Kinetics of pressure induced disorder-order transition in symmetric poly(styrene-bloc-butadiene) copolymer melts.

C. Cassignol, W. De Odorico, G. Schreyeck, R. Weidisch, J. S. Gutmann, R. Döhrmann\textsuperscript{1}, A. Meyer\textsuperscript{1} and M. Stamm\textsuperscript{2}.

Max-Planck-Institut für Polymerforschung, Postfach 3148, D-55021 Mainz, Germany
\textsuperscript{1}Beamline A2, HASYLAB Geb. 25f/455, Notkestr. 85, D-22603 Hamburg, Germany
\textsuperscript{2}Institut für Polymerforschung Dresden (IPF), Hohe Straße 6, D-01069 Dresden, Germany

In diblock copolymers, the mostly repulsive interactions between A and B segments together with the existence of a chemical bond between A and B gives rise to different ordered structures depending on the composition (volume fraction of the blocks) of the diblock copolymer\cite{1, 3}. In a system with upper (lower) critical solution temperature (U(L)CST), the system gets miscible at higher (lower) temperature and the structure breaks down. This is called the microphase separation transition (MST) which takes place at the temperature $T_{\text{MST}}$.

The dependencies of the MST on temperature, composition and degree of polymerisation have been studied and are now well known \cite{2, 3}. In addition, in previous experiment performed on a symmetric P(S-b-B) sample we showed that pressure is another thermodynamic parameter that causes the MST, shifting the $T_{\text{MST}}$ by an amount of 20°C per Kbar \cite{4}.

In our last study, we used a combination of SAXS and on-line pressure jump experiments carried out with a high pressure cell in order to follow the time evolution of the formation of the lamellar ordered structure in a symmetric P(S-b-B) diblock copolymer. Performing different shallow pressure jumps from the disordered state into the ordered one (at $T=110^\circ$C), we showed the existence of an incubation period after each jump. This observation together with an Avrami fit of the ordering dynamics suggested a one dimensional nucleation and growth process.

In the present study, coming from low pressure (100 bar), we performed on the same P(S-b-B) sample, the same pressure jump from the disordered state into the transition regime but at a lower temperature ($T=105^\circ$C) and we observed a longer incubation period (about 1000 sec) in the previous study (about 300 sec at 110°C) \cite{5}. An Avrami fit of the data shows that the process is still a one dimensional nucleation and growth process but the characteristic time of the relaxation process is larger than at 110°C, so that the kinetics of the ordering process is slower at lower temperature.

In a second part, coming from the lamellar ordered state at high pressure value (1600 bar), we released the pressure in order to reach the transition regime (between the ordered and the disordered state). Then, after various waiting time (larger than the relaxation time of the ordered structure \cite{6}), we performed once again various pressure jumps into the ordered state. Unlike the jumps performed coming from the disordered state, we observed that in all cases no incubation period appears. In addition, the further the final pressure is beyond the MST region the faster is the kinetics. This behaviour suggests that the ordered structure is not totally destroyed when the pressure is released and that it grows then right away, without nucleation step, as soon as the pressure is increased once again. In the transition region, the nuclei and a part of the structure are still present in the sample for more than several hours. This is shown by the Q* values at the beginning of the jump which are similar to the one observed in the ordered state (see Q* value at long time in figure 1a), so that the chains are already stretched \cite{7} and participate to the formation of the ordered structure, then there are only little changes in the Q* values during the pressure jump. Although further data investigation is necessary, we predict a two step ordering process, a fast initial one and a slower second one, as indicated by the double exponential fit in figure 1b.
Figure 1: Morphology peak -position (Q*), -width (σ) and inverse maximum (Io*/I*) as received by fitting a Lorentz function to the Q dependent scattering intensity. Q denotes the scattering vector $Q = (4\pi/\lambda) \sin(\theta/2)$ with $\lambda = 1.54\text{Å}$. Data were taken at the A2 beamline of Hasylab/DESY in Hamburg, Germany. Io* is the maximum intensity of the ordered phase.

(a) Nucleation and growth of the ordered lamellar structure after a pressure jump from the disordered state into the transition regime, coming from low pressure (100 bar). The line is an Avrami fit with an exponent of two.

(b) Growth of the ordered structure after a pressure jump from the transition regime into the ordered state coming from the high pressure value, hence from the ordered state. The line is a double exponential fit with relaxation times of 224 and 3183 seconds respectively.

References