Dynamics of a Triblock Copolymer in a Selective Solvent for the Middle Block Investigated Using Pulsed Field Gradient NMR

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ABSTRACT: The concentration dependence of the self-diffusivity of a hydrogenated polystyrene-*block*-polybutadiene-*block*-polystyrene triblock copolymer in an *n*-heptane solution ($c = 0.58-6.9$ g/100 mL) was investigated using the pulsed field gradient NMR at 20−35 °C. The solvent is a preferential solvent for the middle block. At low concentrations, micelle-like aggregates (flowers) are observed. With increasing concentration larger aggregates (animals) are formed. These aggregates show a tendency to anomalous diffusion: exchange of micelles between the aggregated and the nonaggregated state as well as restricted diffusion. At the highest concentrations, individual diffusion of insoluble domains (nodes) is observed, but no transient network behavior. The width of the distribution of self-diffusivities corroborates the findings. Our results are in agreement with light scattering results published previously.

Introduction

Block copolymers can order in a large variety of structures in the melt if the temperature is decreased below the disorder-to-order transition temperature.[1] In solutions of block copolymers, a selectivity of the solvent for different blocks influences the structure. A preferential solvent for one block leads in diblock copolymers to micelle-like structures in which the blocks that are not dissolved form the core and the blocks that are soluble in the solvent form the coronas.[2] In triblock copolymers ABA we have two different cases: the solvent can dissolve either only the outer blocks or only the inner block. In the first case micelles similar to those of diblock copolymers are formed; in the latter case the situation is more complicated. There are two possibilities for the outer blocks to order: the two outer blocks of a triblock copolymer molecule can be trapped in one common node (or core), or the two outer blocks are trapped in different nodes by which a transient network starts to form.[3,4]

We have investigated a triblock copolymer, hydrogenated polystyrene-*block*-polybutadiene-*block*-polystyrene, dissolved in *n*-heptane, a nonsolvent for the polystyrene chain parts, by pulsed field gradient (PFG) NMR. With PFG NMR, the self-correlation function of individual chains is measured, i.e., the self-diffusion. The same system was recently investigated by quasi-elastic light scattering (QELS) spectroscopy [5,6] and, in an earlier work, also by small-angle X-ray scattering (SAXS) and viscosimetry.[7] The main result of these investigations at low copolymer concentrations was proof of the existence of micelle-like aggregates, so-called flowers. With increasing concentration, larger aggregates, so-called animals, with a high inner mobility start to form. At high concentrations, of the order of 5−7 g/100 mL, three dynamic modes were observed in QELS measurements: (i) the fast diffusive mode (the decay rate is linear function of the scattering vector squared), (ii) the middle mode with relaxation behavior (the decay rate is independent of the scattering vector), and (iii) the slow diffusive mode. The fast mode is the collective diffusion in physical gel, the middle, relaxation mode, is probably due to a local movement of nodes trapped in the network of the physical gel, and the slow diffusive mode implies the existence of large-scale inhomogeneities in the system. A similar system, polystyrene-*block*-polyisoprene-*block*-polystyrene in *n*-heptane, was thoroughly investigated by Lairez et al. with QELS, SAXS, SANS, and viscosimetry[3,8,9] At still higher concentrations, a cubic lattice structure is formed.[10,11]

In this paper, the self-diffusion in the solutions of hydrogenated polystyrene-*block*-polybutadiene-*block*-polystyrene in *n*-heptane was investigated by PFG NMR. We have been interested in additional information to the QELS results of our preceding work.[5,6] Several questions arise: Can we detect a transition from flowers to micellar aggregates called animals by self-diffusion experiments? Can we get information about the inner dynamics of animals? Is there any indication of formation of a transient network in concentrated solutions?

Experimental Section

Samples. A triblock copolymer, hydrogenated polystyrene-*block*-polybutadiene-*block*-polystyrene (Shell product, Kraton G-1650), was fractionated,[12] and the middle fraction (15 wt % of the crude sample) was used in this study. The molar mass of the sample was $M_w = 7.0 \times 10^4$ g mol^{-1} with a polydispersity $M_w/M_n = 1.05$ and the mass fraction of polystyrene of 0.28.[6] As a solvent, protonated *n*-heptane was used. We have also prepared solutions with fully deuterated *n*-heptane, but these solutions have shown phase separation at room temperature. Lairez et al. have observed a cloud point of their polystyrene-*block*-polyisoprene-*block*-polystyrene copolymers in *n*-heptane solutions at temperatures near 15 °C.[3] Obviously, our solutions are not very far from the phase separation temperature, and the isotope effect of the solvent is sufficient to shift it close to the room temperature.

