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Chain diffusion in the melt of an asymmetric diblock copolymer in the disordered and ordered state

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Abstract The self-diffusion in a polystyrene-b-polyisoprene diblock copolymer with a strongly asymmetric composition was investigated with dependence on temperature by pulsed field gradient (PFG) NMR. The diblock shows with decreasing temperature a disorder-to-order-transition at $T_{\mathrm{ODT}} = 393$ K from a micellar liquid-like to a bcc ordered state which was recently measured by SAXS [M. Schwab and B. Stühn, Phys. Rev. Lett. (1996) 76: 924]. Two diffusivities were observed, one of the free diblock chains and one of the diblock chains fixed in micelles. The volume fraction of free chains decreases with decreasing temperature. The diffusivity of the free chains must be related to chain stretching. The experiments show that within the time of the NMR experiment (300 ms) there is no exchange between the diblock chains in the free state and those fixed in the core of the micelles.

Key words Polymer melt – asymmetric diblock copolymer – polyisoprene-b-polystyrene – disorder-to-order transition – micelles – chain self-diffusion

Introduction

Block copolymers exhibit interesting structural properties since the interplay between thermodynamic repulsion of the chemically different chain parts and entropy effects leads to a large variety of microphase separation phenomena [1]. Diblocks show, depending on composition, essentially lamellar, cylindrical or spherical structures in the ordered state. The molecular transport in these microphase-separated block copolymers is more complicated than in homopolymer melts and solutions. The structures, resulting in a non-homogeneous composition of the solution or melt, may give rise to diffusion barriers or at least to a retardation of the diffusion process.

The diffusion in lamellar disordered and ordered symmetric diblocks was studied by Lodge and coworkers [2–4] with the forced Rayleigh scattering technique (FRS). They have shown that the influence of the disorder-to-order transition on the chain diffusion is only weak in non-entangled melts whereas in entangled melts the repulsive interaction of the two chain parts in combination with the existence of entanglements (a tube) leads to a more or less dramatic slowing down of the chain mobility with increasing entanglement density and in different segregation states [4]. Using field gradient NMR measurements it was shown in detail that the disorder-to-order transition in a symmetric diblock copolymer polystyrene-b-polyisoprene (PS-b-PI) led to a confinement of the chain diffusion to within the macrocrystalline grains [5].

In the melt, the chains of asymmetric diblocks can be arranged in micellar structures with cores formed by the shorter chain parts. In this asymmetric ordered diblock melts not all chains are included in the micellar cores but also free chains exist in the ordered state [6–8]. An additional effect is that the micelles can undergo a transition from a liquid-like structure into a macrocrystalline bcc ordered array. Such ordering was also observed in micellar solutions of block copolymers at higher polymer concentrations [9, 10]. The present paper is concerned with the chain diffusion in a diblock copolymer with strongly asymmetric composition in which the chains arrange in a micellar structure. The transition from the homogeneously mixed, disordered state to a macrocrystalline state is preceded by an intermediate structure of micelles with liquid-like order. This sequence of states has been observed recently [8, 11]. In particular, in this state of liquid-like order not all chains are included in micelles. A fraction of the chains is free and forms a continuous matrix. Lowering the temperature reduces the number of free chains and finally leads to a transition to a bcc ordered macrocrystalline state.

Since the micellar structures in asymmetric ordered diblocks resemble structures in micellar polymeric solutions, in sterically stabilized polymeric colloids and also the structure of star polymers, a study of their diffusion properties is of general interest. In an earlier FRS study of a solution of styrene-b-ethylenebutylene-b-styrene triblock copolymer in which the styrene chain parts form the core of micelles, two diffusivities were observed which were attributed to micelles and free chains [6]. Recently, Schaertl and coworkers have investigated the diffusion of an asymmetric PS-b-PI diblock with added PI homopolymer, one with a chain length shorter than the diblock PI chain part (wet brush behavior) and one with a chain length longer than the PI chain part of the diblock (dry brush behavior) [7]. SAXS experiments have shown a bcc order of micellar structures in both systems, whereas FRS experiments have found one diffusivity in the dry brush system and two diffusivities in the wet brush system, the last differ by about one order of magnitude. The temperature dependence of the diffusion was found to be approximately equal to that of pure polyisoprene, the experimental scatter was, however, considerable. The optically labeled chain part was the polystyrene, and an interference with the glass transition in the cores of the micelles was probably the reason of this scatter.

