Self-Diffusion in a Lamellar and Gyroid (Ordered) Diblock Copolymer Investigated Using Pulsed Field Gradient NMR

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ABSTRACT: We report about self-diffusion experiments on a compositionally asymmetric poly(ethylene-*co*-propylene)-*block*-poly(dimethylsiloxane) diblock copolymer exhibiting the lamellar and the gyroid morphology. The echo attenuation curves were analyzed by fitting a logarithmic normal distribution function. The self-diffusion coefficients were broadly distributed compared to the distribution caused by the polydispersity alone. This is attributed to the onset of anisotropic diffusion in the lamellar morphology and to unavoidable traces of homopolymers. The most probable self-diffusion coefficients and the values calculated for a hypothetical disordered diblock copolymer melt are lower than the self-diffusion coefficients of the constituent homopolymers having the same molar mass. This is explained by entanglements of the majority block which hinder single-chain diffusion parallel to the interfaces formed due to the microphase separation of the different blocks.

1. Introduction

Block copolymers form different microphase-separated morphologies, such as the lamellar, the hexagonal cylindrical, the gyroid, and the spherical cubic one. They can serve as models system for studying the relationship between morphology, interfaces, and molecular dynamics. The state and morphology of diblock copolymers are usually described by the volume fraction of one block, f, the overall degree of polymerization, N, and the Flory−Huggins interaction parameter, χ, which is inversely proportional to temperature.[1,2] Due to the repulsive interaction between different chain segments, microphase separation takes place below the order-to-disorder (ODT) temperature. The value of $(\chi N)_{\mathrm{ODT}}$ depends strongly on the value of f. Above $(\chi N)_{\mathrm{ODT}}$, a variety of different morphologies are observed depending on the composition of the diblock copolymer, e.g., the lamellar structure, the hexagonal structure consisting of cylinders, and the cubic structure consisting of micelle-like entities.[1,2] The mechanisms of self-diffusion of the block copolymers in different ordered morphologies as functions of the volume fraction and chain length are still under investigation.[3] They are, among others, important for understanding the kinetics of order-to-order transitions (OOT).[4,5]

The collective dynamics of diblock copolymers have mainly been studied using quasielastic light scattering,[6] the segmental dynamics using dielectric spectroscopy,[7] and the translational dynamics using forced Rayleigh scattering (FRS)[8] and pulsed field gradient (PFG) NMR.[9] Lodge et al. investigated the tracer and self-diffusion in a series of lamellar ordered diblock copolymer melt using macroscopically oriented samples.[8] In the case of nonentangled block copolymers, the diffusion is found to be anisotropic: i.e., the diffusion along the lamellae (parallel diffusion) is not retarded, while the diffusion across the interface (perpendicular diffusion) is strongly slowed down as a consequence of the thermodynamic repulsion between the two blocks.[8] In entangled symmetric diblock copolymers, on the other hand, the diffusion both along and across the lamellar interfaces is strongly retarded because, in addition to the thermodynamic repulsion hindering the perpendicular diffusion, the entanglements prevent the motion of the chains parallel to the interface.[8,10,11]

The dynamics of asymmetric diblock copolymers in the cylindrical and the spherical ordered state have been investigated much less than the dynamics of symmetric diblock copolymers. Lodge et al. investigated a poly(ethylene-*co*-propylene)-*block*-poly(ethylethylene) (PEP−PEE) diblock copolymer showing an OOT from cylinders to spheres and did not find a discontinuity in the self-diffusion coefficient crossing the OOT temperature.[8] Fleischer et al. studied two strongly asymmetric diblock copolymer samples (polystyrene-*block*-polyisoprene and poly(ethylene-*co*-propylene)-*block*-poly(dimethylsiloxane); PEP−PDMS) using PFG NMR.[9,12] The OOT and the ODT were found to have only minor effects on self-diffusion in these samples as well. In all spherically ordered phases the self-diffusivities were broadly distributed, and their magnitude suggested that not the

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[‡] We dedicate this paper to the memory of the deceased Gerald Fleischer, who has initiated the described research.

