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Dynamics of Structure Formation at the Microphase Separation Transition in Diblock Copolymers

M. Schuler and B. Stühn*

Fakultät für Physik, Universität Freiburg, Hermann-Herder Strasse 3, D-7800 Freiburg, Germany

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ABSTRACT: Time-resolved small-angle X-ray scattering is used to investigate the time dependence of structure formation at the ordering transition in bulk diblock copolymers. After a quench from the disordered into the ordered state two relaxation processes are found on well-separated time scales. The slow process displays an unusual temperature dependence and is discussed as a nucleation phenomenon.

The microphase-separation transition (MST) in diblock copolymers is characterized as a disorder-to-order transition.[1] Even for the case of symmetric composition it is weakly first order and is induced by concentration fluctuations. The structural properties and the thermodynamics of such systems have been extensively studied in the past.[2]

Only a few papers, however, have been devoted to the problem of the phase-transition kinetics concerning block copolymer/solvent systems.[3-5] In bulk block copolymer systems rheological measurements were used to study the kinetics of the transition from the disordered into the ordered state.[6,7] From the ordering kinetics it was concluded that heterogeneous nucleation governed the ordering process.

The kinetics of the MST is of particular interest as it combines the properties of the disorder-to-order transition with the specific dynamics of polymeric systems. As a result of this combination one finds a coupling of the glass transition of the hard block to the MST in the case of short-chain diblock copolymers of polystyrene and polyisoprene.[8] In order to avoid these complications the glass transition temperature is normally shifted by adding a solvent to the polymer. The resulting system is of course more complicated due to the specific interactions between solvent and the constituent blocks of the polymer.

In this paper we report results on the phase-transition kinetics of two bulk diblock copolymers of polystyrene/*cis*-1,4-isoprene. The properties of the polymers are compiled in Table I. They differ in their composition and in their relation between the phase-transition temperature T_{MST} and the glass transition of the polystyrene block T_g^{PS}. Whereas polymer 1 is unable to form a macrolattice with long-range order,[8] polymer 2 was shown to develop a lamellar structure with a period of 16.2 nm. The average stacking height of the lamellae within an ordered domain is 310 nm.[8]

The following results were obtained with time-resolved small-angle X-ray scattering (SAXS) during a quench of the block copolymer from the homogeneously disordered state into the ordered, microphase-separated state. The sample was contained in a small brass sample holder of low heat capacity, which was kept at the initial temperature T_i. It was then pushed into the oven of a Kratky SAXS camera which was set to the final temperature T_f. The variation of temperature with time was continuously monitored using a platinum sensor located directly in the sample material. The typical time for T to reach T_f is $\tau_T \approx 10$ s. During the quench experiment the structure factor of the diblock copolymer changes drastically from a liquidlike, broad peak to an intense Bragg peak (see Figure 1) reflecting the transition from correlation hole scattering to long-range order. In our experiment we integrate the peak intensity over a range of scattering vectors q using a detector slit of 1-mm width. It is thus possible to measure the time dependence of peak intensity with a resolution better than 1 s at a standard laboratory X-ray source. The maximum time in these experiments was 8000 s.

Table I
Properties of the Polystyrene/*cis*-1,4-Isoprene Diblock Copolymers

polymer	vol. fraction of PS	mol wt M_N	M_W/M_N	T_{MST}/°C
1	0.77	20 800	1.06	69[a]
2	0.44	15 700	1.04	89

[a] T_{MST} was not observed. Here T_S was extrapolated from SAXS measurements in the disordered state.[8]

The time evolution of the peak intensity is shown in Figure 2 for sample 2. The quench was from $T_i = 140$ °C to $T_f = 80$ °C, and the transition temperature for this sample is 89 °C. The figure clearly shows the existence of two distinctly different time scales for the relaxation of the structure factor. A quick response at short times that cannot be resolved in this experiment is followed by a slow relaxation at times τ_{slow} of several hundred seconds. Similar results are obtained for sample 1. However, in this case the fast relaxation τ_{fast} is resolved.

