Self-Diffusion of a Symmetric PEP−PDMS Diblock Copolymer above and below the Disorder-to-Order Transition

G. Fleischer* and F. Rittig

Universität Leipzig, Fakultät für Physik und Geowissenschaften, Institut für Experimentelle Physik I, Linnestrasse 5, D-04103 Leipzig, Germany

P. Štěpánek

Institute of Macromolecular Chemistry of the Academy of Sciences of the Czech Republic, Heyrovsky sq. 2, CZ-16206 Prague, Czech Republic

K. Almdal and C. M. Papadakis

Condensed Matter Physics and Chemistry Department, Risø National Laboratory, P.O. Box 49, DK-4000 Roskilde, Denmark

Received June 30, 1998; Revised Manuscript Received December 14, 1998

ABSTRACT: The self-diffusion of a lamellae-forming nonentangled PEP−PDMS diblock copolymer was investigated with pulsed field gradient (PFG) NMR in dependence on temperature. The order-to-disorder transition (ODT), which occurs at $T = 64$ °C, was traversed. Coming from the disordered state, a sudden increase of the width of the distribution of self-diffusivities was observed (an increase of the nonexponentiality of the echo attenuation) when crossing the ODT. This is caused by the onset of anisotropic diffusion along the lamellae whose orientations are isotropically distributed. The weakness of the nonexponentiality leads to the conclusion that the range of local order in the grains is much smaller than the grain size (determined by small-angle light scattering). In addition, the temperature dependence of the self-diffusivity shows a substantial slowing down when approaching the ODT from the disordered state which is attributed to the effect of concentration fluctuations. The self-diffusion measurements are compared with earlier measurements of the zero shear viscosity and dynamic light scattering on this polymer and with Monte Carlo simulations from the literature. The results from all of these methods are consistent.

1. Introduction

Diblock copolymers consisting of monomers A and B are an interesting class of polymers since they form different ordered structures below the disorder-to-order transition (ODT) temperature, e.g., lamellar, cylindrical, and spherical structures, depending on the composition f, i.e., the volume fraction of monomeric units A.[1] The disorder-to-order transition occurs at a temperature T_{ODT} which is controlled by the parameter χN, where χ is the Flory−Huggins interaction parameter between the monomeric units A and B and N the overall chain length.[2] Recently, additional structures have been found in the phase diagram of a diblock copolymer.[3] Whereas in the literature the main interest has been devoted to the elucidation of these ordered structures, less is known about the dynamics, especially about the self-diffusion.[4] Lodge and co-workers have investigated the self-diffusion and tracer diffusion in entangled and nonentangled as well as in oriented and nonoriented symmetric diblock copolymers with forced Rayleigh scattering (FRS).[5] Even though the self-diffusion along the lamellae is locally anisotropic, they have found exponential signal decays in the FRS experiments. Whereas the ODT had no marked influence on the self-diffusion of nonentangled diblock copolymers, the influence of entanglements combined with the thermodynamic repulsion between the two chain parts in the lamellar state results in an appreciable slowing down of the self-diffusivity. Hashimoto et al. have observed a non-Fickian FRS diffusion decay in ordered diblock copolymers which they attributed to the influence of grain boundaries in the system.[6] This effect was directly seen in pulsed field gradient (PFG) NMR investigations on a symmetric polystyrene-*b*-polyisoprene diblock copolymer (PS−PI) in the ordered state by Fleischer et al., the grain size being 300 nm.[7]

Information about the self-diffusion can also be obtained by dynamic light scattering (DLS) through the measurement[8−13] of the diffusion coefficient D_{H} of the heterogeneity mode, which is related to the self-diffusion coefficient, D_{s}, by the equation[14]

$$D_{\mathrm{H}} = D_{\mathrm{s}}(1 - \kappa\chi N) \qquad (1)$$

Here, the parameter κ describes the compositional heterogeneity of the block copolymer. For anionically synthesized block copolymers with small polydispersity index, $\kappa\chi N$ is a small correction of the order of a few percent,[11] i.e., $D_{\mathrm{H}} \approx D_{\mathrm{s}}$. DLS results[11−13] also indicate that self-diffusion is not visibly influenced by the ODT; however, an additional low-amplitude diffusive component is systematically observed in the spectra of relaxation times (X-mode with diffusion coefficient D_{x}), being approximately an order of magnitude faster than the heterogeneity mode, but with a dependence on temperature different from that of D_{s}.[12] Figure 3 reproduces a typical distribution of relaxation times obtained from DLS, on the same polymer as examined in the present work. One possible explanation for D_{x} suggested in ref

---

* To whom correspondence should be addressed.

