TX, USA

We have developed a novel bubble inflation method to determine the rheological response of ultrathin polymer films. The method shows,consistent with other methods, dramatic reductions of the glass transition (Tg) of polystyrene of high molecular weight. We have also discovered a major stiffening of the material in the rubbery plateau regime. New information for polycarbonate shows that, like polystyrene it can exhibit strong reductions in the Tg and rubbery stiffening. We also report the first evidence of terminal flow in the bubble inflation experiment using polycarbonate having thicknesses from 3 nm to 9 nm. We have also performed liquid film dewetting experiments for both polystyrene and polycarbonate systems. The results for the polystyrene are consistent with literature reports of little change in the glass transition and no change from macroscopic behavior for the rubbery plateau regime. On the other hand, for polycarbonate we observe both a reduction in the Tg and moderate stiffening in the rubbery regime. These results will be discussed in detail.

Invited Talk CPP 13.2 Tue 11:00 ZEU 160
Molecular dynamics at nanometric length-scales — •Friedrich Kremer — Universität Leipzig, Fak. f. Physik u. Geowissensch., Inst. f. Experimentelle Physik I, Linnéstr. 5, D-04103 Leipzig

Broadband Dielectric Spectroscopy, Spectroscopic vis-Ellipsometry, X-Ray Reflectometry, Alternating and Differential Scanning Calorimetry are combined to study glassy dynamics and the glass transition in nanometric thin (about 5 nm) layers of polystyrene (PS) having widely varying molecular weights and Polymethylmethacrylate (PMMA) deposited on different substrates. For the dielectric measurements two sample geometries are employed, the common technique using evaporated electrodes and a recently developed approach taking advantage of nanostructures as spacers. All applied methods deliver the concurring result that deviations from glassy dynamics and from the glass transition of the bulk never exceed margins of nearly 3 K independent of the layer thickness, the molecular weight of the polymer under study and the underlying substrate. Our findings are discussed in the context of the highly controversial literature and prove that an appropriate sample preparation is of paramount importance in order to avoid artefacts. References: 1.Erber et al., Macromolecules 43, 7729 (2010). 2.Mapesa et al., Europ. Phys. J. - Special Topics 189, 173-180 (2010). 3.Treß et al., Macromolecules (2010). DOI:10.1021/ma 102031k.

Invited Talk CPP 13.3 Tue 11:30 ZEU 160
On the origin of the deviations from bulk behavior in ultrathin polymer films: from glass transition to tracer diffusivity — •Simone Napolitano, Michael Wübbenhorst, and Cinzia Rotella — Department of Physics and Astronomy, Katholieke Universiteit Leuven, Celestijnenlaan 200D, Leuven, 3001, Belgium

We show clear evidence that the changes ultrathin films undergo during annealing are strongly correlated to the amount of chains irreversibly adsorbed at the interface. An analysis of the time evolution of the dielectric function during annealing steps above Tg revealed three different regimes: at times much shorter than the adsorption time, the thickness of the adsorbed layer is constant and the incomplete interface mimics the effect of a free surface (packing frustration); upon increase of surface coverage, the films undergo a series of metastable states characterized by the largest changes in the deviations from bulk behavior; finally the system approach a new equilibrium whose properties are fixed by the new interfacial configurations. Our picture is confirmed by further investigation of the distribution of glass transition temperatures, tracer diffusivity and dielectric relaxation strength at different distances from the adsorbing interface. We show that during annealing ultrathin films evolve towards a steady state whose properties might still differ from bulk. In particular, for polystyrene, the lack of specific interactions with the substrate results in slow adsorption kinetics, keeping the deviations from bulk behavior in steady states with an extremely long lifetime.