In this paper, we report on the self-diffusion studies of an asymmetric PS-b-PI diblock of $M_w = 46{,}000$ and a volume fraction of polystyrene $f = 0.11$ dependent on temperature using pulsed field gradient (PFG) NMR. The structure of the melt was well characterized by SAXS [8]. In our study, two diffusivities were observed, one of the free chains and one of the micellar structures. Especially, the diffusion of the free chains is strongly affected by the presence of the micelles.

Experimental

Diblock copolymer

The investigated diblock copolymer is a poly(styrene-b-1,4-isoprene) with a molecular weight $M_w = 46{,}000$ and an M_w/M_n of 1.09. The volume fraction of polystyrene f_{ps} is 0.11. The polymer was synthesized by standard anionic polymerization techniques. From known densities and monomeric molecular weights of polystyrene and polyisoprene, we obtain for the molecular weight of the PS-part $M_{ps} = 5500$ and for that of the PI-part $M_{PI} = 40{,}500$. The respective chain lengths (degree of polymerization) are $N_{PS} = 53$ and $N_{PI} = 650$. The entanglement chain length N_e is estimated from the formula $N_e^{-1} = (fN_{e,ps}^{-0.5} + (1-f)N_{e,PI}^{-0.5})^2$ [12] to $N_e = 79$ for our diblock using the entanglement molecular weights of PS and PI of 17,500 and 5000, respectively. N_e is mainly determined by the longer polyisoprene chain part, and the result for N_e does not sensitively depend on the relation used to calculate N_e. The diblock melt is well entangled, $N/N_e = 8.2$ in the disordered state.

The unperturbed end-to-end distances of the two chain parts are $\langle R^2\rangle_{PS}^{0.5} = 5$ nm and $\langle R^2\rangle_{PI}^{0.5} = 16$ nm using $\langle R^2/M\rangle_{PS} = 4.6 \times 10^{-21}$ m^2 and $\langle R^2/M\rangle_{PI} = 6.4 \times 10^{-21}$ m^2. The $\langle R^2\rangle^{0.5}$ of the diblock chain in a completely disordered state is $(\langle R^2\rangle_{PS} + \langle R^2\rangle_{PI})^{0.5} = 16.8$ nm.

Self-diffusion measurements

The self-diffusion coefficients of the diblock chains in the melt have been measured by pulsed field gradient NMR. The spectrometer used was the home-built FEGRIS 400 with a proton resonance frequency of 400 MHz [13]. With PFG-NMR, the displacement of the proton-bearing chain segments is measured [14]. In the diffusion limit, i.e. for root mean square displacements $\langle z^2\rangle^{0.5}$ much larger than the possible diffusion constraints in the system which can act as a source of anomalous diffusion, the measured echo attenuation is given for one kind of diffusing species by

$$S_{inc}(q, t) = \exp(-q^2Dt)\,, \qquad (1)$$

where we have used the analogy of field gradient NMR with the quasielastic incoherent scattering experiment [15, 16]. D denotes the self-diffusion coefficient and t the diffusion or observation time which in our experiment is equal to the separation of the two field gradient pulses. The generalized scattering vector q is the product of the gyromagnetic ratio of the proton γ, the magnitude g and the duration δ of the field gradient pulses: $q = \gamma\delta g$. We always have worked under the narrow pulse approximation, i.e. at $\delta \ll t$.

The stimulated echo pulse sequence was used: $\pi/2 - \tau - \pi/2 - t - \pi/2 - \tau$ echo with the pulse distance $\tau = 3$ ms and the diffusion time $t = 300$ ms except at $T = 333$ and 342 K where $t = 200$ ms was used because of the shorter relaxation time T_1 at lower temperatures. The field gradient pulses were applied after the first and the third $\pi/2$-rf pulse, respectively. The effective field gradient pulse width was $\delta_{\text{eff}} = 1.85$ ms. In the experiment, g was increased from 0 to 25 T/m.