10.1021/ma981029e CCC: $18.00

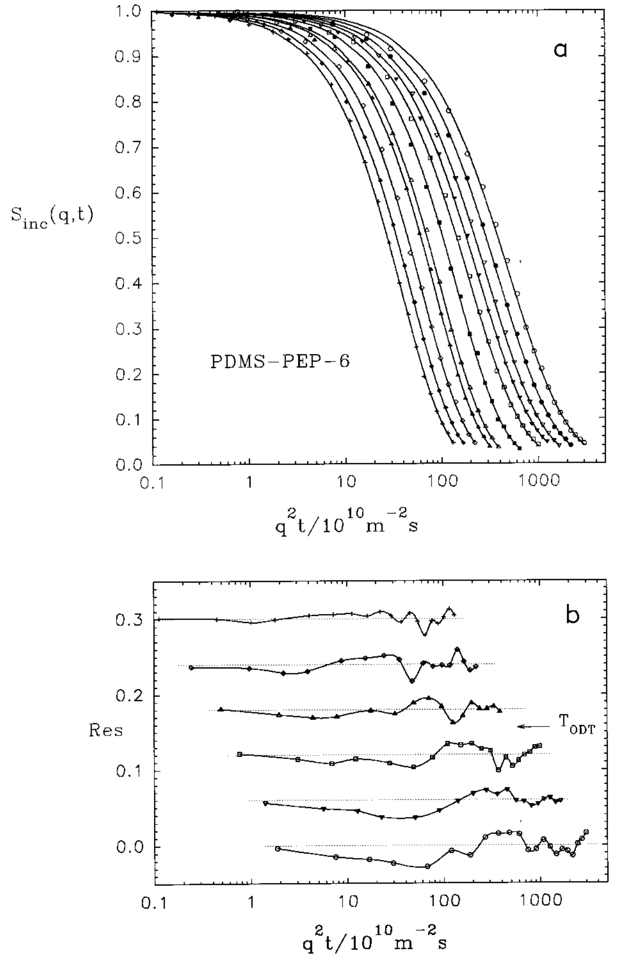

Figure 1. (a) Echo attenuations $S_{inc}(q,t)$ vs q^2t for the diblock PDMS−PEP6. From right to left: $T = 36$ (○), 41 (●), 46.5 (▽), 51 (▼), 56.5 (□), 62 (■), 67 (△), 72 (▲), 77 (◇), 82 (◆), and 87 °C (+). The lines are fits of a log-normal distribution of self-diffusivities D as described in the text. (b) Residuals of the fit of a log-normal distribution of self-diffusion coefficients to $S_{inc}(q,t)$. Symbols as in (a). For clarity of representation, data of only every second temperature are depicted and successively shifted upward by 0.06.

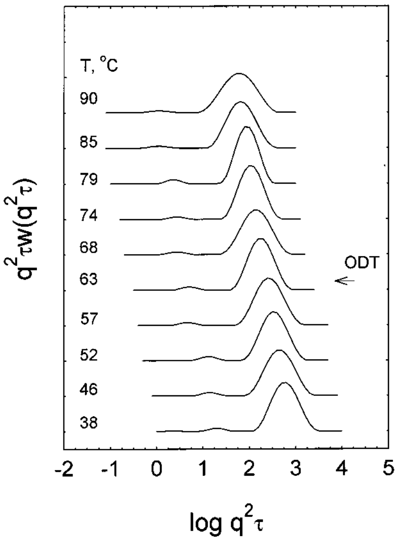

Figure 2. Distribution of relaxation times, in units of $q^2\tau$ as obtained from the measured $S_{inc}(q,\tau)$ by inverse Laplace transformation, for the temperatures indicated.

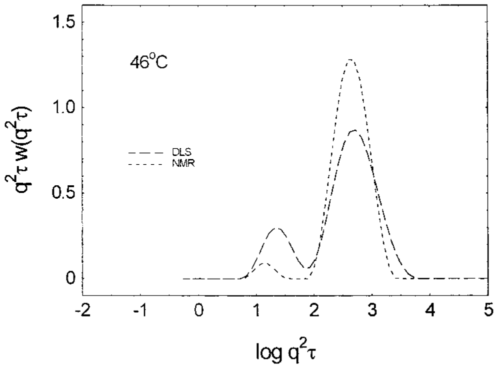

Figure 3. Comparison of distributions of relaxation times obtained at 46 °C from dynamic light scattering and PFG NMR. The time scale of the DLS data has been multiplied by q^2 to make it coincide with that of PFG NMR. D_H (right peak) and D_x (left peak) indicate the heterogeneity diffusion and X-diffusion components (from ref 12).

12 is that this mode is due to self-diffusion of a certain, relatively small, percentage of homopolymers of one block which failed to copolymerize to form the diblock copolymer. Such self-diffusion of a second component might be resolvable in a finely recorded incoherent dynamic structure factor of a PFG NMR experiment.