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Different concentrations were prepared by dilution or evaporation of a stock solution of 2 g/100 mL. The stock solution was prepared by dissolution of the polymer in n-heptane in a sealed glass flask at 80 °C for several days.

Pulsed Field Gradient (PFG) NMR. The self-diffusion measurements were carried out with a home-built spectrometer FEGRIS 400 operating at a resonance frequency of 400 MHz.[13] Field gradients g up to 25 T/m have been applied, the pulse duration δ was varied between 0.3 and 1.85 ms, and the distance between the field gradient pulses, t, which is equal to the diffusion or observation time, was varied between 13 and 603 ms.

In the diffusion limit and narrow pulse approximation, $\delta/3 \ll t$; the echo attenuation A/A_0 (where A is the echo amplitude and A_0 the echo amplitude without applied field gradients) is equivalent to the incoherent intermediate scattering function, $S_{\mathrm{inc}}(q,t)$[14,15]

$$A/A_0 = S_{\mathrm{inc}}(q,t) = \exp(-q^2tD) \tag{1}$$

for a system with one of self-diffusion coefficient D and $q = \gamma\delta g$ with γ denoting the gyromagnetic ratio of the proton. Both assumptions were always fulfilled in the experiments. In eq 1, an analogy of PFG NMR and QELS experiments was used.[15]

Since the difference between the diffusivities of n-heptane (3×10^{-9} m^2 s^{-1}) and micelles or micellar agregates is several orders of magnitude, the subtraction of the fast echo decay of n-heptane in the NMR signal is easily possible. After the subtraction, the echo attenuation was generally proved to be nonexponential. We have used two functions to describe the nonexponential echo decay. The first is the Kohlrausch–Williams–Watts function (KWW)

$$S_{\mathrm{inc}}(q,t) = \exp(-(q^2tD)^{\beta}) \tag{2}$$

This expression is well-known for describing nonexponential relaxation processes of nonequilibrium states in condensed matter physics.[16] The KWW function is frequently used to describe time autocorrelation functions in QELS experiments.[5,17] The smaller the parameter β, the broader is the distribution of self-diffusivities. $\beta = 1$ means a single-exponential behavior. An average diffusivity D_{KWW} can be calculated:

$$D_{\mathrm{KWW}} \equiv \langle 1/D\rangle^{-1} = \beta D/\Gamma(1/\beta) \tag{3}$$

with $\Gamma(z)$ denoting the Γ-function, $\int_0^{\infty} e^{-t}t^{z-1}\,dt$.

Second, we have fitted the echo attenuation to a log-normal distribution of self-diffusivities:

$$S_{\mathrm{inc}}(q,t) = \int w(\ln D)\exp(-q^2tD)\,d\ln D \tag{4}$$

with

$$w(\ln D) \propto \exp\{-\ln^2(D/D_0)/2\ln^2\sigma\} \tag{5}$$

where D_0 denotes the median D of the distribution and $\ln \sigma$ the distribution width. Using the relation

$$D_{\max} = D_0\exp(-\ln^2\sigma) \tag{6}$$

the most probable self-diffusivity $D_{\max}$ can be calculated; it is the maximum of the distribution $w(D)$. The use and benefit of this kind of analysis have been shown previously.[18] As we will see in the further text, neither a KWW fit nor a fit with a log-normal distribution of D gives good results in all cases.

In our experiments, we also expect the presence of non-Fickian, anomalous diffusion. Anomalous (restricted) diffusion in fractal-like systems is characterized by a weaker dependence of the mean-squared displacement of the diffusing species than with the first power of the diffusion time t. In such experiment, a time-dependent, apparent self-diffusivity D_{app} is observed:[14,19]

$$D_{\mathrm{app}} \propto t^{\kappa-1} \tag{7}$$

with $\kappa < 1$. D_{app} decreases with increasing observation or diffusion time. In the case of normal diffusion, all echo attenuations measured at different observation times merge to one master curve in the so-called master representation $S_{\mathrm{inc}}(q,t)$ vs q^2t. On the other hand, the echo attenuations are split for different observation times due to anomalous diffusion. The curvature of $S_{\mathrm{inc}}(q,t)$ becomes larger with increasing observation time.

