

CPP 21: Poster: Confinement of Polymers in Nanoscopic Layers - How Much do Properties Change?

Time: Tuesday 18:00–20:00

Location: P2

CPP 21.1 Tue 18:00 P2

Glassy dynamics of polymers in thin films and monomolecular layers — ●MARTIN TRESS¹, EMMANUEL MAPESA¹, ANATOLI SERGHEI², and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Leipzig — ²Université Lyon 1, Villeurbanne, France

The glassy dynamics of nanometer thin polymer layers supported on a solid substrate was investigated by Broadband Dielectric Spectroscopy (BDS). The thickness was systematically reduced finally resulting in randomly distributed polymer coils. Highest priority was put on an appropriate sample preparation including an annealing procedure for sufficient long time at elevated temperatures in inert atmosphere to avoid effects due to remaining solvent and chemical degradation. Further, detailed checks of the surface topology by atomic force microscopy (AFM) were performed to verify stability of the samples during the whole measurement. The dynamics is compared to the bulk to trace changes due to the impact of the interface and to give a length scale for the interfacial interactions.

CPP 21.2 Tue 18:00 P2

Glassy dynamics of ultra-thin layers of polyisoprene — ●EMMANUEL MAPESA, MARTIN TRESS, and FRIEDRICH KREMER — Universität Leipzig, Leipzig

Broadband Dielectric Spectroscopy (BDS) - in combination with a nanostructured electrode arrangement - is used to study thin layers of polyisoprene. In the view of BDS, polyisoprene belongs to a special type of polymers because a part of its molecular dipole moment attached to each monomer unit is aligned along the main chain. These fraction adds up to one dipole moment of the whole polymer chain corresponding to the end-to-end vector of the molecule. This enables the investigation of two distinct relaxation modes taking place at two different length scales: the segmental motion which involves structures of about 1 nm in size (2 to 3 monomer units) and the so-called normal mode which represents the dynamics of the whole macromolecule. By making measurements on identical samples in capped and uncapped geometries, and systematically reducing the layer thicknesses, we show clearly the changes that occur in these two relaxation processes due to the presence of a solid interface. Special attention is given to sample preparation and treatment.

CPP 21.3 Tue 18:00 P2

Dynamic Glass Transition of Thin Poly(Bisphenol A Carbonate) Films — ●HUAJIE YIN and ANDREAS SCHÖNHALS — BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

The dynamic glass transition (α relaxation) of thin poly(bisphenol A carbonate) films (down to 10 nm) capped between two aluminum electrodes is investigated by dielectric relaxation spectroscopy. There is no thickness (polymeric layer) dependence of the dynamic glass transition temperature down to a critical thickness of 20 nm. For thickness below ~ 20 nm, an increase of dynamic glass transition temperature is observed. The Vogel-Fulcher-Tammann (VFT) equation is further applied to fit the data of relaxation rate vs dynamic glass transition temperature which reveals that the Vogel temperature increases with decreasing film thickness d . These peculiar properties are discussed in terms of the formation of a top layer of adsorbed poly(bisphenol A carbonate) segments having a reduced molecular mobility with regard to bulk poly(bisphenol A carbonate) at the experimental time scale. Contact angle measurement is performed to confirm the strong interaction between the aluminum layer and poly(bisphenol A carbonate). The interfacial energy between them is calculated to be 3.1 mJ/m² which is related to an increase of dynamic glass transition temperature.

CPP 21.4 Tue 18:00 P2

Calorimetric Glass Transition of Thin Poly(Bisphenol A Carbonate) Films — ●HUAJIE YIN and ANDREAS SCHÖNHALS — BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

The differential alternating current chip calorimeter with the sensitivity of a few tens of pJ/K was applied to study the glass transition of thin poly(bisphenol A carbonate) films with thickness ranging

from 35 nm to 230 nm. The temperature dependent measurement (393.15–463.15 K) of complex heat capacity of nanometer-thin films was carried out in the frequency range typically from 1 Hz to 1000 Hz. Amplitude and phase angle of the complex differential voltage as a function of the temperature, respectively, were attained in the measurement, which can be used to determine the calorimetric glass transition temperature. No thickness dependency of calorimetric glass transition temperature was observed within an uncertainty of ± 3 K at every setting frequency. The frequency dependence of calorimetric glass transition temperatures was further analyzed by the fitting of Vogel-Fulcher-Tammann (VFT) equation. It is shown that there is no deviation from the common VFT behavior.