A number of factors may influence the self-diffusion of polymer chains in ordered lamellar diblocks that are not effective in homopolymer systems.[5] The diffusion in the ordered lamellar state is a priori anisotropic since the diffusivity parallel to the lamellar interfaces D_{par} differs from the diffusivity perpendicular to the lamellar interfaces D_{perp}. The boundaries between the stacks of lamellae or grains may act as diffusion barriers. Also, entanglements in ordered lamellar systems lead to a strong slowing down of the self-diffusivity, and finally the effective monomeric friction is expected to change at the ODT, since the composition of the environment of each block becomes more and more enriched with alike monomers. Already above the ODT, temperature−concentration fluctuations set in and lead to a reduction of the self-diffusivity of homopolymer tracers and diblocks, as theoretically predicted by Barrat and Fredrickson,[15] Leibig and Fredrickson,[16] and Tang and Schweizer.[17] These effects were qualitatively verified.[5,18,19]

In this contribution, we present results of self-diffusion measurements carried out using PFG NMR on a compositionally symmetric nonentangled poly(ethylenepropylene)-*b*-poly(dimethylsiloxane) (PEP−PDMS) diblock copolymer. The PEP−PDMS system exhibits a larger thermodynamic repulsion between the two chain parts than the thoroughly investigated systems PS−PI and PEP−PEE. The ODT of PEP−PDMS diblocks lies in a well accessible temperature range for moderate chain lengths and, hence, still not too small self-diffusivities.Therefore, this system is well-suited for investigations with PFG NMR, where the lower limit of measurable self-diffusivities is many orders of magnitude higher than in forced Rayleigh scattering. We have carefully investigated the deviation of the echo attenuation from exponentiality and found a discontinuity at the ODT, indicating a broadening of the distribution of self-diffusivities upon cooling. In addition, the temperature dependence of D shows a slowing down when approaching the ODT from higher temperatures. The self-diffusion results are in remarkable agreement both with DLS and viscosity measurements carried out on this diblock[12,20] and with computer simulations.[21,22]

2. Experimental Section

The block copolymer used is poly(ethylenepropylene)-*b*-poly(dimethylsiloxane), PEP−PDMS, synthesized anionically as described elsewhere[20] having $M_n = 6300$ g/mol and a polydispersity $P = M_w/M_n = 1.07$. The volume fraction of PEP monomers is $f_{\mathrm{PEP}} = 0.48$. This polymer, named PEP−PDMS-6, is nearly nonentangled. The order−disorder transition temperature was established by rheological measurements[20] and by static birefringence measurements to be $T_{\mathrm{ODT}} = 64$ °C. An appropriate amount of the polymer was inserted in an NMR tube and sealed under vacuum.

The labels in PFG NMR are the protons of the diffusing molecules (when using ^{1}H NMR); therefore, no chemically labeling of the chains is necessary. The spin-echo attenuation measured with PFG NMR is equivalent to the incoherent intermediate dynamic structure factor $S_{\mathrm{inc}}(q,t)$ of all the protons in the sample.[23,24] We used the stimulated echo experiment $\pi/2-\tau-\pi/2-t-\pi/2-\tau-$echo. After the first and third $\pi/2$ radio-frequency pulse, two field gradients of magnitude g and duration δ are applied. In the case of ordinary diffusion and a single self-diffusion coefficient D in the sample, the measured spin-echo attenuation $S_{\mathrm{inc}}(q,t)$ is equal to $\exp(-q^2Dt)$ with the generalized scattering vector $q = \gamma\delta g$ and γ denoting the gyromagnetic ratio of the proton.[23,24] If we have reasons to assume a distribution $w(D)$ of self-diffusion coefficients in the sample, e.g., due to the polydispersity of the polymer, then the measured $S_{\mathrm{inc}}(q,t)$ is a Laplace transformation of this distribution:

$$S_{\mathrm{inc}}(q,t) = \int w(D)\exp(-q^2tD)\,\mathrm{d}D \qquad (2)$$

The diffusion times t range between about 10 ms and some 100 ms. τ was fixed to 3 ms and δ to 1.85 ms. To vary q, g was incremented, the maximim value being 25 T/m. The measurements were carried out using the home-built spectrometer FEGRIS 400 operating at a resonance frequency of 400 MHz. The accuracy of the temperature control is ±1 K.

Depending on the value of D of the diffusing molecular species, the typical root-mean-square displacements in PFG NMR experiments $\langle z^2\rangle^{0.5} = (2Dt)^{0.5}$ ranges from ≈0.1 to ≈10 μm. Therefore, the center-of-mass diffusion in case of polymer diffusion is measured. D was not found to depend on the observation time t; therefore always ordinary, no anomalous or restricted, diffusion proceeds.

3. Results and Discussion

In Figure 1 the echo attenuations $S_{\mathrm{inc}}(q,t)$ for a set of temperatures above and below the ODT together with the fits of log-normal distributions of self-diffusion coefficients (see below) are shown. We could measure the echo attenuations very precisely and down to an attenuation of a few percent. For $T < T_{\mathrm{ODT}}$, the $S_{\mathrm{inc}}(q,t)$ are markedly nonexponential. In this temperature region the sample has the lamellar structure. It consists of grains formed by isotropically oriented stacks of more or less parallel lamellae. In a birefringence measurement[12] we have determined the grain size of the ordered lamellar domains according to the method of Garetz et al.[21] Both from the far field intensity profile and from the integral birefringence we have obtained an average size of the birefringent grains $l_{\mathrm{av}} = 2.5$ μm at a temperature 20 K below the ODT temperature. This length is by far larger than the displacements of the diblock chains $\langle z^2\rangle = 2Dt$ monitored in our experiment with values for $\langle z^2\rangle^{0.5}$ between 0.1 and 0.4 μm. We expect that only very few chains cross to an adjacent grain during the diffusion time t. $S_{\mathrm{inc}}(q,t)$ should thus obey the laws of two-dimensional diffusion between isotropically distributed parallel planes with $D_{\mathrm{par}} = D$ and $D_{\mathrm{perp}} \approx 0$. The resulting distribution of self-diffusivities measured in one dimension along the z-coordinate (what PFG NMR does) then leads to the echo attenuation