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diffusion of single copolymers but rather the diffusion of the entire micelles was observed.[12] Yokoyama and Kramer investigated an asymmetric polystyrene-*block*-polyvinylpyridine diblock copolymer (PS−PVP) forming a spherical structure using forward recoil spectroscopy.[13] The self-diffusion is slowed by a factor of up to 10^{-4} compared to that of the homopolymers, although the monomeric friction coefficients of both blocks are similar in magnitude and temperature dependence. For the cylindrical and the lamellar morphology in the PEP−PDMS system we have observed a difference in single-chain diffusion parallel and perpendicular to the interfaces.[14,15] The diffusion coefficient across the interface was slowed by a factor of up to 60 compared to the diffusion along the interface.[15] Hamersky et al. investigated a poly(ethylene oxide)-*block*-poly(ethylethylene) (PEO−PEE) diblock copolymer forming the hexagonal cylindrical and the gyroid morphology using FRS[16] and report an anisotropy of self-diffusion of about 80 for the cylindrical phase. FRS decays from the gyroid phase were single-exponential and gave a diffusivity consistent with the diffusivity parallel to the cylinder axis reduced by the tortuosity of the gyroid network. However, the copolymer diffusivity was lower than that of either of the constituent homopolymers or other disordered PEO−PEE diblock copolymers, even after accounting for differences in molar mass. This was attributed to the onset of entanglement effects.

To observe the anisotropy of diffusivities, two protocols can be followed: (i) to investigate a macroscopically oriented (e.g., shear-aligned) diblock copolymer sample as a function of rotation angle or (ii) to investigate isotropically oriented samples and to extract the (different) diffusion coefficients from the nonexponentiality of the signal decays.[15] In the present study, we report on PFG NMR investigations of the self-diffusion of PEP−PDMS block copolymers forming the lamellar and gyroid morphology using the second protocol. The results are compared with the self-diffusivities of the corresponding homopolymers. With the investigated sample, we continue our studies of the diffusion mechanisms in PEP−PDMS diblock copolymers in different morphologies. The results from the lamellar and the disordered phase are compared to former investigations,[3,14] and the results from the gyroid morphology are discussed in the framework of the reduction of the self-diffusivities due to the bicontinuous network.[17] The gyroid morphology has an $Ia\bar{3}d$ symmetry[4] that divides the volume into two interpenetrating continuous and equally sized networks. This morphology consists of cylinders connected three by three, building up a three-dimensional network. This structure has also been observed in lipid systems.[18] The PEP−PDMS system has a larger χ parameter than the thoroughly investigated systems PS−PI or PEP−PEE; thus, the ODT temperatures of the PEP−PDMS diblock copolymers lie in an experimentally accessible temperature range for moderate molar masses. This system is well-suited therefore as a model system for investigations using PFG NMR in a wide temperature range crossing the ODT temperature.

2. Experimental Section

2.1. The Sample. The poly(ethylene-*co*-propylene)-*block*-poly(dimethylsiloxane) (PEP−PDMS) diblock copolymer was anionically synthesized[19] and termed PEP−PDMS 7. The molar mass $\bar{M}_n$ is 1.06×10^4 g mol^{-1} ($N = 181$), and the polydispersity index $P = \bar{M}_w/\bar{M}_n = 1.04$.[19] The χ parameter was determined by $\chi = -63.3/T - 0.04$.[20] The volume fraction of the majority block, f_{PEP}, is 0.654.[19] The entanglement molar mass M_e of PEP is 1500 g mol^{-1} at 25 °C and 2300 g mol^{-1} at 140 °C;[21] thus, the PEP matrix is entangled. The PDMS block is nonentangled ($M_e = 1.3 \times 10^4$ g mol^{-1}).[21] With increasing temperature the sample shows the phase sequence lamellar−gyroid−disordered. The OOT and ODT temperatures are 122 and 172 °C, respectively[4,19] An appropriate amount of the copolymer was inserted into an NMR tube, which was evacuated for 24 h and sealed under high vacuum.

