CPP 17 Physics of polymers I

Zeit: Dienstag 09:45–11:00 Raum: TU C130

CPP 17.1 Di 09:45 TU C130

A first order crystallization process in poly(ethylene-co-octene) by way of transient phase formation. — •Andreas Häfele, Barbara Heck, Thomas Hippler, Takahiko Kawai, Peter Kohn, and Gerd Strobl — Physikalisches Institut der Albert-Ludwigs-Universität Freiburg, Hermann-Herder-Str. 3, 79104 Freiburg

Samples of poly(ethylene-co-octene) with different content in co-units show peculiarities in their crystallization behavior. When cooled from the melt to a fixed crystallization temperature, at first a structure of diffuse appearance with variations on the length scale of micrometers is observed in the polarizing optical microscope. The transformation into the final semi-crystalline state then proceeds in two ways, by a continuous change of the inner structure of micrometer-sized objects and the growth of spherulites. Time dependent small angle and wide angle X-ray scattering experiments corroborate the occurrence of two crystallization mechanisms. Atomic force microscopy indicates that the change of the inner structure of the preformed objects is due to an in-filling of crystallites. This first order crystallization process is responsible for a pronounced melt memory effect: shapes of dilatometry isotherms and characteristic times vary systematically with the temperature of the melt prior to cooling to the crystallization temperature. The temperature range of the effect is limited; crystallization kinetics remains constant below a melt temperature Tml and above a melt temperature Tmh and varies only in-between.

CPP 17.2 Di 10:00 TU C130

Stiffness variations across epoxy-interphases — •Martin Munz, Jaeun Chung, and Heinz Sturm — Bundesanstalt für Materialforschung und -Prüfung (BAM), Div. VI.2, Unter den Eichen 87, D-12205 Berlin

Interfacial effects in thermosetting systems are of particular interest, since significant diffusional effects can be induced during the crosslinking reaction. When starting from a two-component system consisting of an epoxy resin and an amine curing agent, stoichiometric imbalances can occur in the vicinity of the interface via the preferential ad- or absorption of one of the components. Via the crosslink reaction the chemical gradients are converted into spatial variations of the final network structure, thus resulting in gradients of local mechanical properties. In this study, scanning force microscopy (SFM) and depth-sensing microindentation were employed in order to map interphasial stiffness variations. Two different systems were employed, namely a copper/epoxy- and a polyvinylpyrrolidone(PVP)/epoxy-system. In the former case, SFM-based stiffness mapping revealed interphasial stiffness gradients extended over 3 microns. However, in the case of the thermoplastic/epoxy-system, much more extended interphases were found (210 microns). Using EDX, a zone of amine (diaminodiphenylsulfone, DDS) depletion was identified within the interphase and a non-zero amine-concentration was detected within PVP. The observation of local increase of epoxy modulus with a decrease of amine-epoxy concentration ratio is consistent with results from DMA. The observed increase of the room temperature modulus can be rationalised in terms of antiplasticisation of the beta transition.

CPP 17.3 Di 10:15 TU C130

Ageing of biosynthetic PHB — •Antje Bergmann and Anthony J. Owen — Fakultät für Physik, Universität Regensburg

The semicrystalline polymer polyhydroxybutyrate (PHB) is a bacterially processed polyester and therefore biocompatible and completely biodegradable. Its properties are similar to those of some conventional plastics such as polyethylene (PE). However, its mechanical characteristics show detrimental changes with time - an ageing process occurs. It is not yet satisfactorily understood why samples crystallised at room temperature embrittle increasingly with time, whereas annealing treatments may restore the excellent mechanical properties of freshly moulded material. Using wide-angle x-ray diffraction we analysed the crystal structure of samples annealed at various temperatures after several storage times. Differential scanning calorimetry experiments were carried out to observe melting and crystallisation processes. The results of our research seem to be interpretable in a remarkably simple way: We found that only a specific structural state is thermodynamically stable enough not to be prone to further crystallisation and ageing. This state is characterised by certain elementary cell dimensions, degree of crystallinity and crystal size.

CPP 17.4 Di 10:30 TU C130

Annealed Polyelectrolytes in a Poor Solvent — •Christian Seidel and Sahin Uyaver — Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Abt. Theorie, 14476 Potsdam-Golm

In weak (so-called annealed) polyelectrolytes (PELs) the degree of charging is not fixed but can be tuned by changing the solution pH. Due to dissociation and recombination of ion pairs the charge can move along the chain. This extra degree of freedom gives rise to new and nontrivial features. In particular, for PELs in a poor solvent, the annealing of charges can have strong effects.

Using (semi-)grand canonical Monte Carlo simulations of a chain of contour length Nb we focus on the conformational properties in the close-to-Θ-point regime $\tau = (\Theta - T)/\Theta < \tau^* \sim N^{-1/5}u^{3/5}$ ($u = \lambda_B/b$ with λ_B being the Bjerrum length) as well as in the deep-poor-solvent regime $\tau > \tau^*$. In the latter case we find the first-order transition between a weakly charged globule and a highly charged extended chain predicted by theory [1]. For $\tau < \tau^*$ we demonstrate that a cascade of pearl-necklace transitions can be initiated by changing the pH [2]. This result is in fact very similar to recent experimental date [3].

[1] S. Uyaver, C. Seidel, Europhys. Lett. **64** (2003) 536.
[2] 2. Uyaver, C. Seidel, J. Phys. Chem. **108** (2004) to appear in Dec.
[3] L.J. Kirwan et al., Nano Lett. **4** (2004) 149.

CPP 17.5 Di 10:45 TU C130

Simulations and experiments of star-like polylectrolytes — •Arben Jusufi — a

We present a study of star-like polyelectrolyte systems (PE-stars) which consist of polyacrylic acid chains attached to a common cyclodextrine core, which size is microscopic in comparison to the extension of the PE-star (ca. 20nm). We have carried out theoretical investigations, computer simulations and experimental studies in order to determine the osmotic coefficient, effective interactions, and structural correlations of the system. First experimental results for the osmotic coefficient (which gives the ratio between the measured osmotic pressure of the counterions to the corresponding ideal osmotic pressure) of PE-stars in the dilute limit [1] has been shown to be almost constant over a wide range of PE-star concentration. This is confirmed theortically, and by recent results obtained from Molecular Dynamics simulations, as was presented in Ref. [2]. Results for structural correlations are additionally compared with anomalous small angle X-ray scattering (ASAXS). These experiments offer novel insight into the counterion distribution of PE-stars.

[1] X. Guo and M. Ballauff, Phys. Rev. E 64, 051406 (2001); B. Das, X. Guo and M. Ballauff, Progr. Colloid Polym. Sci. 121, 34 (2002).
[2] A. Jusufi, C. N. Likos, and H. Löwen, Phys. Rev. Lett. 88, 018301 (2002); J. Chem. Phys. 116, 11011 (2002).