$$S_{\mathrm{inc}}(q,t) = \int \exp(-q^2tD\sin^2\theta)\,\mathrm{d}\cos\theta \qquad (3)$$

integrated from $\theta = 0°$ to $\theta = 90°$ where θ is the angle between the direction of the field gradient (z-direction) and the normal of the lamellae.[26] Equation 3 contains no adjustable parameter. However, our measured $S_{\mathrm{inc}}(q,t)$ show a substantially smaller nonexponentiality than calculated with this model. We conclude that the diblock molecules change the direction of diffusion several times during the observation time t. This can be achieved in two ways: either the lateral size of the lamellae is much smaller than our shortest displacement $\langle z^2\rangle^{0.5}$ in the ordered state which lies between 0.2 and 0.3 μm and, hence, much smaller than the diameter of a grain or the degree of order in the grains is very weak, the correlation length of the normal to the lamellar planes being much smaller than the grain size. Lodge et al. have always observed an almost perfect exponentiality of the signal decay in their FRS experiments on diblock copolymer diffusion with only a few exceptions at $T \ll T_{\mathrm{ODT}}$.[5,27,28] The nonexponential decays in FRS reported by Hashimoto et al.[6] have been explained by the influence of grain boundaries. The grating distances in the FRS experiments of Lodge et al. are between 1 and 5 μm, thus by an order of magnitude larger than in our experiment, and the grain sizes are reported to be smaller than 1 μm. The more exponential signals in their experiments may have their origin in the stronger averaging of the locally anisotropic diffusion process.

Another estimate of order in the diblock copolymers can be obtained from the width of the first-order Bragg peak in the SANS spectrum.[29] The peak width ξ is determined by the number of parallel oriented lamellae that contribute to the reflection, and from this peak width the average number of parallel correlated lamellae can be calculated to $N_s \simeq 2.75\, q^*\xi/2\pi$ where q^* is the peak position; i.e., the correlation length of the lamellar orientation is $\xi_l = 2\pi N_s/q^* \simeq 2.75\xi$.[29] At a temperature 20 K below T_{ODT}, we obtain from the data of ref 20 $\xi/2\pi = 3.3$ nm leading to $\xi_l \simeq 57$ nm, which corresponds to only 2.3% of the grain size determined using small-angle light scattering. Our results must therefore be interpreted in the framework of grains consting of lamellae having very imperfect order below ODT. Note that the block copolymers can freely diffuse along the lamellar interfaces, even though these are buckled, whereas a grain boundary hinders their diffusion substantially.

The experimental $S_{\mathrm{inc}}(q,t)$ curves can be quantitatively analyzed in several ways: with a cumulant fit, a fit of one or two stretched exponentials, $\exp(-(q^2t/q^2\tau)^\beta)$ where $D = 1/q^2\tau$, a log-normal distribution of self-diffusivities, and by Laplace inversion of eq 2 using the routine Repes, for instance.[30] A cumulant fit and one stretched exponential failed to fit $S_{\mathrm{inc}}(q,t)$, mainly at large q^2t. The most successful fit of the observed $S_{\mathrm{inc}}(q,t)$ was obtained using a log-normal distribution of self-diffusivities:

$$w(\ln D) \sim \exp[-(\ln^2(D/D_0))/2\ln^2\sigma] \qquad (4)$$

A five-parameter fit of a sum of two stretched exponentials was equally successful. The fit of a log-normal distribution is particularly useful, since it has only two adjustable parameters that can be determined with a relatively small uncertainty. This is supported by the following: if the distribution of the molecular weight is log-normal and D depends on M with a power law $D \sim M^{-\alpha}$, the distribution of D is also log-normal with $\ln^2 \sigma = \alpha^2 \ln P$ where P is the polydispersity of the molecular weight, $P = M_w/M_n$.[31] A log-normal distribution of M is often rather well fulfilled for anionically polymerized samples where the GPC traces are nearly Gaussian. From our measured value $\ln^2 \sigma \approx 0.065$ in the disordered state and $\alpha = 1$ (Rouse dynamics), we obtain a polydispersity $P = 1.067$, in complete agreement with the polydispersity of the diblock copolymer. Thus, in the disordered state, the observed distribution of D seems to be caused exclusively by the distribution of M. The fits of $S_{\mathrm{inc}}(q,t)$ with eq 2 using a log-normal distribution of D, eq 4, are shown in Figure 1a. The residuals, shown in Figure 1b, do not systematically deviate from zero; only at low q^2t values are the experimental $S_{\mathrm{inc}}(q,t)$ values systematically slightly below the fitted curve, indicating a larger amount of fastly diffusing species in the sample than described by the log-normal distribution. This is most pronounced at the lowest temperatures.