To diffusivities were observed in the diblock melt. In this case the echo amplitude A is described by

$$A/A_0 = \sum \phi_i \exp(-2\tau/T_{2,i})\exp(-t/T_{1,i})S_{\text{inc},i}(q,t) \Big/ \sum \phi_i \exp(-2\tau/T_{2,i})\exp(-t/T_{1,i}) \,, \tag{2}$$

with $i = 1$ and 2 characterizing the two kinds of species (in our case, fast and slowly diffusing chains). A_0 denotes the echo amplitude without applied field gradients. The $T_{1,i}$ and $T_{2,i}$ are the longitudinal and transverse NMR relaxation times of the two species, respectively. The ϕ_i denote the relative number of protons of each kind of species in the sample. We can set ϕ_i equal to the volume fraction of the species under consideration since the signal amplitude is predominantly determined by the polyisoprene protons.

In an overview experiment we have proved that $T_{2,i}$ of the two species are long in comparison with the time $2\tau = 6$ ms in which transverse relaxation occurs, therefore the terms $\exp(-2\tau/T_{2,i})$ were set equal to one. At $T = 458$ K, the transverse relaxation was found to be monoexponential with a T_2 of 60 ms. Also the longitudinal magnetization decay was found to be almost exponential with the $T_{1,i}$ values being nearly identical for the two species. Therefore, Eq. (2) may be simplified to

$$A/A_0 = \phi_1 S_{\text{inc},1}(q,t) + \phi_2 S_{\text{inc},2}(q,t) \,, \tag{3}$$

neglecting the small differences in the relaxation behavior in the two kinds of species. The influence of longitudinal relaxation on ϕ_i was checked in a separate experiment in which the stimulated echo pulse sequence was preceded by a π-rf pulse with a distance of 300 ms to the first $\pi/2$-rf pulse. In this time interval an additional longitudinal relaxation proceeds [17, 18]. This additional relaxation led to a change of the experimentally determined ϕ_i of a few percent only indicating that the slowly diffusing chains have very slightly shorter T_1 than the fast diffusing chains.

Equations (2) and (3) are valid for the case of slow exchange between the diblock chains in the free state and being fixed in the core of micelles (see below). Our experimental echo attenuations were fitted with one diffusion coefficient D_{fast} for the fast diffusion (Eq. (1)). The $S_{\text{inc,slow}}(q,t)$ is non-exponential due to a distribution of self-diffusion coefficients. The experimental accuracy of the measured echo attenuation is not good enough to determine the exact distribution function. There are different mathematical expressions to approximate a distribution function. We have tested a log-normal distribution and a normal (Gaussian) distribution of self-diffusion coefficients and a stretched exponential (KWW-expression) $\exp(-(q^2tD_{\text{KWW}})^\beta)$ for fitting $S_{\text{inc,slow}}(q,t)$. The fit with a log-normal distribution was poor while the two other fits turned out to be sufficiently good with comparable quality. In this paper, we present the results of the KWW-fit which is the most simple one mathematically and which is often used for the interpretation of PFG-NMR measurements [19]. The self-diffusion coefficients given in Results and Discussion are the averaged $\langle D\rangle_{\text{slow}}$ calculated with $\langle D\rangle = \beta D_{\text{KWW}}/\Gamma(1/\beta)$ with Γ denoting the Gamma function.

The polymer was sealed under vacuum in an NMR sample tube of 7.5 mm o.d. The temperature was varied between 333 and 458 K, the temperature accuracy in the probe head was ± 1 K. There was no change of the echo attenuations after several repeated measurements with their heating–cooling cycles indicating that no degradation or other chemical reactions occur during the elevated temperatures.