CPP 21.5 Tue 18:00 P2

Structure-Property Relationships of Plasma Deposited Poly (acrylic acid) Thin Films — ●ALAA FAHMY, RENATE MIX, ANDREAS SCHÖNHALS, and JÖRG FRIEDRICH — BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany

Poly (acrylic acid) films with a thickness of about 150 nm were deposited in the pulsed plasma regime onto aluminium and glass substrates. The structure/property relationships of these samples were studied in dependence on the duty cycle (DC) of the plasma by a broad combination of different techniques and probes. For the first time volume sensitive methods (FTIR, dielectric spectroscopy, and differential scanning calorimetry) are combined with surface analytics by employing XPS. For an unambiguous identification of COOH groups by XPS, derivatisation with trifluoroethanol was accomplished. Quantitative FTIR investigations give qualitatively the same dependence of the concentration of COOH groups on DC like XPS investigations. The dielectric measurements reveal that the structure of the plasma deposited films is different from that of the bulk material. Especially a lower glass transition temperature is observed. This result points to a highly branched structure of the plasma deposited polymer with a high number of dangling chains. Moreover, the dielectric measurements show that the plasma deposited films are not thermally stable but undergo a post plasma chemical reaction during heating, where the reaction kinetics depends on DC.

CPP 21.6 Tue 18:00 P2

Form factor of polymer melts: Deviations from ideal Gaussian behavior — ●JULIA ZABEL¹, CALEB DYER², MARK DADMUN², HENDRIK MEYER¹, JOACHIM WITTMER¹, and JOERG BASCHNAGEL¹ — ¹Institut Charles Sadron, CNRS, 23 rue du Loess, 67037 Strasbourg, France — ²Univ Tennessee, Dept Chem, Knoxville, TN 37996 USA

With a disarmingly simple argument Flory predicted that a flexible polymer in a melt behaves as an ideal, 3 dimensional random walk, its step length Gaussian distributed. This hypothesis is based on excluded volume screening in a dense melt. The Gaussian coil gives rise to such important scaling laws as $R_g \sim N^{1/2}$ which are fundamental in modern polymer physics. Over the last decade the Flory hypothesis has been revisited and corrections suggested [Semenov et al, Euro Phys. J. E, 12 (2003)]. Coarse grained simulation models support these corrections [Wittmer et al, EPL, 77 (2007)]. Most recently small angle neutron scattering experiments have been performed on high molecular weight PIB and PDMS melts. The results will be presented here and their deviations from ideal behavior discussed.

CPP 21.7 Tue 18:00 P2

Effect of substrate on the formation of polyelectrolytes multilayers — ●MAXIMILIAN ZERBALL, SAMANTHA MICCIULLA, CHLOÉ CHEVIGNY, and REGINE VON KLITZING — Stranski-Lab., TU Berlin, Institut für Chemie, Sekr. TC 9, 10623 Berlin

For the past twenty years, the Layer-by-Layer technique (LbL) has made it possible to modify surfaces by covering them with thin films. This technique opened the door for a wide variety of potential applications for polyelectrolyte multilayers (PEM), for example chemical reactors, antireflective coatings, containers or filtration membranes. The deposition of PEMs is influenced by various parameters, such as ionic strength, pH value and charge density. But a systematic study of the substrate effect on this deposition is still missing: this poster

will present results which focus on the influence of the substrate on the formation of the multilayers. For this purpose different substrates are studied: by directly changing the nature of the substrate (Silicon or Gold), but also by chemically modifying the silicon surface using silanization (change of both substrate charge and interactions with polyelectrolytes). For polyelectrolytes we chose to use the two most widely spread systems, PSS/PAH and PSS/PDADMAC, both either with long or short chain lengths. The thickness, roughness and aspect of the PEM are monitored as a function of the number of layers deposited by a complementary use of ellipsometry (with humidity control) and AFM. We can then very finely determine the substrate influence zone, and what the vicinity to the substrate changes inside this zone.

CPP 21.8 Tue 18:00 P2

Fluidics of confined liquid films: Impact of slippage on spinodal dewetting — •MATTHIAS LESSEL, OLIVER BÄUMCHEN, SABRINA HÄFNER, and KARIN JACOBS — Department of Experimental Physics, Saarland University, D-66041 Saarbrücken, Germany

We investigate the dewetting dynamics of short-chained polystyrene

(PS) films with thicknesses in the range of a few nanometers. According to the stability criteria derived from the effective interface potential, capillary waves are amplified and cause film thickness variations, a scenario termed spinodal dewetting. By in situ AFM investigations, the dynamics of spinodal dewetting is quantified [1, 2]. Due to confinement of the polymer in a thin film, physical properties such as the glass transition temperature change compared to the bulk properties. Recently, Yang et al. [3] were able to provide evidence for a highly mobile surface layer at the air/liquid interface of unentangled PS films. Bäumchen et al. showed for entangled PS films that the inter-chain entanglement density is reduced close to the interface [4]. An interfacial layer is capable to influence significantly the flow dynamics of the polymer. Polymer dewetting is studied by using substrates with different hydrophobic coatings like self-assembled monolayers of silanes or an amorphous fluoropolymer (AF 1600) coating.

[1] R. Seemann et al., Phys. Rev. Lett., 86 (2001), 5534.

[2] R. Fetzer et al., Phys. Rev. Lett., 99 (2007), 114503.

[3] Z. Yang et al., Science, 328 (2010), 1676.

[4] O. Bäumchen et al., Phys. Rev. Lett. 103 (2009) 247801.