2.2. PFG NMR. The incoherent intermediate dynamic structure factor, $S_{inc}(q,t)$, of the diblock copolymer was measured using PFG NMR. A detailed description of this method has been reported.[22−24] The NMR signal was generated by the stimulated-echo rf pulse sequence: $\pi/2-\tau-\pi/2-t'-\tau/2-\tau-$echo. The measured spin-echo attenuation A/A_0 due to field gradient pulses applied after the first and third $\pi/2$ rf pulse is equivalent to the incoherent intermediate scattering function known from neutron scattering:[25]

$$\frac{A}{A_0} = S_{inc}(q,t) = \int \exp(iqz)\, P(z,t)\, dz \qquad (1)$$

A and A_0 are the spin-echo amplitudes with and without field gradients applied, respectively. $P(z,t)$ is the so-called propagator[22] or the probability density for a displacement of a polymer segment over the distance z within the diffusion time $t = t' + \tau$. $q = |\mathbf{q}| = \gamma\delta g$ is a generalized scattering vector with γ denoting the gyromagnetic ratio of the proton, δ the width, and g the magnitude of the gradient pulse. With a Gaussian propagator, we obtain from eq 1

$$S_{inc}(q,t) = \exp(-q^2tD) \quad \text{with } \langle z^2\rangle = 2Dt \qquad (2)$$

where D denotes the self-diffusion coefficient and $\langle z^2\rangle$ the mean-square displacement of the polymer segments in the z-direction during t.

The PFG NMR experiments were carried out with a home-built NMR spectrometer operating at a ^{1}H resonance frequency of 400 MHz.[26] In each experiment, τ was chosen to be 3 ms. In each experimental run, δ and t were fixed and g was incremented. The maximum g value was 25 T m^{-1} and the maximum δ value 1.85 ms. The length scales probed by PFG NMR, therefore, lie between $1/q \simeq 80$ nm and a few micrometers. The diffusion times t were varied between 13 and 603 ms. Equation 2 represents the so-called narrow-pulse approximation $\delta \ll t$ which is fulfilled in our experiments. The experimental error of the temperature is ±1 K. The upper experimental limit is 200 °C.

3. Results

Typical PFG NMR echo attenuation curves in the three phases (lamellar, gyroid, and disordered) are shown in Figure 1. Two main observations are made: The echo attenuations are nonexponential, but the deviation from exponential behavior is less pronounced than in the cylindrical case.[15] The echo attenuations for different observation times, t, lie on a master plot $S_{inc}(q,t)$ vs q^2t over the complete temperature range. This master plot indicates the occurrence of unrestricted, ordinary diffusion over the considered time and length scales; i.e., no diffusion barriers influencing the diffusion of the diblock copolymers are present on the length scales monitored in our experiment.

In the lamellar phase we thus assign the nonexponentiality of $S_{inc}(q,t)$ to a distribution of self-diffusion coefficients along the z-direction. In the PFG NMR experiment, the self-diffusion is measured only in the direction of the gradient (z-direction). The case of diffusion along randomly oriented (straight) lamellae has been calculated previously.[22,23,27] The mean-square

