

**Experiment title:**

Pressure and Temperature Dependence of the Phase Behavior and its Kinetics in Diblock Copolymers

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Report:

Different polymers in general show no or little tendency to mix on a molecular level. The reason is the nearly vanishing contribution of entropy to the free energy of mixing. An interesting phenomenon results when two polymers are chemically connected to form a block copolymer. The repulsive interaction between the constituent blocks now leads to supramolecular order: the different blocks form domains which order on lattices with well defined symmetry and lattice constants of the order of several nanometers. Such structures may be investigated with small angle x-ray scattering. The small angle camera of the ESRF makes it possible to obtain scattering patterns in very short time and at high resolution which enables a detailed study of the line shape and its dependence on external parameters. It was observed recently that at a pressure of 1 bar the order-to-disorder transition of a polystyrene/polyisoprene diblock copolymer was accompanied by a density discontinuity'. The density of the ordered state was lower than that of the disordered state. The Clausius-

Clapeyron equation then implies a shift of the transition temperature to lower values with increasing pressure. We have therefore measured the variation of structure with pressure at a temperature just below the transition temperature of 1 bar. The results are shown in the figure 1. At 1 bar the scattering pattern exhibits a narrow peak of high intensity as a result of the lamellar order. The second order peak is suppressed due to the nearly symmetric composition of the block copolymer. Increase of pressure broadens the peak and lowers its intensity thus indicating the transition to the disordered state. At high pressure, however, this trend is reversed and the systems returns to the ordered state. Figure 2 displays the variation of peak width Δ and the maximum intensity $I(q^*)$ with p . Measurements at different temperatures indeed reveal a decrease of the transition temperature with pressure⁷. The opposite behavior has been found for high pressure³ above 25bar. It remains an open question whether the existence of a minimum in the pressure dependence of the transition temperature is a specific phenomenon for a certain class of block copolymers or a general feature.

- (1) H. Kasten, B. Stuhn, *Macromolecules* 1995,28,4777
- (2) B: Steinhoff et al, *Macromolecules*, submitted
- (3) D. Hajduk et al, *Macromolecules*, 1996,29, 1473

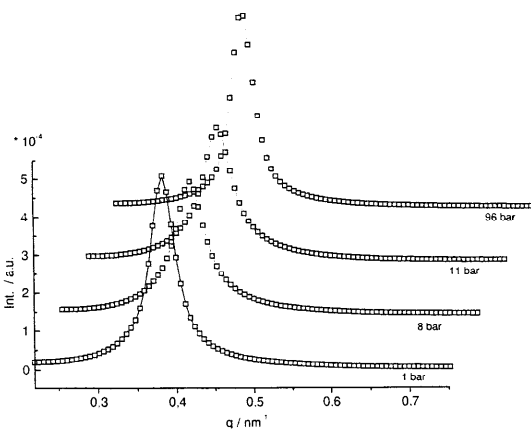


Fig. 1

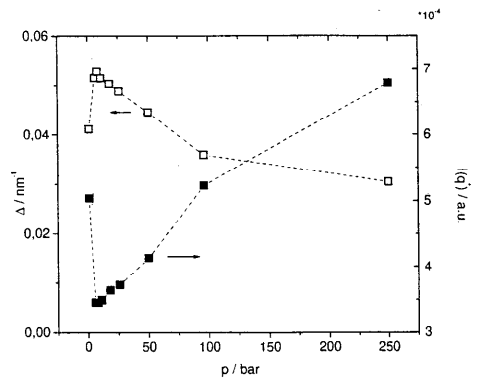


Fig. 2