In general, after a temperature jump, one expects the peak intensity to relax into the new equilibrium according to the microscopic relaxation times.[10] In the case of two subsequent processes we write phenomenologically for the integrated peak intensity

$$I_{peak} = \Delta I_{fast}\left[1 - \exp\left[-\left(\frac{t}{\tau_{fast}}\right)^{\beta_{fast}}\right]\right] + \Delta I_{slow}\left[1 - \exp\left[-\left(\frac{t}{\tau_{slow}}\right)^{\beta_{slow}}\right]\right] \quad (1)$$

In eq 1 we have used stretched exponentials for the relaxation functions. ΔI_{fast} and ΔI_{slow} are the intensity changes caused by the fast and slow components, respectively. The intensities at $t = 0$ and $t \to \infty$ are known from the measurements of the equilibrium structure factor. It is indeed found that the exponent $\beta_{fast} \approx 1$, whereas β_{slow} differs significantly from 1 for both copolymers. The symmetric diblock (sample 2) goes through the MST without being stopped by the glass transition. Its β_{slow} is larger than 1 for temperatures $T_f \gtrsim 70$ °C, as would be expected for a nucleation process of the Avrami type.[4] At lower T_f it tends to $\beta_{slow} \approx 0.5$. For the asymmetric diblock (polymer 1) we find $\beta_{slow} \approx 0.5$ for all temperatures.

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* To whom correspondence should be addressed.

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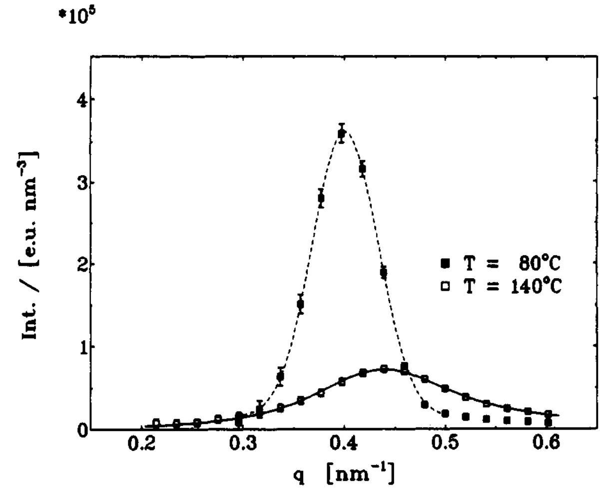

Figure 1. Comparison of the equilibrium SAXS structure factor in the disordered (open squares) and in the ordered (filled squares) states of polymer 2. The drawn line is a fit of RPA theory corrected for polydispersity.[12] The broken line is a Gaussian fit.

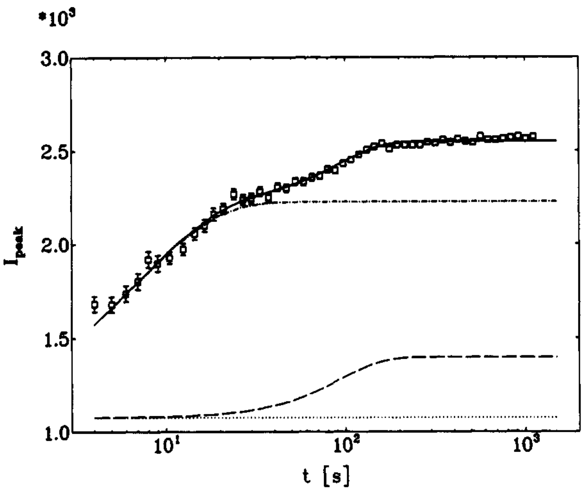

Figure 2. Time dependence of the integral peak intensity for polymer 2 during a quench from $T_i = 140$ °C to $T_f = 80$ °C. The lines show the decomposition into two modes according to eq 1.

A second interesting feature of the relaxation behavior is contained in the temperature dependence of the relaxation rates τ_{fast}^{-1} and τ_{slow}^{-1} (see Figure 3). Only those values of τ_{fast} which are significantly larger than τ_T are included in the figure. For polymer 1 the rates follow a straight line in the Arrhenius representation of Figure 3. However, the slow relaxation shows a larger activation energy.

For polymer 2 we only present the result for the slow relaxation which is well resolved on the time scale of our experiment. Its temperature dependence exhibits a clear maximum in between the transition temperature and the glass transition of the hard block.