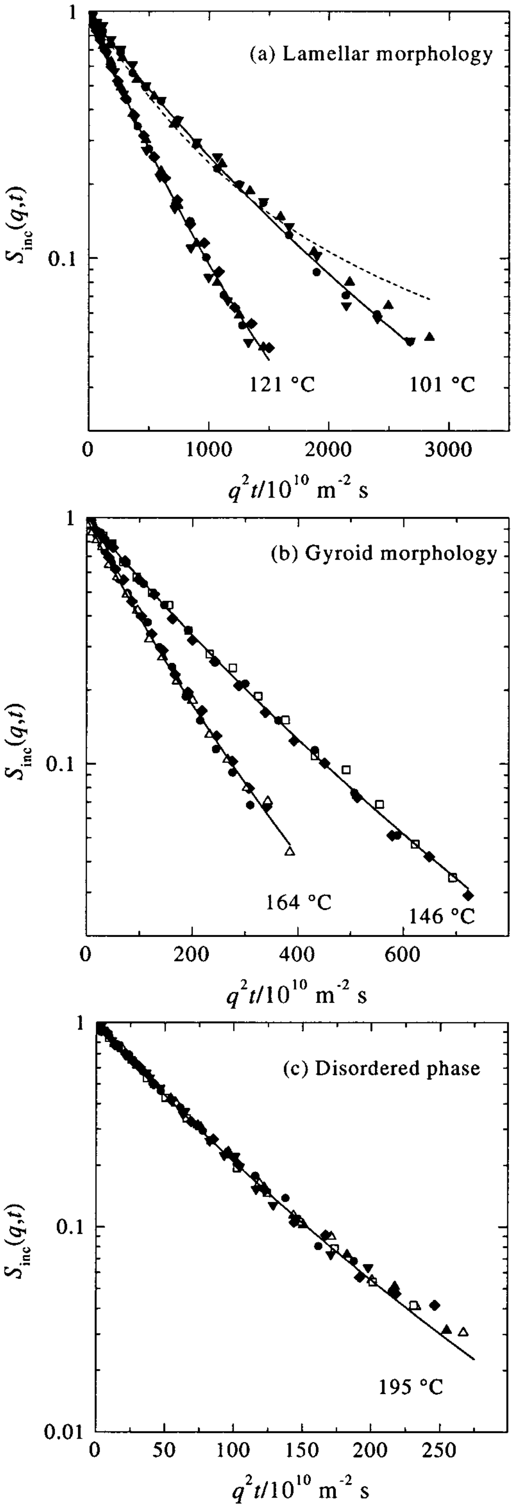

Figure 1. Echo attenuations $S_{inc}(q,t)$ vs q^2t for the diblock copolymer PEP−PDMS 7 at the indicated temperatures and for observation times $t = 33$ (△), 53 (□), 103 (◆), 203 (▼), 303 (▲) and 603 ms (●). (a) Lamellar, (b) gyroid, and (c) disordered phase. The full lines indicate fits with eq 5 and the dashed line in (a) with eq 3 with ($D_{perp} = 0$) for 101 °C.

displacement along the z-axis by diffusion within one lamella $\langle z^2\rangle$ is equal to $2D_{par}t \sin^2\theta$, where D_{par} is the self-diffusion coefficient for the motion in the lamellar plane and where θ denotes the polar angle between the z-axis and the normal to the lamellae.[23,27] Whereas $S_{inc}(q,t)$ for spins residing in a given element (grain) is assumed to be Gaussian, the powder average is not. By averaging eq 2 over all element orientations for the spin echo attenuation,[22,23,27] one obtains

$$S_{inc}(q,t) = \int_0^1 \exp(-q^2tD_{par}\sin^2\theta)\, d\cos\theta \qquad (3)$$

The result is a strongly nonexponential echo attenuation which is indicated by the dashed curve in Figure 1a. This deviation from the exponential behavior is far more pronounced than observed in the experiment. If diffusion perpendicular to the lamellae interface is permitted ($D_{perp} > 0$), the local mean-square displacement is given by $\langle z^2\rangle = 2t(D_{par}\sin^2\theta + D_{perp}\cos^2\theta) = 2t(D_{par} + (-D_{par} + D_{perp})\cos^2\theta)$. For this modified expression averaging over all element orientations leads to

$$S_{inc}(q,t) = \exp(-q^2tD_{par})\int_0^1 \exp(-q^2t(D_{perp} - D_{par})\cos^2\theta)\, d\cos\theta \quad (4)$$

Fitting eq 4 to the data yields two parameters: the diffusion coefficient parallel to the lamellae plane, D_{par}, and the (inverse) anisotropy of motion: D_{perp}/D_{par}. The integration in eq 4 was carried out numerically, and the expression obtained was fitted to the experimental data. This type of analysis has also been successfully applied in studies of the diffusion in the cylindrical morphology[15] and in channels of mesoporous adsorbents of type MCM 41.[28] The fits in the lamellar morphology lead to anisotropies $D_{par}/D_{perp} \approx 5-7$. These are rather small values compared to previously reported anisotropies by Hamersky et al.[29] which amount to ~40. In contrast to our experiments, Hamersky et al. investigated a macroscopically oriented sample. The correlation length of parallel aligned lamellae has been found to be small (≈60 nm).[14] Consequently, we conclude that during the observation time the diblock copolymers change their direction of motion several times and average out the possible anisotropy of diffusion coefficients. The results must therefore be interpreted in terms of grains consisting of imperfectly ordered lamellae due to defects as well as to undulations of the lamellar planes which are observable by dynamic light scattering.[30]