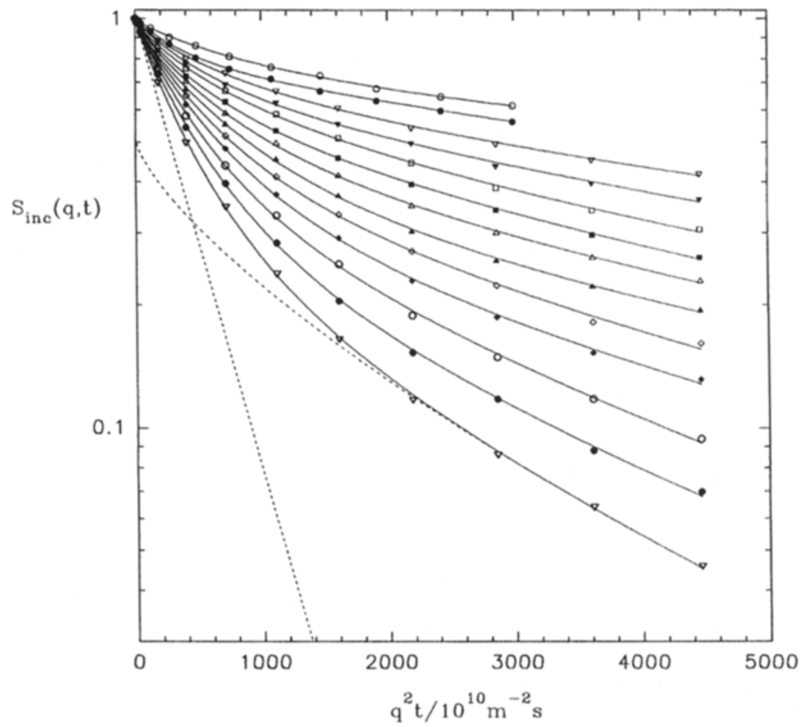
Results

The measured echo attenuations for 13 different temperatures between 333 and 458 K are shown in Fig. 1. They consist of two parts, a fast and a slow decay. Following the observation of two kinds of species in the SAXS experiments of Schwab and Stühn [11] we have fitted our echo attenuations with a sum of a fast and a slow decay. A good fit was achieved with a single exponential for the fast decay and a stretched exponential for the slow decay. A fit with only one stretched exponential fails considerably, therefore the assumption of two kinds of species is unavoidable in our investigation also. The signal in the fast decay very probably contains small contributions from low molecular weight traces (which is often observed in PFG-NMR studies of polymer melts). Therefore, the measured self-diffusion coefficient D_{fast} and the ϕ_{fast} can be slightly too large at lower temperatures. This influence reduces with increasing temperature, the values at the higher temperatures are reliable.

In Fig. 2 the temperature dependence of the two self-diffusivities derived from the echo attenuation are shown in an Arrhenius plot. They are discussed in the next section.

In Fig. 3 the contribution of the fast diffusing species to the signal, ϕ_{fast}, determined by PFG-NMR in this work

Fig. 1 Echo attenuation plots at different temperatures. From top to bottom: $T = 333$, 344, 354, 364, 375, 385, 395, 406, 417, 428, 438, 448 and 458 K. The experimental error is about the symbol size. The lines are fits with a sum of an exponential and a stretched exponential. Both functions are separately shown as dashed lines for $T = 458$ K



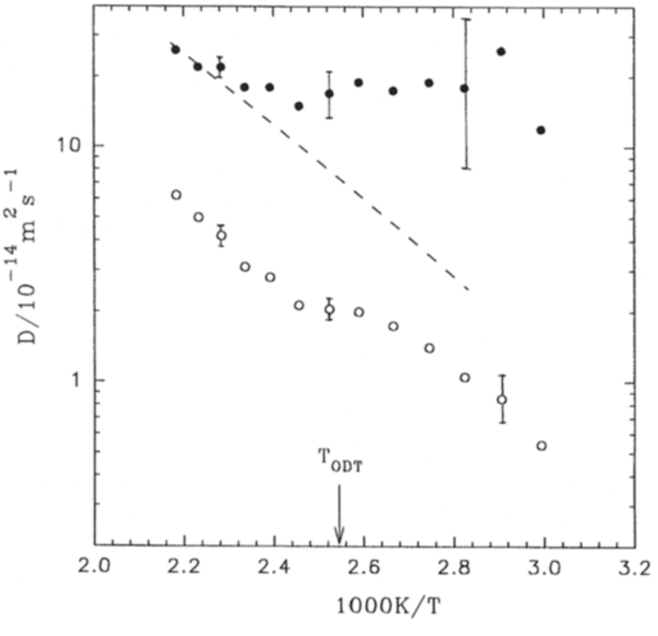


Fig. 2 Arrhenius plot of the self-diffusion coefficients. ●: D_{fast}; ○: D_{slow} (averaged diffusion coefficient $\langle D \rangle$); dashed curve: self-diffusivity of a polyisoprene with $M_n = 45{,}000$ from Ref. 21. Typical error bars are given. T_{ODT} is indicated by an arrow