If the diffusing species can form aggregates in solution with a lifetime τ in one aggregate, they can be found in the aggregated and the nonaggregated free states. Two limiting situations can be distinguished: the case of fast exchange between the two states for times $t \gg \tau$ and the case of slow exchange for times $t \ll \tau$.[14,20] In the case of fast exchange, we measure in the experiment one average self-diffusivity D

$$D = p_1D_1 + p_2D_2 \tag{8}$$

in which p_i denotes the probability of finding the species in the state with self-diffusivity D_i.

In the case of slow exchange, we observe a superposition of exponentials in the echo attenuation according to

$$S_{\mathrm{inc}}(q,t) = p_1\exp(-q^2tD_1) + p_2\exp(-q^2tD_2) \tag{9}$$

The transition from slow to fast exchange can be monitored in the experiment if the lifetime τ lies within the time window of the diffusion experiment (which is in our case between about 10 and 600 ms). With increasing diffusion time the echo attenuation becomes more and more exponential. We have the opposite tendency to the case of anomalous diffusion: the curvature of the echo attenuation $S_{\mathrm{inc}}(q,t)$ becomes smaller with increasing observation time.

In our system, an exact evaluation of data from the echo attenuation is impossible in both cases of an anomalous diffusion and exchange dynamics because the nonexponentiality of $S_{\mathrm{inc}}(q,t)$ caused by the anomalous diffusion is partly superimposed by the always present distribution of self-diffusivities due to the size polydispersity of species. Therefore, only qualitative results can be obtained. In PFG NMR experiments, the NMR signal arises from aliphatic protons of the chains. Aromatic protons provide no NMR signal because their relaxation time T_2 is too short (see Results and Discussion section). This behavior is opposite to light scattering investigations where the scattered light mostly comes from the polystyrene nodes in the system formed by insoluble polystyrene blocks. Since PFG NMR monitors root-mean-squared displacements of polymer molecules larger than its chain end-to-end distance, this fact is without consequences in PFG NMR investigations.

High-Resolution Liquid NMR. ^{1}H NMR spectra of 1.5 g/100 mL solutions of the triblock copolymer in fully deuterated n-heptane were recorded with a spectrometer (Bruker DRX-400). The solution was heated to 50 °C before each measurement. No phase separation occurred within the recording time of the NMR spectrum.

Results and Discussion

Self-Diffusion of Micelles in Dilute Solutions. In Figures 1 and 2, we show two examples of the echo attenuations, $S_{\mathrm{inc}}(q,t)$, of triblock solutions of concentrations 0.58 and 2.07 g/100 mL, respectively, for a variety of observation (diffusion) times. The signal of the solvent, n-heptane, was subtracted. We can immediately see that normal diffusion occurs in those solutions; i.e., the curves for different observation times merge to one master curve. The echo attenuation is nonexponential

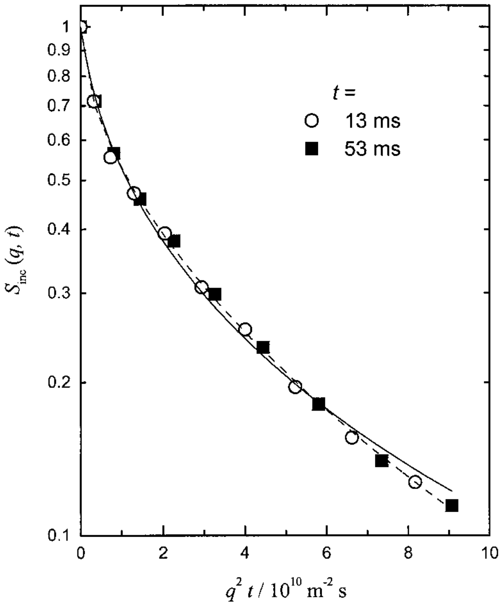

Figure 1. Echo attenuation, $S_{inc}(q,t)$, at room temperature for a 0.58 g/100 mL solution of the triblock copolymer in *n*-heptane for the diffusion times indicated in the figure. The dashed line is a fit with a KWW function, eq 2; the full line is a fit with a log-normal distribution of self-diffusivities, eqs 4 and 5.