Alternatively, the echo attenuations were analyzed using a log-normal distribution of self-diffusivities:

$$S_{inc}(q,t) = \int w(\ln D)\exp(-q^2Dt)\, dD$$

with

$$w(\ln D) \propto \exp\left(-\frac{\ln^2(D/D_0)}{2\ln^2\sigma}\right) \qquad (5)$$

where the parameter D_0 is the median of the distribution of the diffusivity, σ is the width of the distribution, and $w(\ln D)\, d\ln D$ denotes the mass of chains having their logarithm of self-diffusivity between $\ln D$ and $\ln D + d\ln D$. The use and benefit of applying this distribution to diffusion phenomena have been demonstrated before.[3,12,14,31] The distribution $w(D)$ has its maximum at $D_{max} = D_0\exp(-\ln^2\sigma)$, the most probable diffusion coefficient.[32]

The application of this distribution function is supported by the following: Approximating the distribution of molar masses with a log-normal distribution leads to the following relationship between the polydispersity

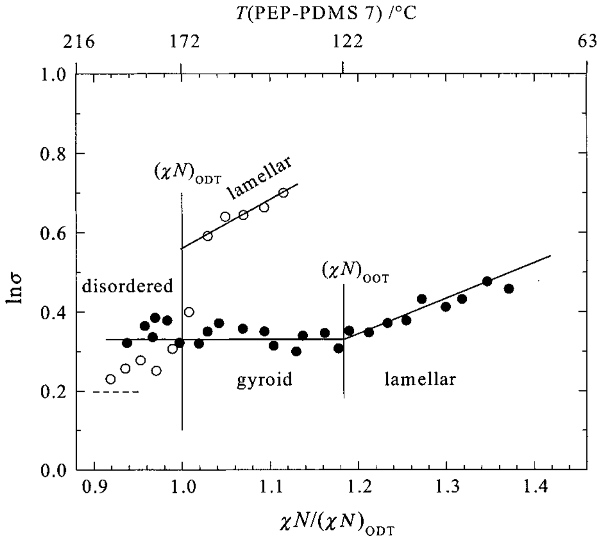

Figure 2. Distribution widths σ of the self-diffusivities in a log-normal distribution of D in dependence on $\chi N/(\chi N)_{\mathrm{ODT}}$ for PEP−PDMS 7 (●) and PEP−PDMS 6 (○).[14] The horizontal dashed line indicates the distribution of self-diffusivities of the PEP−PDMS 7 sample corresponding to polydispersity alone (eq 6). The full lines are guides to the eye.

index P ($= \bar{M}_w/\bar{M}_n$) and the distribution width of the self-diffusivity, ln σ.

$$\ln^2 \sigma = \beta^2 \ln P \qquad (6)$$

This relation is valid only if $D \propto M^{\beta}$ holds. β is related to the diffusion regime (Rouse model, $\beta = -1$; reptation, $\beta = -2$). GPC traces of anionically synthesized polymers with a small P are very often similar to a log-normal distribution.[32] Figure 2 shows the dependence of the distribution width σ on the ratio $\chi N/(\chi N)_{\mathrm{ODT}}$ of PEP−PDMS 7 and a previously investigated diblock copolymer forming the lamellar morphology (T_{ODT} = 64 °C; $\bar{M}_n$ = 6.3 × 10^4 g mol^{-1}).[14] For PEP−PDMS 7 no discontinuity is observed, either at the ODT or at the OOT temperature. Using eq 6 and the value of P known from GPC on PEP−PDMS 7, we obtain, for Rouse diffusion in the disordered and lamellar phase, a distribution width (dashed line in Figure 2) which is constant over the whole temperature range and lower than the values from the PFG NMR experiments. Thus, the observed distribution of the diffusivity is not exclusively caused by the polydispersity. In the lamellar phase, the distribution width of both samples increases with decreasing temperature, which reflects the onset of two-dimensional diffusion. For the disordered phase of PEP−PDMS 6 and PEP−PDMS 7 and the gyroid morphology of PEP−PDMS 7, the distribution width is rather high and temperature-independent.

In the disordered phase the lowest χN value (at 200 °C) is 17. A blend of the two homopolymers PEP and PDMS having the same chain lengths as the two blocks of PEP−PDMS 7 would demix at a χN value of ~4.4, following mean-field arguments.[2] Between these two χN values concentration fluctuations occur; i.e., the sample is heterogeneous. The consequence of the concentration fluctuations is a distribution of diffusion coefficients on top of the one from polydispersity, as observed.