Invited Talk CPP 13.4 Tue 12:00 ZEU 160
Calorimetry of Thin Films – From Single Layer Glass Transitions to Inter-layer Diffusion in Double Layers — •Christoph Schick[1], Dongshan Zhou[2], and Heiko Huth[1] — [1]Institute of Physics, University of Rostock, Germany — [2]State Key Laboratory of Coordination Chemistry, Nanjing University, China

Nanocalorimetry allows studying the glass transition in nanometer thin films. One of the striking results of fast scanning (FSC) as well as alternating current (AC) calorimetry is the commonly observed constant Tg in thin films down to a few nm. Blends of polystyrene and poly(phenylene oxide) (PS/PPO) confined in thin films were investigated by AC nanocalorimetry. For this blend, we see even for the thinnest films (6 nm, corresponding to about half of PPO radius of gyration Rg) only one unchanged glass transition. The good miscibility between PS and PPO remains even in ultrathin films. Finally, we show that our chip calorimeter is sensitive enough to study the inter-layer diffusion in ultrathin films. The PS chains in a 150 nm PS/PPO double layer that is prepared by spin coating PPO and PS thin films in tandem gradually diffuse into the PPO layer when heated above the Tg of PS, forming a PSxPPO(100-x) blend. However, on top of the PSxPPO(100-x) blend, there exists a stable pure PS like layer (ca. 30nm in our case) that does not diffuse into the blend beneath even staying at its liquid state over 10 hours.

CPP 13.5 Tue 12:30 ZEU 160
Chain Dynamics of Polymers Confined to Ordered Nanoporous Alumina Membranes — •Cornelius Franz[1], Salim Ok[2], Gopalakrishnan Rengarajan[2], Fabián Vaca Chávez[1], Christian G. Hübner[3], Martin Steinhart[2], and Kay Saalwächter[1] — [1]Institut für Physik - NMR, Universität Halle, Betty-Heimann-Str. 7, 06120 Halle — [2]Institut für Chemie, Universität Osnabrück — [3]Institut für Physik, Universität Lübeck

The nanoscopic confinement effect of hard neutral or attractive walls on the dynamics of polymer chains in the melt is studied by solid-state NMR. We apply a variety of NMR techniques to the characterization and the elucidation of chain dynamics in true model composites based on self-ordered nanoporous alumina with well-defined geometry and the possibility to tune the properties of the inorganic surface.

The long-time dynamics of entangled melts is significantly different from the bulk and rather anisotropic in a layer of a few nm close to the weakly interacting wall, and that the effect appears to scale with the entanglement spacing. Further preliminary studies demonstrated that these effects are orientation dependent, and also occur for nominally unentangled melts.

We also studied the large-scale diffusion by pulsed-gradient NMR and the infiltration kinetics by confocal fluorescence microscopy where we have monitored the infiltration of dye-doped polymer into self-ordered AAO in situ. Pore-wall modification experiments were verified by quantitative high-resolution NMR.

CPP 13.6 Tue 12:45 ZEU 160
Polymer melt dynamics in confinement: Reduction of the inter-chain entanglement density close to an interface — •Oliver Bäumchen, Renate Fetzer, and Karin Jacobs — Department of Experimental Physics, Saarland University, D-66041 Saarbrücken, Germany

Fluids in confinement may exhibit properties that differ strongly from bulk behavior. One example is the reduction of the glass transition temperature in thin polymer films, whether above or below the entanglement length of the polymer. Another example is the inter-chain entanglement density in the bulk compared with the one in the vicinity of an interface. Dewetting experiments of thin (<200 nm) polystyrene films reveal that the inter-chain entanglement density close to an interface can be reduced by a factor 3 to 4, depending on interfacial properties [1,2]. Parameters that control the reduction will be detailed. Our findings shed new light on the solid/liquid boundary condition of liquid flow [3], on the molecular structure of this interface and possible reasons for a reduction of the glass transition temperature.

[1] O. Bäumchen, R. Fetzer and K. Jacobs, *Phys. Rev. Lett.* **103**, 247801 (2009).

[2] O. Bäumchen and K. Jacobs, *Soft Matter* (2010), DOI: 10.1039/C0SM00078G.

[3] O. Bäumchen and K. Jacobs, *J. Phys.: Condens. Matter* **22**, 033102(21pp) (2010).