

CPP 37: Molecular Dynamics

Time: Friday 10:30–12:30

Location: C 230

CPP 37.1 Fri 10:30 C 230

Investigation of polymer dynamics in acrylonitrile butadiene rubber — ●JULIANE FRITZSCHE and MANFRED KLÜPPEL — Deutsches Institut für Kautschuktechnologie e.V., Eupener Straße 33, D-30519 Hannover, Germany

The field of application of elastomers is determined by their frequency dependent dielectric and dynamic-mechanical properties. The dynamic spectrum of such materials becomes very important for understanding the correlation between parameters of the molecular and supramolecular structure on one hand and macroscopic properties on the other.

The frequency dependent mechanical behaviour is obtained by dynamic-mechanical analysis (DMA) and dielectric spectroscopy. Dielectric broadband relaxation spectroscopy covers a frequency range between 10-1 and 109 Hz. In this range molecular and collective dipolar fluctuations, charge transport and polarization effects at inner and outer boundaries take place and determine the dielectric properties of the material. However, molecular and collective dipolar fluctuations are related to characteristic parts of a molecule (functional group) or the molecule as a whole and give raise to characteristic relaxation processes. The investigation of these processes is one of the most important applications of this method as information about the polymer dynamics can be obtained.

In this presentation we will show the investigation of a acrylonitrile butadiene rubber unfilled and filled with different loadings of silica and carbon black. We obtained the dynamic-mechanical behaviour and the dielectric properties in a wide frequency range.

CPP 37.2 Fri 10:45 C 230

Molecular dynamics simulations of polymer brushes — ●GUI-LI HE¹, HOLGER MERLITZ^{1,2}, JENS-UWE SOMMER², and CHEN-XU WU¹ — ¹Xiamen University, Department of Physics, 361005 Xiamen, China — ²Leibniz-Institut für Polymerforschung Dresden, 01069 Dresden, Deutschland

We have carried out molecular (Langevin) dynamics simulations of polymer brushes up to very high grafting densities. We report on the fluctuation properties, the excess free energy and the brush-crystallization at extreme grafting densities. The importance of finite extensibility in order to understand chain properties at high substrate coverage is demonstrated. Recent simulation results of mixed binary brushes are shown.

References: 1. Gui-Li He, Holger Merlitz, Jens-Uwe Sommer and Chen-Xu Wu, Static and dynamic properties of polymer brushes at moderate and high grafting densities: A molecular dynamics study, *Macromolecules* 40, p. 6721 (2007)

2. Gui-Li He, Holger Merlitz, Jens-Uwe Sommer and Chen-Xu Wu, Polymer brushes near the crystallization density, *Eur. Phys. J. E* (in press)

CPP 37.3 Fri 11:00 C 230

Interfacial dynamics of polymers in contact with solid substrates — ●ANATOLI SERGHEI and FRIEDRICH KREMER — University of Leipzig, Linnestr. 5, Leipzig, 04103, Germany

Polymers exhibit alterations of their microscopic (and hence macroscopic) properties in the vicinity of solid interfaces. In the present contribution a novel experimental approach is demonstrated which enables one to investigate molecular fluctuations of polymer segments in the immediate (nanometric) vicinity of solid substrates. This development, employing nanostructures as spacers, renders to Broadband Dielectric Spectroscopy - traditionally a volume specific technique - the ability to measure the interfacial dynamics of organic materials in contact with solid substrates. The method readily allows to adjust the interfacial interactions by a controlled deposition of various (metallic but as well organic) layers onto the surface of the supporting electrodes. Experimental results on the interfacial dynamics of several polymers will be discussed, in systematic dependence on the interfacial interactions.

CPP 37.4 Fri 11:15 C 230

Surface diffusion of single polymer chains - a molecular dynamics study — ●CHRISTIAN VREE and S. G. MAYR — I. Physikalisches Institut, Universität Göttingen, Friedrich-Hund-Platz 1, 37077

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Bulk diffusion and transport of polymers in melts and solutions have attracted large scientific interest during the past decades in particular with respect to the influence of solvents, chain length, conformation and temperature. Contrary, surface kinetics of polymers are still poorly understood, although there is increasing interest in this field. Surface diffusion is of great importance in thin film physics, i.e. in physical vapor deposition methods. Therefore it is essential to understand the microscopic mechanisms of surface diffusion in more detail.

Here we present molecular dynamics studies of a polymer chain on a surface of a thin film of the same type of polymer. A cubic box with periodic boundary conditions in x- and y-direction and free surfaces in z-direction with typical dimensions of $42\sigma \times 42\sigma \times 30\sigma$, where σ is the bond length in Lennard-Jones units, acts as the substrate, where a single chain is placed on. Non-bonded particles interact via a truncated Lennard-Jones potential, while bonded particles interact via the FENE-potential suggested by Kremer and Grest (*J. Chem. Phys.* **92**, 5057, 1990). We find that the mobility on the surface is increased compared to the bulk value by about a factor of 2, while the time scaling does not change significantly.