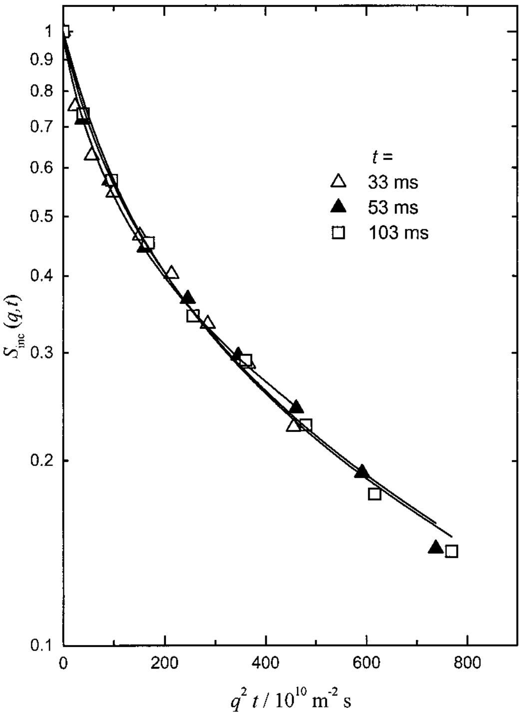

Figure 2. Same as in Figure 1 but for a concentration of 2.07 g/100 mL.

because of distribution of self-diffusivities. In Figure 1 two fits are also shown: the KWW fit (dashed line) and the fit with a log-normal distribution (full line) of self-diffusivities. The difference between the two fits is not very large with only a slightly larger curvature of the log-normal fit. At 0.58 g/100 mL, the KWW fit is better, and at 2.07 g/100 mL, the log-normal fit is better. Our measurements show, in accord with the light scattering experiments of ref 5, that at the lowest concentrations micelles exist in a triblock copolymer solution which show a size distribution. We call such structures flowers on the basis of the paper of Lairez et al.[3] Using viscosity of *n*-heptane, we have calculated from our self-diffusion measurements (D_{KWW} at $c = 0.58$ g/mL) a particle hydrodynamic radius of $R_H = 26$ nm, which is in a good agreement with the QELS result of 23.8 nm.

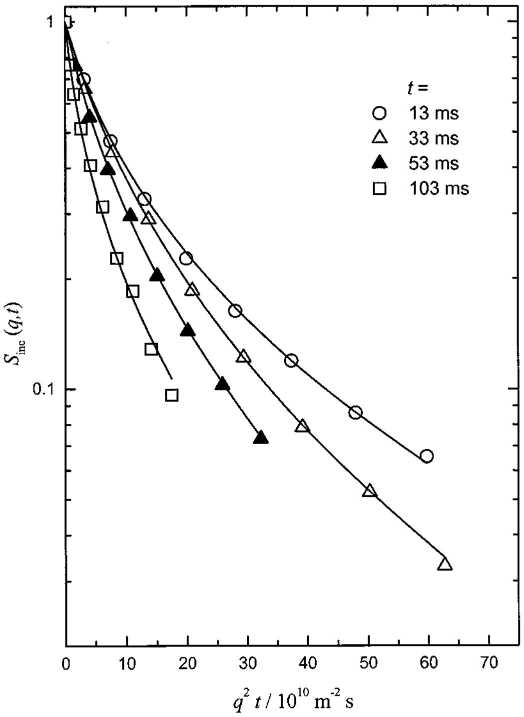

Figure 3. Echo attenuations at $T = 35$ °C for a 2.56 g/100 mL solution for the diffusion times indicated in the figure. For line denotations, see Figure 1.

Transition from Free Micelles to Micellar Aggregates at Intermediate Concentrations. At concentrations higher than 2 g/100 mL, a transition from free to aggregated micelles is observed. We call these micellar aggregates animals again according to ref 3. Since the self-diffusivity slows down very strongly with increasing concentration (see below), we were rather limited in variation of the observation time at high concentrations. To overcome this problem, the echo attenuation measurements of highly concentrated solutions were also performed at 35 °C where the diffusivity is rather strongly enhanced, in accord with measurements of the temperature dependence of the decay rates by QELS.[5,17] In Figures 3−5, the echo attenuations, $S_{inc}(q,t)$, for 2.56, 4.0, and 6.9 g/100 mL solutions of the triblock copolymer measured at 35 °C are shown. The self-diffusion coefficients strongly drop with increasing concentration. For a 2.56 g/100 mL solution, splitting of echo attenuations for different diffusion times t is observed. The reason for this splitting is an exchange process: with increasing observation time, the curvature of $S_{inc}(q,t)$ vs q^2t becomes smaller, and the initial slope is nearly independent of t. As an alternative explanation for these diffusion patterns, one might consider the existence of different relaxation times T_1 for different species and variation of the individual signal of the species in the NMR signal when changing the observation time. However, due to spin diffusion, we expect averaging of the T_1 times.[21] Additionally, we have measured the T_1 decays for the triblock at different concentrations dissolved in deuterated *n*-heptane and have found only one T_1 in the solutions. Thus, an exchange of chains or complete flowers between animals