and by SAXS from Ref. [8] is shown to be dependent on temperature. ϕ_{fast} rather strongly decreases on lowering the temperature, a fact which is already seen in Fig. 1. The width of the distribution of the low self-diffusivities is characterized by the exponent β of the KWW expression. The β-values are shown in Fig. 4 in dependence on temperature. β is of the order of 0.7, the distribution of self-diffusivities of the micelles is rather broad. A weak minimum of β and, hence, a maximum of the distribution

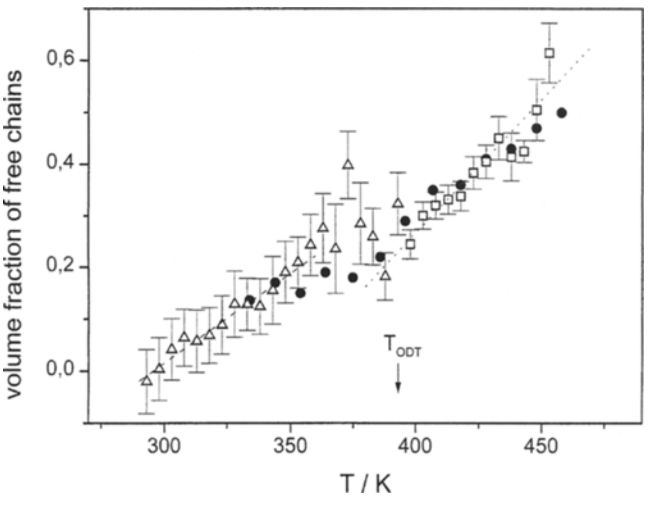


Fig. 3 Volume fraction of free chains (fast diffusing part) in the spin echo (●) and from SAXS data of Ref. [8] (□, △) dependent on temperature

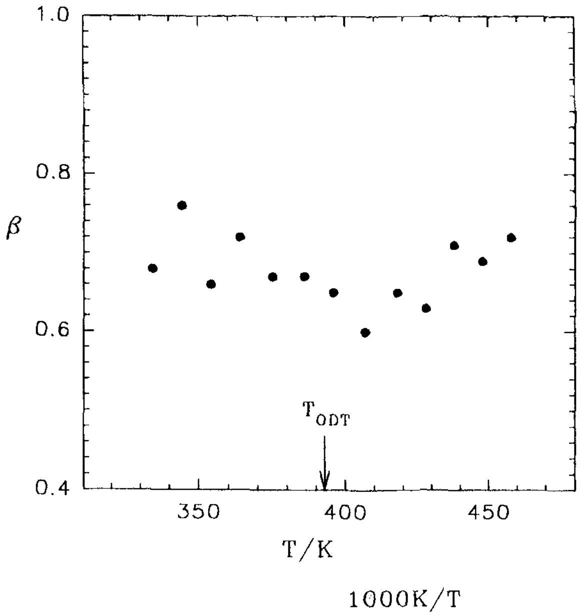


Fig. 4 The stretching parameter β of the fit of the slowly diffusing part in the spin echo attenuation with a stretched exponential dependent on temperature

width of diffusivities is observed around the temperature of the disorder-to-order transition T_{ODT}.