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CPP 37.5 Fri 11:30 C 230

Disentanglement in thin polymer films — ●HENDRIK MEYER — Institut Charles Sadron, CNRS UPR22, Strasbourg, France

Molecular dynamics simulations of thin polymer films confined between structureless walls show accelerated in-plane dynamics with decreasing film thickness. Using the primitive path analysis (PPA) introduced by Everaers et al [*Science* 303 (2004) 823] for chain length up to $N=1024$, we can show that the entanglement density decreases with decreasing film thickness. However, the effect becomes pronounced only for films thinner than the bulk radius of gyration where also the structure of the chains becomes modified by the confinement [1]. The PPA algorithm can be modified to estimate the contribution of self-entanglements: The latter become more important for thinner films, however, they do not counterbalance the global decrease of entanglements.

[1] H. Meyer et al *Eur. Phys. J. Sp.Top.* 141 (2007) 167.

CPP 37.6 Fri 11:45 C 230

Binding and Diffusion of individual dye molecules in ultrathin liquid films — ●DANIELA TÄUBER, JÖRG SCHUSTER, and CHRISTIAN VON BORCZYKOWSKI — Research G.: From local constraints to macroscopic transport, TU-Chemnitz, Institut für Physik, 09107 Chemnitz

The structure and dynamics of liquids close to solid interfaces is of central interest for numerous practical applications involving microfluidic structures. By tracking of single dye molecules we have been able to reveal details of the molecular structure of ultrathin liquid films on interfaces in previous work [1].

Molecular motion in thin liquid film is not purely diffusive but includes also temporary sticking or binding of probes to the solid surface. Based on a series of recent experiments we demonstrate that sticking probabilities as well as the diffusion constants of various dyes in ultrathin TEHOS films are slowly changing on a time scale of days. Although the two phenomena are strongly interconnected, we can show that they are caused by two independent processes, namely i) the thinning of the film due to evaporation, and ii) a change of the chemical composition of the surface which will lead to a decrease of the sticking probability a few days after sample preparation. A simple surface chemistry model is presented to explain those observations. In addition we show that thinning of the films is accompanied by a slow down of diffusional motion, which supports further our findings of a strongly anisotropic diffusion due to the layering structure of the films [1].

[1] J. Schuster, F. Cichos, Ch. von Borczykowski: *Euro. Phys. J. E.* 12 (2003), 75-80

CPP 37.7 Fri 12:00 C 230

Chain motion in poly(ethylene oxide) crystallites as studied by NMR — ANJA ACHILLES, ALBRECHT PETZOLD, THOMAS THURN-ALBRECHT, and ●KAY SAALWACHTER — Institut für Physik, Martin-Luther-Universität Halle Wittenberg, 06099 Halle (Saale)

Many stereoregular polymers exhibit pronounced large-scale dynam-

ics in the crystalline phase. “Helical-jump” processes mediate chain transport over large distances through the crystallites, and they are often related to the mechanically active $\alpha_{(c)}$ relaxation and macroscopic properties such as yield processes and ultradrawability. While the timescale of such processes has been studied for many different polymers [1], their dependence on morphological parameters, such as crystalline and amorphous layer thickness, has received less attention.

In this contribution, we report on NMR investigations of helical jumps in PEO crystallites, using advanced high-resolution ^{13}C exchange spectroscopy as well as simple analyses of the ^1H time-domain signal. These results are correlated with SAXS-determined changes in the morphology and crystallinity as a function of molecular weight and the crystallization conditions.

[1] W.-G. Hu, K. Schmidt-Rohr, *Acta Polym.* **50**, 271 (1999)

CPP 37.8 Fri 12:15 C 230

Morphological Differences in Semi-crystalline Polymers: Its Implications on Local Dynamics and Chain Diffusion —

•ROBERT GRAF¹, YEFENG YAO¹, SANJAY RASTOGI², and HANS WOLFGANG SPIESS¹ — ¹Max-Planck-Institut für Polymerforschung, 55128 Mainz, Deutschland — ²Eindhoven University of Technology, 5600MB Eindhoven, The Netherlands

Morphological differences in semi-crystalline polymers due to different crystallization conditions have strong implications on the chain motion. Using a broad variety of solid state NMR techniques probing the molecular dynamics on different time and length scales, the local dynamics in the non-crystalline regions of solution crystallized linear polyethylene was found to be lower than in a melt crystallized sample under the same conditions, but the opposite is observed for chain diffusion between non-crystalline and crystalline regions. The activation enthalpy for chain diffusion, however, is the same, indicating that entropic differences in the non-crystalline regions strongly influence the chain diffusion of the same polymer in different morphologies.

Reference:

Y-F. Yao, R. Graf, H.W. Spiess, D.R. Lippits, S. Rastogi, *Phys. Rev. E*, in press.