Let us consider the gyroid phase. Since the repeat distance of the lattice of the gyroid morphology is $2\pi/q^*$ ≈ 15 nm (from SANS at 150 °C[19]) and the PFG NMR probes length scales larger than 80 nm, every anisotropy of diffusion is averaged out in the PFG NMR experiment. Consequently, the distribution of the diffusivity cannot be explained by polydispersity alone. The fact that the width of the distribution in the gyroid phase is similar to the one in the disordered phase shows that the local structure is not appreciably different in these two phases. Concentration fluctuations in the disordered state and in the gyroid morphology impose similar hindrance to chain diffusion. To explain the higher width of the distribution, grain size effects, where unavoidable traces of homopolymers and other admixtures are collected, must be considered.

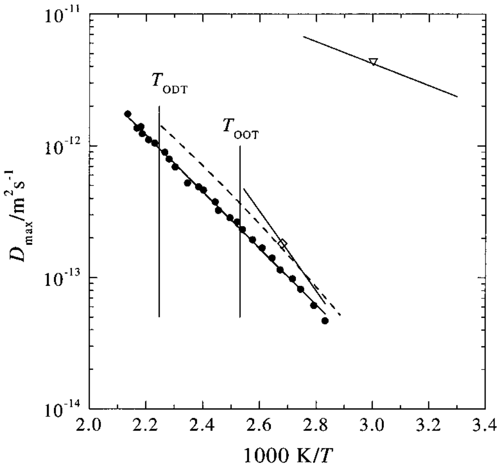

Figure 3. Arrhenius plot of the most probable self-diffusion coefficent $D_{\max}$ of the PEP−PDMS 7 diblock copolymer (●). The self-diffusivities of a PEP homopolymer of M_n = 1.1 × 10^4 g mol^{-1} from ref 33 (◇) and a PDMS homopolymer from ref 34 (▽) and their temperature dependencies (solid lines) are also depicted. The dashed line indicates the self-diffusivity of a hypothetical disordered diblock copolymer (see text).

The diffusivity distribution width increases in the lamellar morphology and can be explained by the anisotropy which is not fully averaged out.[14] In Figure 2 the distribution width in the lamellar phase is seen to be different for both diblock copolymer melts. Because the distribution in the lamellar morphology of the recently investigated PEP−PDMS 6 diblock copolymer is broader than in the PEP−PDMS 7 diblock copolymer, the lamellar order is higher in PEP−PDMS 6 than in the PEP−PDMS 7 sample. The diblock copolymer samples differ in composition and molar mass. However, a higher molar mass leads to a higher χN value and a stronger segregation between the PEP and PDMS blocks. It seems reasonable that the higher composition asymmetry leads to a weaker order indicated by a lower distribution width of the self-diffusivities.

In Figure 3 the temperature dependence of the self-diffusivities of PEP−PDMS 7 and the homopolymers PEP and PDMS, having the same molar mass as the overall block copolymer mass, are depicted.[33,34] The temperature dependence of the diffusivity of the diblock copolymer can be described by an Arrhenius law over the whole temperature range with an activation energy E_A = 41 ± 1 kJ mol^{-1}. Again, there is no discontinuity, either at the ODT temperature or at the OOT temperature.