Discussion

The structures in the melt of the diblock were extensively studied by means of SAXS by Schwab and Stühn [8]. At high temperatures ($T \approx 480$ K) they have found a liquid-like order of micellar structures and free diblock chains. The micellar structures are formed by cores of the polystyrene chain parts with diameters between 15 and 18 nm surrounded by a corona of the polyisoprene chain parts. The interaction between micelles is described by a hard-sphere diameter which is about 1.8 times the diameter of the polystyrene core. At $T_{ODT} = 393$ K a disorder-to-order transition occurs, which appears as a transition from the liquid-like to a bcc ordered array of the micelles. There is a continuous increase of the diameter of the polystyrene cores when decreasing the temperature, simultaneously the volume fraction of the free diblock chains becomes smaller.

In view of these results, the two self-diffusivities observed in our experiments have to be attributed to the free diblock chains and to the micelles. Let us at first discuss the fast self-diffusion coefficient which is shown in the upper curve of Fig. 2. The free diblock chains consist of 11% polystyrene and 89% polyisoprene. The polystyrene part has a higher monomeric friction coefficient than the polyisoprene part. The total friction coefficient of the chain is the sum of $N_{PS}\zeta_{PS} + N_{PI}\zeta_{PI}$, where the ζ_{PS} and ζ_{PI} are now the monomeric friction coefficients of styrene and polyisoprene, resp., in the real matrix consisting of the free chains and polyisoprene chains in the corona of the micelles. Unfortunately, there exists no well-founded theoretical model which predicts the chain friction in diblocks from the monomeric friction coefficients of its chain parts [20]. We assume a self-diffusion coefficient of our diblock equal to that of a polyisoprene of a molecular weight $M = 45{,}000$. For estimating M we have taken into account that the contour length of the polystyrene chain part is shorter than that of a polyisoprene chain of equal molecular weight and that the free diblocks move in a polyisoprene-rich matrix, i.e. the styrene–isoprene monomeric friction is assumed not to be very enhanced with respect to the isoprene–isoprene monomeric friction in a melt well above the glass transition temperature.

The temperature and molecular weight dependence of the self-diffusion of polyisoprenes are known from an earlier investigation [21], and we have depicted the data for a polyisoprene 45,000 in Fig. 2 as a dashed line, mildly extrapolated to 460 K. The agreement with the diffusion of the free diblock chains at high temperatures is very good. When lowering the temperature the self-diffusivity of the free diblock chains decreases much weaker that the self-diffusivity in a pure polyisoprene melt. This is a surprizing result. One has to take into account that space filling conditions disturb the Gaussian conformation of the free chains in the diblock melt. The smallest average distance between the surfaces of two polystyrene cores is about 12 nm on average, whereas the end-to-end distance of an unperturbed diblock chain is about 16.8 nm. A steric repulsion in addition to the thermodynamic repulsion between the free chains and the micellar core arises from the fact that the polyisoprene corona is strongly ordered near the core surface due to packing conditions. This leaves little volume available for the free chains in the system. Therefore, they must be stretched to a considerable amount. In the homogeneous melt the self-diffusivity of entangled chains is given by $D = D_{\text{tube}} N_e / 3N$ [22], where D_{tube} is the self-diffusion coefficient along the tube (the Rouse diffusivity). If the tube is stretched to a linear chain conformation, then D turns out to be $D = D_{\text{tube}}/3$ (the factor $\frac{1}{3}$ stemming from the isotropic directions of diffusion). The diffusion is a factor of N/N_e faster than the diffusion of Gaussian entangled chains of equal chain length in a tube of entanglement chain length N_e. N/N_e has a value of 8.2 for our diblock in the disordered melt. This chain stretching can qualitatively explain the enhanced diffusion of the free diblock chains in our system, at least down to the disorder-to-order transition at $T = 393$ K. We avoid a discussion at the low-temperature end because of the increasing uncertainties of the data.

The agreement between the PFG-NMR and the SAXS measurements of the volume fraction of free chains is surprisingly good which can be seen in Fig. 3. The data from the PFG-NMR and the SAXS experiment are consistently evaluated with respect to the two kinds of species in the diblock melt. This further supports our assignment of the fast mode to the diffusion of free chains in the matrix.