At low temperatures the rates τ_{slow}^{-1} of both polymers are the same (see Figure 3). The stretched form of the time dependence as well as the large value of the apparent activation energy (290 kJ/(mol K)) indicates that the process is governed by the glass transition of the polystyrene-rich domains.

Finally we propose an explanation of the two relaxation processes observed in the relaxation of the structure factor of a bulk diblock copolymer during a quench from the disordered into the ordered regime. They are related to the formation of concentration fluctuations in a first step and the subsequent arrangement of these structures onto a macrolattice. The first step leads to the separation of the subchains within one polymer and is facilitated by intramolecular modes. At this stage relaxation processes are fast as the relevant glass transition temperature is that of the mixture of polystyrene and polyisoprene.

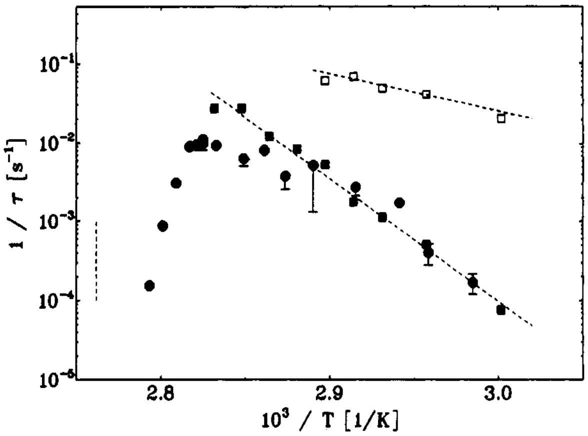

Figure 3. Temperature dependence of the relaxation rates τ_{slow}^{-1} (filled symbols) for sample 1 (squares) and sample 2 (circles). τ_{fast}^{-1} was only resolved for sample 1 (open squares). The maximum in τ_{slow}^{-1} for sample 2 occurs in between its T_{MST} (see broken line) and the glass transition T_g^{PS}.

The second step affords diffusion of the center of mass of the polymer to form the macrolattice. This process may now couple to the glass transition of the polystyrene-rich domain. For polymer 2 this coupling becomes dominant in the lower T_f regime.

The maximum in the rate τ_{slow}^{-1} for polymer 2 is supposed to be caused by the increasing thermodynamic driving force with supercooling below T_{MST} on one side and the slowing down of transport processes in the vicinity of the glass transition on the other side. The existence of a nucleation process is closely related to the weak first-order nature of the MST.[11] In this respect the formation of the macrolattice in a block copolymer melt follows mechanisms similar to those of the crystallization of a polymer from the melt.

References and Notes

(1) Leibler, L. *Macromolecules* **1980**, *13*, 1602–1617.
(2) Bates, F.; Frederickson, G. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525–527.
(3) Hashimoto, T.; Kowsaka, K.; Shibayama, M.; Suehiro, S. *Macromolecules* **1986**, *19*, 750–754.
(4) Harkless, C.; Singh, M.; Nagler, S.; Stephenson, G.; Jordan-Sweet, J. *Phys. Rev. Lett.* **1990**, *64*, 2285–2288.
(5) Connell, J.; Richards, R.; Rennie, A. *Polymer* **1991**, *32*, 2033–2042.
(6) Rosedale, J.; Bates, F. *Macromolecules* **1990**, *23*, 2329–2338.
(7) Bates, F.; Rosedale, J.; Frederickson, G. *J. Chem. Phys.* **1990**, *92*, 6255–6270.
(8) Stühn, B. *J. Polym. Sci., Polym. Phys.* **1992**, *30*, 1013–1019.
(9) Stühn, B.; Mutter, R.; Albrecht, T. *Europhys. Lett.* **1992**, *18*, 427–432.
(10) Binder, K. *J. Chem. Phys.* **1983**, *79*, 6387.
(11) Frederickson, G.; Binder, K. *J. Chem. Phys.* **1989**, *91*, 7265.
(12) Holzer, B.; Lehmann, A.; Stühn, B.; Kowalski, M. *Polymer* **1991**, *32*, 1935.