«EFFECT OF PRESSURE ON THE DYNAMICS OF HOMOPOLYMERS AND POLYMER BLENDS»

Ph.D. Dissertation

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ABSTRACT

In the present thesis we studied the origin of (i) the *glass transition* in homopolymers, and of (ii) *dynamic heterogeneity* in polymer blends. For this purpose we employed, dielectric relaxation spectroscopy (DRS) as a function of temperature and pressure, and pressure-volume-temperature (PVT) experiments. In addition, the structure was studied by means of x-ray scattering, the thermal properties by differential scanning calorimetry (DSC), and for the dynamics we used additionally, rheology. In order to elucidate the origin of the glass transition, different homopolymers were investigated. Using DRS (estimation of $\tau(T,P)$) and independent PVT (estimation of $V(T,P)$) experiments, the ratio of activation energies (E^*_V/H^*) was used in order to quantify the relative importance of volume and temperature in determining the origin of the liquid-to-glass transition. It was found that both, monomer volume (V_m) and local packing (q^*) play a key role in controlling this ratio and thus the dynamics of glass-formers near T_g. In addition, the origin of the "mixed" (αβ)- process (which is closely related with the glass transition) was studied. It was found that the (αβ)- process is practically a continuation of the α-process at higher temperatures. In order to investigate the dynamic heterogeneity in polymer blends we studied (i) a compatible (due to hydrogen bonds) polymer blend, (ii) a partially compatible copolymer, and (iii) a thermodynamically compatible blend. The investigation of the hydrogen-bonded blend revealed that the increase of temperature and pressure results in the broadening of the distribution of relaxation times through the weakening of hydrogen bonds and the associated decoupling of the segmental dynamics. A central result of that study was the identification of a critical temperature (T_c) above which the system becomes increasingly heterogeneous. The investigation of the copolymer has shown that the increase of pressure, unlike temperature, enhances the dynamic heterogeneity. This effect originates from the distinctly different pressure sensitivities of the homopolymers and can be traced back to differences in local packing. The investigation of the thermodynamically compatible blend revealed that the self-concentration model is able to describe the dynamics of the high-T_g component. In addition, a critical test of the model was made -for the first time- examining its ability to describe the segmental dynamics at elevated pressures. It was found that the model describes reasonable well the segmental dynamics at elevated pressures for the high-T_g component. The extracted relevant length scale (Kuhn length) was found to display only a weak P-dependence in accord with earlier experimental findings and recent simulations. Finally, a comparison of the segmental dynamics was made, with experimental results from quasi-elastic neutron scattering (QENS), neutron spin echo (NSE), and nuclear magnetic resonance (NMR) for the same polymer blend.