The self-diffusion coefficients of the diblock copolymer sample in all phases are lower than the ones of the slowest constituent homopolymer having the same molar mass as the overall diblock copolymer molar mass. This is surprising, because the diffusion coefficient of the diblock copolymer is given by the averaged friction coefficient of the two blocks which is between the homopolymers having the same molar mass as the diblock copolymer. One could argue that these slow diffusivities of the diblock copolymer are caused by the different morphologies keeping in mind that the diffusion path follows the interfaces of these structures. To eliminate this effect, we have calculated a diffusion coefficient for a hypothetical disordered diblock copolymer melt using the data of the diffusion coefficients in the lamellar morphology and assuming that the self-diffusion coefficients in the lamellar morphology are reduced by a factor of $^3/_2$ compared to the hypothetical disordered phase ($D_{\text{par}} \gg D_{\text{perp}}$).[14] For the gyroid morphology we must consider the geometric confinement due to the bicontinuous network, i.e., the tortuosity factor of the gyroid morphology. The effects arising from the network connection and the orientation of the cylinders forming the gyroid phase are collected as a single tortuosity factor.[35] This tortuosity factor was calculated for the gyroid morphology by Hamersky et al.[16] with $(3.5/5)^2 \approx {}^1/_2$, in agreement with their experimental findings ($\approx$1/1.5).[16] In this calculation the diffusion paths along the surface of the gyroid network were not considered when the diffusion equations were solved[17] although the chains diffused over the whole interface.The geometric considerations by Hamersky et al.[16] are nonetheless reasonable for their diblock copolymer sample, since the volume fraction of the minority block is small and there are two interpenetrating networks in the gyroid phase. According to their results, Anderson et al. computed the so-called obstruction factor (reduction of D compared to the disordered phase; tortuosity factor) for several surfactant systems in the bicontinuous cubic, the L_3, and the microemulsion phase.[17] They obtained that in total the diffusivity is reduced by a factor of 1/1.5 for particle diffusion on a minimal surface exhibiting cubic symmetry. We use this factor for the gyroid morphology. The diffusion coefficient for the hypothetical disordered state (D_{hy}) is given by $D_{\text{hy}} = 1.5\ AD_{\max}$ with $D_{\max}$ denoting the measured most probable self-diffusion coefficient in the gyroid morphology.

Although we expected the diffusivity of the hypothetically disordered diblock copolymer melt to lie between the diffusivities of the homopolymers PDMS and PEP having the same molar mass, this was not the case. The diffusivity of the hypothetical disordered diblock copolymer in Figure 3 is lower than the one of the slowest homopolymer, PEP. We thus must consider therefore that the PEP matrix is entangled. While the homopolymer in an entangled melt can follow its tube, a diblock copolymer in the ordered state cannot because the tube is perpendicular to the interface. This reduction for entangled block copolymers has been described by Lodge and Dalvi[36] as an activated reptation[36,37] and, for high χN values, as a block retraction mechanism.[36,38] For the activated reptation across the interface the chain has to overcome an enthalpic barrier which determines the diffusivity by $D \propto \exp(-\chi N)$.[36] In the case of a block retraction mechanism the enthalpic barrier is so high that the diffusivity depends only on the number of entanglements,[36,38] and the self-diffusion coefficient is given by $D \propto \exp(-N/N_{\text{e}})$ where N_{e} is the number of monomers between two entanglements. Both mechanisms lead to a dramatical reduction of the diffusion coefficient. Since the PDMS block is not entangled and the χN values are relatively high, we believe that the diffusion can be described by a block retraction mechanism where the copolymer junction points are confined to the interfacial zone, and diffusion along the interfaces proceeds only when the PEP block retracts through the entanglements into the interfacial zone and then relaxes into a new configuration.[36,38] The diffusivities of both the hypothetical diblock copolymer and the real one are lower than the PEP homopolymer having the same molar mass.

4. Summary

The self-diffusion of a PEP−PDMS diblock copolymer was measured using PFG NMR in the lamellar, gyroid, and disordered phases. The spin-echo attenuation curves were analyzed using a log-normal distribution as well as a model of anisotropic diffusion in the lamellar morphology. Because the values found for the anisotropy $D_{\text{par}}/D_{\text{perp}}$ are small, we conclude that the length of the straight parallel (ordered) lamellae (grain size) is lower than the smallest monitored displacement ($\approx$80 nm).

The fits from the log-normal distribution yield two parameters: the width of the distribution of the self-diffusivies and the most probable self-diffusion coefficient. In all phases, a relatively broad distribution of the self-diffusivities is found. In the lamellar morphology the increase in the distribution width reflects the onset of anisotropic diffusion which is not fully averaged out. In the gyroid and the disordered phases the distribution of the self-diffusivities is wider than one would expect from the polydispersity alone. This is attributed to the fact that the local structure of the ordered morphology and of the concentration fluctuation is not appreciably different in these two phases. Grain size effects in the gyroid morphology, where unavoidable traces of homopolymers or other admixtures are collected, as well as concentration fluctuations in the disordered phase also increase the width of the distribution.

Both the measured self-diffusion coefficients and the values of a hypothetical diblock copolymer having the same composition are smaller than the ones of the constituent homopolymers having the same molar mass. This can be explained by the entanglements in the PEP matrix which reduce the self-diffusivities along the interface. The reduction of the diffusivity is explained by the block retraction mechanism.[36,38]

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