Figure 2 shows the Laplace inversions of the measured $S_{\mathrm{inc}}(q,t)$ at various temperatures obtained with the program Repes.[30] The main peak of the distribution is well described by the log-normal distribution. In addition to this dominant component arising from the self-diffusion of the copolymer chains, there is a weak faster component which may be attributed to trace amounts of free homopolymer chains in the system, as explained above. Figure 3 compares the distribution of relaxation times obtained at 46 °C in the present experiments by PFG NMR with that obtained by DLS;[12] the horizontal axis of the latter has been corrected by the factor q^2 to make it equivalent to the PFG NMR scale. The position of the dominant peaks is almost identical, confirming that the diffusion coefficient of the heterogeneity mode measured by DLS is essentially identical to the self-diffusion coefficient measured by NMR. The scatter in the positions of the fast peak in the NMR data is rather large, as seen in Figure 2, which does not allow a quantitative comparison with DLS experiments; nevertheless, it is plausible to assume that the fast weak component describes the same process in both experiments. The activation energy of the D_x mode in DLS, the faster mode, was found to be 27 kJ/mol. This relatively low value rules out the possibility that PEP homopolymer diffusion is the origin of the fast mode in DLS because the PEP homopolymer is dissolved in the PEP part of the lamellae and where it has a higher activation energy of self-diffusion. For the activation energy of pure PEP see Figure 5a. It may be that the fast diffusing signal in NMR arises from PDMS homopolymer traces (which cannot be excluded completely) or from low molecular traces which have been not detected by GPC. Low molecular traces are often strongly weighted in the NMR signal due to their long nuclear magnetic relaxation times. In DLS, cooperative motion of these low molecular traces relative to the diblock chains may lead to a slow diffusive mode in DLS, which should be faster than the heterogeneity mode which is controlled by polymer diffusion only.

Figure 4 shows the temperature dependence of the width of the log-normal distribution, $\ln^2 \sigma$, obtained from the fits (eq 4). There is a clear discontinuity at the ODT; the distribution width increases strongly upon cooling into the ordered state, reflecting the onset of two-dimensional diffusion. At $T > T_{\mathrm{ODT}}$, there is no indication of two-dimensional diffusion, as expected, and the distribution width is only determined by the polydispersity of the polymer as explained above.

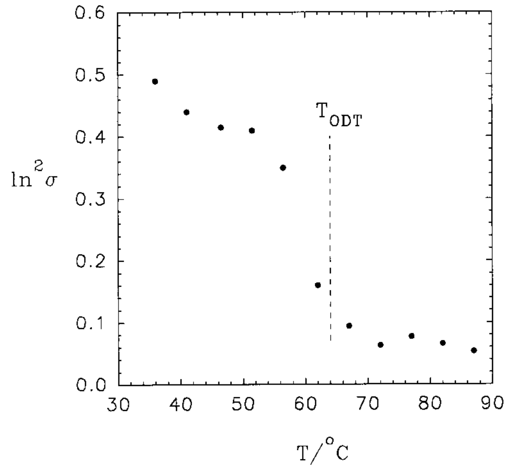

Figure 4. Distribution width of the self-diffusivities given as $\ln^2 \sigma$ of a log-normal distribution of D in dependence on temperature.