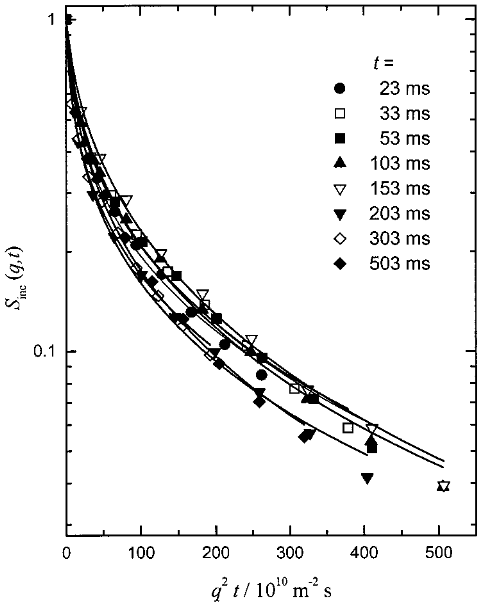

Figure 4. Same as in Figure 3 for a concentration of 4.0 g/100 mL. For line denotations, see Figure 1.

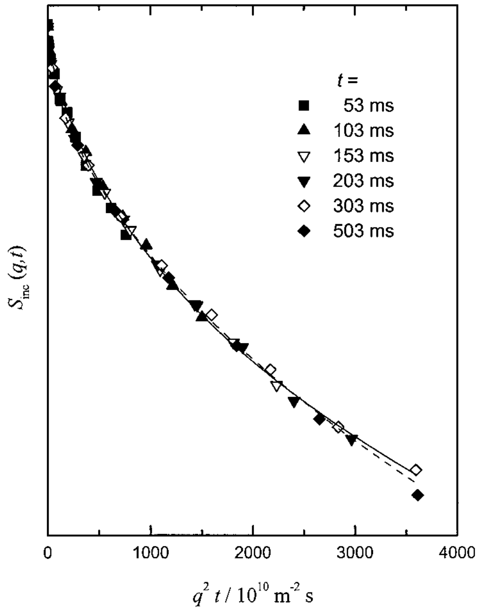

Figure 5. Same as in Figure 3 for a concentration of 6.90 g/100 mL. For line denotations, see Figure 1.

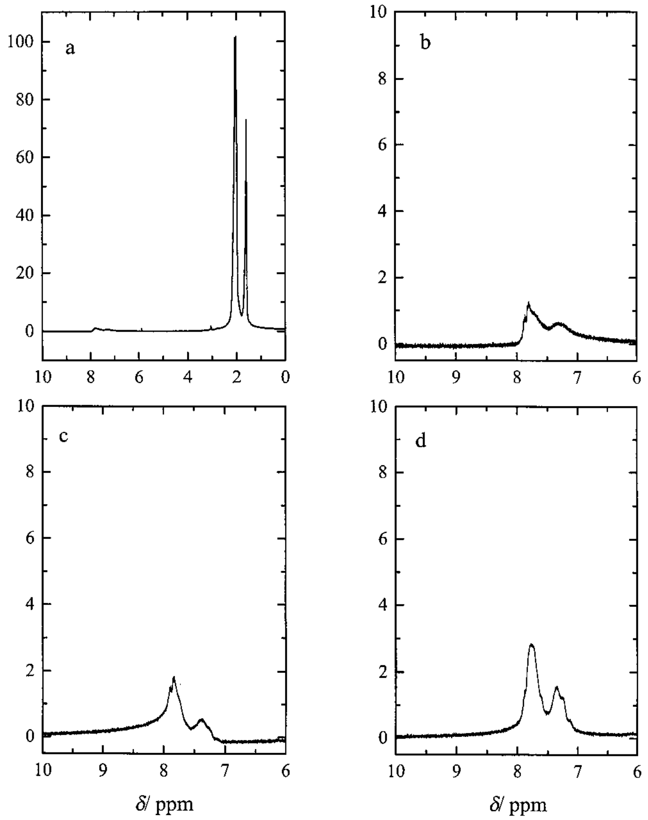

Figure 6. ^{1}H NMR spectra of a 1.5 g/100 mL solution of the triblock copolymer dissolved in fully deuterated *n*-heptane: (a) full spectra at 25 °C; (b) only aromatics groups from polystyrene at 25 °C; (c) the same as in (b) but at 35 °C; (d) the same as in (b) but at 45 °C.