The low diffusion coefficient is attributed to the diffusion of the micelles in the diblock melt. In micellar systems, an exchange between the molecules in the free state and those fixed in micelles is generally expected. The residence time of a chain in the micellar core depends on several factors, e.g. intermicellar potentials, molecular mobility in the core and collision frequencies and distances. There is a large entropic and enthalpic penalty for a jump of the polystyrene chain part from one core through the dense corona to a neighboring one, and the high monomeric friction between the styrene monomeric units in the core is the kinetic reason for long residence times of the chains in a micelle. The observation of two diffusivities provides direct evidence of slow exchange in our system: the residence time of the polystyrene part of the diblock in the core of a micelle is much longer than our diffusion or observation time of 300 ms. Any exchange should appear in a decreasing non-exponentiality of the echo attenuation with increasing molecular mobility, i.e. with increasing temperature. Such a tendency is by no way visible. The slow diffusivity reflects the diffusivity of the micelles as a whole in a surrounding formed by the free diblock chains around them.

The friction between the micelles is strongly dominated by the polyisoprene chain parts. The activation energy of the micelle diffusion is found to be 34 kJ/mol above T_{ODT}, a value not much larger than that of a pure polyisoprene melt [21], see Fig. 2. At the disorder-to-order transition, at $T_{\mathrm{ODT}} = 393$ K, no discontinuity of the micellar diffusivity is observed, but the T_{ODT} shows up in a slight plateau in the Arrhenius plot. An indication of a plateau near T_{ODT} is also seen in the temperature dependence of the volume fraction of free chains, and the β-value of the KWW function goes through a minimum at T_{ODT}.

At T_{ODT}, in the diffusion time of 300 ms, the micelles move only over a distance of $\langle z^2 \rangle^{0.5} = 2Dt = 110$ nm, which is only four times the micellar diameter. Therefore, the micelle diffusivities reflect the structural and, hence, dynamic inhomogeneities of the diblock melt. This leads to a broader distribution of micelle self-diffusivities as compared with the distribution width of the polystyrene core radii of $\sigma = 2$ nm. Approaching the T_{ODT}, fluctuations in the structure enhance the observed distribution width of the diffusivities. We also assume that these fluctuations and the appearance of a higher order in the system is the reason of the plateau in the D vs. T dependence. The fluctuations promote micellar displacements. This is opposite to the behavior of homogeneously mixed symmetric diblocks at the disorder-to-order transition where the chain parts demix into a lammellar state and fluctuations in the local concentration decrease the diffusivity of the chains when approaching the ODT. The latter effect is theoretically predicted [23, 24] and experimentally observed [3, 4, 25]. In our system, however, fluctuations in local order occur at the disorder-to-order transition.

Unfortunately, we have no viscosity data of the diblock, therefore we cannot confirm the validity of the Stokes law in our polymer. Using the equivalent hard-core radius R_{HS} of 14 nm [8] and the value $D = 5 \times 10^{-14}\,\mathrm{m^2\,s^{-1}}$ for $T = 450$ K, via Stokes law $\eta = kT/6\pi D R_{\mathrm{HS}}$ one obtains $\eta = 4.7$ P as a reasonable value for the viscosity.

Summary and conclusions

We have investigated the self-diffusivity of diblock chains in the melt of a strongly asymmetric polystyrene-b-polyisoprene with a volume fraction of polystyrene of 0.11. From SAXS-investigations [8] it was known that the polymer forms micelle-structures with cores of polystyrene at high temperatures in a liquid-like order. A transition to a bcc order of the micelles on cooling at $T_{\mathrm{ODT}} = 393$ K was observed. The SAXS investigations have also detected free diblock chains with decreasing volume fraction on cooling.

The PFG NMR measurements revealed two diffusivities, one of the free chains and one of the micelles as a whole. No exchange of diblock chains between different micelles was observed within the time scale of the experiment of 0.3 s. The volume fraction of free chains found in the PFG-NMR experiment is in very good agreement with the SAXS data, The diffusion of the free chains is enhanced when decreasing the temperature from 460 K in comparison with a bulk polyisoprene melt. This is explained by successive chain stretching due to packing conditions in the system where the volume fraction of free chains decreases on cooling. At T_{ODT} the diffusivities of the micelles show a slight plateau while the distribution width of the micelle diffusivities passes a maximum. Fluctuations of local order at T_{ODT} are suggested as a possible explanation of this behavior.

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