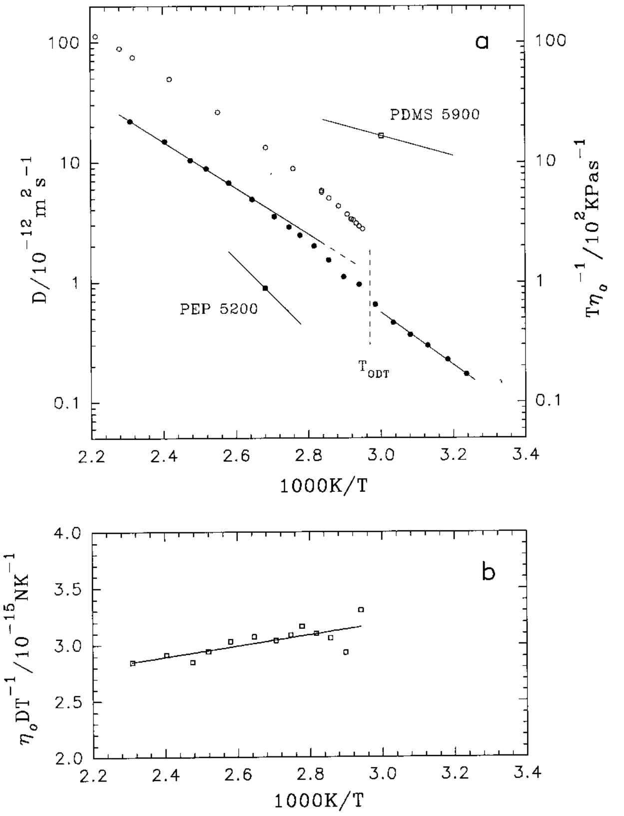

Figure 5. (a) Arrhenius plot of the self-diffusivity of the PEP−PDMS-6 diblock (●). The most probable diffusivity $D_{\max} = D_0/\exp(\ln^2 \sigma)$ of the log-normal distribution of self-diffusivities is given. The experimental errors do not exceed the symbol size. Additionally, the self-diffusivities of a PDMS with $M_w = 5900$ g/mol from ref 38 and that of a PEP with $M_w = 5200$ g/mol from ref 39 are shown together with lines representing the temperature dependence of the self-diffusion of PDMS having an activation energy $E_A = 16$ kJ/mol, value from ref 38, and of PEP having $E_A = 58$ kJ/mol, value from ref 40. On the right ordinate, the zero shear viscosity η_0 given as T/η_0 (○) is displayed, data from ref 20. (b) Arrhenius plot of the quantity $\eta_0 D/T$.

Figure 5 displays an Arrhenius plot of the PFG NMR self-diffusion coefficients given as $D_{\max} = D_0/\exp(\ln^2 \sigma)$, the most probable self-diffusivity of the distribution.[31] Two linear relationships describe the data: one in the ordered state having an activation energy of 45 kJ/mol another one in the disordered state for temperatures larger than $T_{\mathrm{ODT}} + 50$ K with an activation energy of 36 kJ/mol. The region between 64 and 110 °C is a transition region.

Unfortunately, we cannot compare with the diffusion in a hypothetically disordered state since no diblock of same composition but shorter chain length is available. The values of D and the activation energy of self-diffusion are between the values of two homopolymers PEP and PDMS with comparable chain length; cf. Figure 5. The temperature dependence of D of the diblock should be Arrhenius-like at high temperatures far above T_g, as observed for the two homopolymers PDMS and PEP, but about 50 K above T_{ODT} a retardation of D sets in upon cooling. As expained subsequently, the self-diffusion coefficients show the same temperature dependence as the zero shear viscosity data from ref 20. The temperature dependence of the zero shear viscosity of PEP obeys a VFT equation with $T_0 = -138$ °C and that of PDMS with $T_0 = -192$ °C, but for the PEP−PDMS-6 diblock a considerably larger T_0 (−72 °C) was found. This finding is attributed to concentration fluctuations which slow D when approaching the ODT from higher temperatures already before the ODT is reached. Extrapolating the temperature dependences from below and above the ODT, a jump of the diffusion coefficient just at the ODT by a factor very close to $^2/_3$ is observed, the factor by which the diffusion is reduced during a transition from 3- to 2-dimensional diffusion.[32]

In ref 20 the zero shear viscosity η_0 of this diblock was measured. Note that the slow collective dynamical processes seen in the low-frequency behavior of $G'(\omega)$ and $G''(\omega)$ and which give rise to a failure of the temperature−time superposition[33] do not influence the zero shear viscosity. In Figure 5a we have depicted the zero shear viscosity as T/η_0 in the disordered state. The temperature dependence of this quantity very closely resembles that of the self-diffusitity D. We assume the validity of the Rouse dynamics with the well-known expression $\eta_0 D/T = \rho R\langle r^2\rangle_0/36M$.[34] R is the gas constant and ρ the density ($\rho = 0.95$ g/cm^3 at $T = 100$ °C[35]). From our D and η_0 we get the end-to-end distance of the chain $\langle r^2\rangle_0^{0.5} = 9.3$ nm at $T = 100$ °C. From known $\langle r^2\rangle_0/M$ values for PEP[36] and PDMS[37] we obtain $\langle r^2\rangle_0^{0.5} = 6.7$ nm for our diblock copolymer using $\langle r^2\rangle_0 = \langle r^2\rangle_0^{\mathrm{PEP}} + \langle r^2\rangle_0^{\mathrm{PDMS}}$. SANS measurements give $2\pi/q^* = 10.65$ nm at this temperature.[20] The temperature dependence of $\eta_0 D/T \sim \rho\langle r^2\rangle_0$ is shown in Figure 5b. We get from the slope $\mathrm{d}\ln(\rho\langle r^2\rangle_0)/\mathrm{d}T = -(1.2 \pm 0.3) \times 10^{-3}\ \mathrm{K}^{-1}$. Using $\mathrm{d}\ln \rho/\mathrm{d}T = -0.7 \times 10^{-3}\ \mathrm{K}^{-1}$ [35] for the temperature dependence of the density, we obtain $\mathrm{d}\ln\langle r^2\rangle_0^{0.5}/\mathrm{d}T = 0.5\ \mathrm{d}\ln(\rho\langle r^2\rangle_0)/\mathrm{d}T = -0.25 \times 10^{-3}\ \mathrm{K}^{-1}$ for the temperature dependence of the coil dimension (from the D and η_0 data). From known coefficients of thermal expansion of the PEP and PDMS coils, $\kappa_{\mathrm{PEP}} = -0.58 \times 10^{-3}\ \mathrm{K}^{-1}$ and $\kappa_{\mathrm{PDMS}} = 0.39 \times 10^{-3}\ \mathrm{K}^{-1}$,[20] we obtain $\mathrm{d}\ln\langle r_0{}^2\rangle^{0.5}/\mathrm{d}T \approx (\kappa_{\mathrm{PEP}} + \kappa_{\mathrm{PDMS}})/2 = -0.1 \times 10^{-3}\ \mathrm{K}^{-1}$ assuming equal end-to-end distances for the PEP and PDMS chain parts. Thus, with decreasing temperature, $\langle r^2\rangle_0$ determined from our diffusion and viscosity data increases more strongly than calculated from coil expansivities of the homopolymers. The temperature dependence of the lamellar thickness derived from the peak position in SANS is even larger: $\mathrm{d}\ln(1/q^*)/\mathrm{d}T = -1.0 \times 10^{-3}\ \mathrm{K}^{-1}$. The differences of these temperature coefficients give evidence of chain stretching upon cooling, below the ODT.