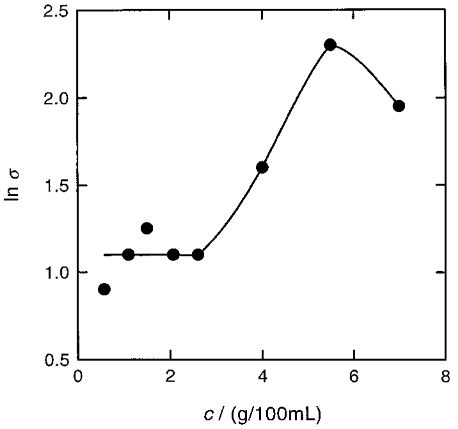

Figure 7. Concentration dependence of the distribution width ln σ of the log-normal distribution of self-diffusivities at room temperature. The line is a guide to the eye.

and solution is observed at this concentration. In other words, a finite lifetime of a chain or a flower within one animal is observed at temperature of 35 °C. The lifetime lies within a time window of the diffusion experiment which is between 10 and 600 ms in the actual case. To specify the exchange dynamics, we have performed NMR measurements of a 1.5 g/100 mL solution at the short T_2 relaxation times of the aromatic protons in the chains. The NMR spectra are shown for three temperatures in Figure 6. We have found that the polystyrene chains are strongly immobilized at least up to 45 °C in the nodes. This implies that the exchange of block copolymer molecules (unimer—micelle) anchored by polystyrene blocks in nodes is suppressed in our experiments at 25 and 35 °C, and therefore, the observed exchange effect is probably due to the exchange of weakly trapped flowers between animals and micellar solution. Moreover, inner motions inside of animals are detected at these intermediate concentrations which manifest themselves in a restricted diffusion detected in the PFG NMR experiments.

The formation of micellar aggregates is underscored by the concentration dependence of the width of the log-normal distribution, ln σ, for short observation times which is depicted in Figure 7 for room temperature. For concentrations between 2 and 3 g/100 mL, where the exchange effect is observed, a distinct increase in ln σ is observed, indicating formation of long-living animal-like structures.

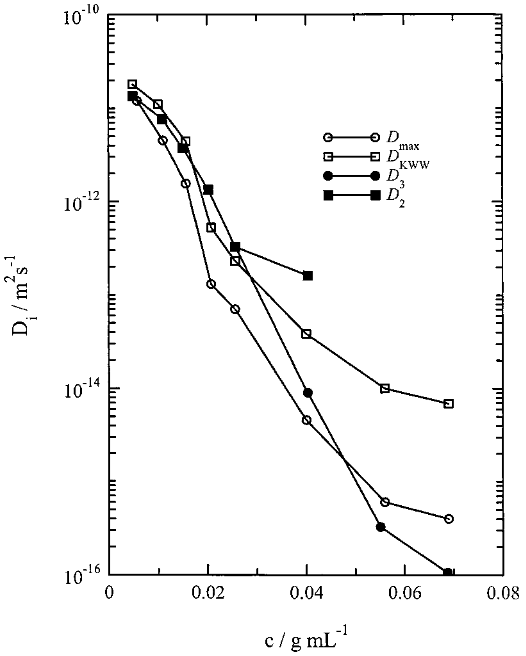

Figure 8. Concentration dependence of the diffusivities of middle and slow modes determined by QELS, D_2 and D_3, and of D_{max} and D_{KWW} from PFG NMR at room temperature.

For a 4.0 g/100 mL solution, the diffusion pattern is more complicated: there is no systematic trend of changing the curvature with the observation time. Probably, effects of restricted (anomalous) diffusion and exchange superimpose. The exchange effects are clearly seen only at larger diffusion times *t*.