Our results are in remarkable accord with the Monte Carlo and molecular dynamics simulations. Hoffmann et al.[21] have caried out Monte Carlo simulations on symmetric diblock copolymer melts. In this study, the center-of-mass diffusivity normalized to the bare diffusivity of a chain of equal chain length but with zero thermodynamic interaction ($\chi = 0$) was found to decrease upon approaching the ODT from higher temperatures to a value of 40% because of the onset of concentration fluctuations. At the ODT itself, however, the sudden decrease of D is only weak. Simultaneously, the radius of gyration and the distance of the centers of mass of the two blocks increase with decreasing temperature, the first one weaker than the second one, reaching a factor of 1.13 and 1.25, respectively, at the ODT. Murat et al. have studied the self-diffusion of a nonentangled symmetric diblock copolymer in a continuum space molecular dynamics simulation.[22] When the ODT is approached (by enlarging the AB segment interaction parameter), the self-diffusion coefficient reduces to about 60% of its value in the completely disordered state. In the ordered state, D_{par} along the lamellar planes does not depend on the interaction parameter; its value is equal to the self-diffusion coefficient in the disordered state just above the ODT. D_{perp}, however, decreases sharply in the ordered state already at low values of the interaction parameter, immediately below the ODT. According to the results of Murat et al.,[22] the self-diffusion coefficient decreases when the ODT is approached; the self-diffusion becomes two-dimensional along the lamellar planes in the ordered state where, in an isotropically ordered sample, $^2/_3$ of the self-diffusivity along the lamellar planes is measured.

4. Conclusion

In conclusion, the full information on the form of the echo attenuation $S_{\mathrm{inc}}(q,t)$ measured using PFG NMR in microphase-separating diblock copolymers leads to deeper insights into the dynamics of diblock copolymers in the ordered and the disordered state. We have observed a sudden broadening of the distribution of self-diffusivities below the ODT which is attributed to the onset of anisotropic diffusion along the planes of the lamellae with isotropically distributed orientations. In contrast to the measurements with FRS, this anisotropic motion is not fully averaged out in the PFG NMR experiment which monitors shorter diffusion distances than FRS. However, the weakness of the observed nonexponentiality of the echo attenuation leads to the conclusion that the correlation length of parallel order of lamellae in the grains is considerably shorter than the grain size determined by small-angle light scattering. Approaching the ODT from the disordered state, the self-diffusion is retarded due to concentration fluctuations. At the ODT itself there is only a weak decrease of D. In addition, we have detected trace amounts of a faster diffusing species in the NMR signal, in both the ordered and the disordered state. The self-diffusivity of the diblock copolymers compares well with the heterogeneity mode detected with DLS on the same sample. The X-mode found using DLS can plausibly be assigned to the cooperative diffusion of the traces found in PFG NMR. The self-diffusivity above the ODT temperature is in good accord with the zero shear viscosity. The value of the end-to-end distance of the diblock copolymer calculated using the Rouse model together with the measured self-diffusion and viscosity and their temperature dependence agrees with the data from SANS. Investigations on an asymmetric PEP−PDMS diblock are now in progress.

Acknowledgment. G.F. and F.R. thank the Deutsche Forschungsgemeinschaft (SFB 294) for financial support. P.S. acknowledges support by Grant A4050604 of the Grant Agency of the Academy of Sciences of the Czech Republic.