Self-Diffusion in Semidilute Solutions. At the two highest concentrations (5.5 and 6.9 g/100 mL), the dynamics behavior of copolymer solutions changes, and we again observe normal self-diffusion of species (see Figure 5), which are stable at least within the time window of our experiment. The measured diffusivities are broadly distributed. No transient entanglement network in the whole sample is formed, but a steep increase in the solution viscosity indicates that the solutions are already approaching the gel point.[7] This observation is in line with viscoelastic (dynamic−mechanical) measurements of Lairez et al. on the polystyrene-*block*-polyisoprene-*block*-polystyrene triblock in *n*-heptane.[3] Small-angle X-ray scattering experiments made on samples with $c = 7$ g/100 mL reveal that a liquidlike order of flowers is predominant in the sample structure.[7,11] With respect to structural results, we can assume that self-diffusion observed at the highest concentrations corresponds to diffusion of flowers inside the liquidlike structure of copolymer solution rather than to diffusion of very large animals.

The concentration dependence of diffusion coefficients D_{KWW}, D_{max} from PFG NMR and D_2 (middle mode), D_3 (slow mode) from QELS[5] for the room temperature are depicted in Figure 8. D_{max} values are systematically lower than D_{KWW} ones. Moreover, the difference between D_{max} and D_{KWW} increases with increasing concentration. This is caused by the different averaging processes used. In the strong asymmetric log-normal distribution, $w(D)$, the maximum of the distribution at D_{max} is situated at rather small self-diffusivities; i.e., self-diffusivities of large species are emphasized. This weighting of large species is less pronounced in D_{KWW}.

Comparison with QELS Data. To compare the really corresponding data of both the PFG NMR and QELS methods, D_{KWW} should be compared with the second dynamic mode of QELS measurements, D_2. (Both the diffusion coefficients were obtained by the KWW fit.) The agreement is quite good up to the concentration 4 g/100 mL. While PFG NMR data at concentrations 5.5 and 6.9 g/mL are diffusive, the second dynamic mode in QELS experiments shows relaxation behavior (the decay rates are independent of the scattering vector) related to a local movement of nodes trapped inside a liquidlike ordered structure of semidilute copolymer solutions.[5,17] The reason for this difference results from a different response of the two techniques to local movements.

The self-diffusion of large heterogeneities (the slow dynamic mode in QELS[5]) was not distinguished in PFG NMR experiments. The reason for this difference is that the two techniques provide average diffusion constants weighted by different factors.[5,22] In PFG NMR, the relative contribution of diffusing particles to total $S_{inc}(q,t)$ is only proportional to the particle concentration, whereas in QELS, a relative contribution to the total light scattering is proportional to the product of the particle concentration and their weight-average molecular weight. Thus, the contribution of large scatterers to the total light scattering is strongly enhanced compared with that of the small ones. Therefore, the relative effect of the slow mode (contribution of large heterogeneities) is negligible in PFG NMR but strong in QELS experiments. This is the reason why clusters often observed in QELS measurements are not detectable in PFG NMR experiments.[22]

Summary and Conclusions

A triblock copolymer dissolved in a selective solvent for the inner block can form different structures in solution: either the two outer blocks are anchored in the same node or they connect two different nodes. We have performed PFG NMR self-diffusion experiments on these solutions. At low concentrations of the triblock copolymer, we observed self-diffusion of micelle-like structures called flowers which show size distribution. On increasing the concentration, aggregation of micelles by bridging sets in (the insoluble blocks are frequently anchored in different cores); the self-diffusivity is dropping rather strongly. Micellar aggregates, called animals, are formed. These aggregates show internal dynamics in the PFG NMR experiment: exchange of copolymer flowers between animals and micellar solution and also indications of anomalous diffusion. At the highest concentrations, normal diffusion was again found. The measured diffusivities were broadly distributed. These findings are corroborated by the concentration dependence of the distribution width of self-diffusivities.

Our results are in accord with the light scattering investigations carried out on the same system.[5,17] Whereas the fast cooperative mode can be only seen in QELS, the middle dynamic mode detected in QELS is well related to self-diffusion coefficients and attributed to the dynamics of animals at intermediate concentrations. The exchange dynamics of flowers between different animals has disappeared at the highest investigated concentrations so that normal diffusion was observed. While the second dynamic mode of QELS shows relaxation behavior at the two highest concentrations, 5.5 and 6.9 g/100 mL, PFG NMR data are further diffusive, related to diffusion of flowers in ordered copolymer solutions. There are still no indications of formation of a transient network in the system up to the concentration of 6.9 g/100 mL.

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