References and Notes

(1) Bates, F. S. *Science* **1991**, *251*, 898.
(2) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(3) Bates, F. S.; Schulz, M. F.; Khandpur, A. K.; Förster, S.; Rosedale, J. H.; Almdal, K.; Mortensen, K. *J. Chem. Soc., Faraday Discuss.* **1994**, *98*, 7.
(4) Fredrickson, G. H.; Bates, F. S. *Annu. Rev. Mater. Sci.* **1996**, *26*, 501.
(5) Lodge, T.; Hamersky, M. W.; Milhaupt, J. M.; Kannan, R. M.; Dalvi, M. C.; Eastman, C. E. *Macromol. Symp.* **1997**, *121*, 219 and references therein.
(6) Ehlich, D.; Takenaka, M.; Okamoto, S.; Hashimoto, T. *Macromolecules* **1993**, *26*, 189. Ehlich, D.; Takenaga, M.; Hashimoto, T. *Macromolecules* **1993**, *26*, 492.
(7) Fleischer, G.; Fujara, F.; Stühn, B. *Macromolecules* **1993**, *26*, 2340.
(8) Jian, T.; Anastasiadis, S. H.; Semenov, A. N.; Fytas, G.; Adachi, K.; Kotaka, T. *Macromolecules* **1994**, *27*, 4762.
(9) Pan, C.; Maurer, W.; Liu, Z.; Lodge, T. P.; Stepanek, P.; von Meerwall, E. D.; Watanabe, H. *Macromolecules* **1995**, *28*, 1643.
(10) Balsara, N. P.; Stepanek, P.; Lodge, T. P.; Tirrell, M. *Macromolecules* **1991**, *24*, 6227.
(11) Stepanek, P.; Lodge, T. P. *Macromolecules* **1996**, *29*, 1244.
(12) Stepanek, P.; Almdal, K.; Lodge, T. P. *J. Polym. Sci., Polym. Phys. Ed.* **1997**, *35*, 1643.
(13) Papadakis, C. M.; Brown, W.; Johnsen, R. M.; Posselt, D.; Almdal, K. *J. Chem. Phys.* **1996**, *104*, 1611.
(14) Stepanek, P.; Lodge, T. P. In *Light Scattering, Principles and Development*; Brown, W., Ed.; Clarendon Press: Oxford, 1996.
(15) Barrat, J.-L.; Fredrickson, G. H. *Macromolecules* **1991**, *24*, 6378.
(16) Leibig, C. M.; Fredrickson, G. H. *J. Polym. Sci., Polym. Phys. Ed.* **1996**, *34*, 163.
(17) Tang, H.; Schweizer, K. S. *J. Chem. Phys.* **1995**, *103*, 6296.
(18) Kannan, R. M.; Su, J.; Lodge, T. P. *J. Chem. Phys.* **1998**, *107*, 4634.
(19) Lodge, T. P.; Blazey, M. A.; Hamley, I. W. *Macromol. Chem. Phys.* **1997**, *198*, 983.
(20) Almdal, K.; Mortensen, K.; Ryan, A. J.; Bates, F. S. *Macromolecules* **1996**, *29*, 5940.
(21) Hoffmann, A.; Sommer, J.-U.; Blumen, A. *J. Chem. Phys.* **1997**, *106*, 6709.
(22) Murat, M.; Grest, G. S.; Kremer, K. *Europhys. Lett.* **1998**, *42*, 401.
(23) Kärger, J.; Pfeifer, H.; Heink, W. *Adv. Magn. Reson.* **1989**, *12*, 1.
(24) Fleischer, G.; Fujara, F. *NMR: Basic Princ. Prog.* **1994**, *30*, 159.
(25) Garetz, B. A.; Newstein, M. C.; Dai, H. J.; Jonnalagadda, S. V.; Balsara, N. P. *Macromolecules* **1993**, *26*, 3151.
(26) Callaghan, P. T. *Principles of Nuclear Magnetic Resonance Microscopy*; Clarendon Press: Oxford, 1993; Chapter 6.3.3.
(27) Lodge, T. P.; Dalvi, M. C. *Phys. Rev. Lett.* **1995**, *75*, 657.
(28) Hamersky, M. W.; Tirrell, M.; Lodge, T. P. *J. Polym. Sci., Polym. Phys. Ed.* **1996**, *34*, 2899.
(29) Papadakis, C. M.; Almdal, K.; Mortensen, K.; Posselt, D. *J. Phys. II (Paris)* **1997**, *7*, 1829.
(30) Jakes, J. *Collect. Czech. Chem. Commun.* **1995**, *60*, 1781.
(31) Booth, C.; Colclough, R. O. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon Press: Oxford, 1989; Vol. 1, Chapter 3.4.4.
(32) Reference 26, Chapter 7.5.2.
(33) Rosedale, J. H.; Bates, F. S. *Macromolecules* **1990**, *23*, 2329.
(34) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, 1978.
(35) Vigild, M. E. PhD Thesis, Risø National Laboratory, Roskilde, Denmark, 1997.
(36) Richter, D.; Farago, B.; Butera, R.; Fetters, L. J.; Huang, J. S.; Ewen, B. *Macromolecules* **1993**, *26*, 795.
(37) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, *5*, 261.
(38) Fleischer, G.; Appel, M. *Macromolecules* **1993**, *26*, 5520.
(39) Pearson, D. S.; Fetters, L. J.; Graessley, W. W.; Ver Strate, G.; von Meerwall, E. *Maromolecules* **1994**, *27*, 711.
(40) Shull, K. R.; Kramer, E. J.; Bates, S. F.; Rosedale, J. A. *Macromolecules* **1991**, *24*, 1383.

MA981029E