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ORIGINAL CONTRIBUTION

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Colloidlike behaviour of a polystyrene-*b*-poly(ethylene-*co*-propylene) diblock copolymer dissolved in *n*-decane investigated by pulsed field gradient nuclear magnetic resonance

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Abstract The self-diffusion of a polystyrene-*b*-poly(ethylene-*co*-propylene) diblock copolymer dissolved in a preferential solvent for the aliphatic block, *n*-decane, was investigated by pulsed field gradient NMR. The diblock copolymer forms micelles in solution, the structure of the solid polymer being preserved in the native solution because the polystyrene is in the glassy state. The equilibrium state is attained upon heating which again freezes in upon cooling to room temperature. The hydrodynamic radius of the micelles decreases by about 50% during this heating–cooling process. The concentration dependence of the self-diffusivity shows typical colloidlike behaviour, and it can be described by a Vogel–Fulcher–Tammann-like equation. No indications of crystallization at higher concentrations are observed in the micellar solution because the micellar sizes are slightly polydisperse. The self-diffusivity was measured up to the glasslike state, where in-cage- diffusion and dynamic heterogeneities could be detected.

Key words Diblock copolymers · Micelles · Solutions · Self-diffusion · Pulsed field gradient nuclear magnetic resonance

Introduction

Diblock copolymers consisting of two chain parts of monomers A and B form micellelike structures if they are dissolved in a preferential solvent for only one chain part [1]. The non-dissolved chain part forms the core of the micelles and the dissolved chain part forms the corona. These micelles are similar to star polymers. The behaviours of star polymers and micelle-forming diblock copolymers have been intensively studied in the past because their behaviour is intermediate between polymers and colloids [2]. The chains are polymerlike on short length scales, smaller than the radius of the stars or micelles. They form blobs but with nonuniform size, i.e. the blob size, ξ, increases with increasing distance from the core as $\xi(r) \sim r/f^{1/2}$ [3], where f is the arm number of the stars. In the case of diblock copolymer micelles f is equal to the aggregation number. With a large core radius, the micelles can serve as model systems for polymer brushes. Micelle-forming diblock copolymers and star polymers show colloidlike behaviour for length scales larger than their diameter: the concentration dependence of the self-diffusion coefficient is nearly identical with that of hard-sphere colloids, it can be described by a Vogel–Fulcher–Tammann (VFT)-like equation, and at a distinct concentration the self-diffusivity goes to zero [4]. In star polymers with very small polydispersity, crystallization occurs at this concentration [5], whereas crystallization is suppressed in our micellar solution of the polystyrene-*b*-poly(ethylene-*co*-propylene) diblock copolymer due to the polydispersity in the size of the micelles.

In recent publications it was attempted to explain the "freezing in" of the molecular mobility of the diblock micelles by aggregation and subsequent gelation [6, 7]; however more recent papers have reported the crystallization of diblock micelles at higher concentrations [8]. Therefore, one question to be answered is what happens at higher concentrations, gelation or crystallization or a colloidal glass transition? Gelation manifests itself in pulsed field gradient (PFG) NMR self-diffusion measurements by a dramatically increasing distribution width of self-diffusivities when approaching gelation (cluster diffusion near the percolation threshold) [9], whereas in case of crystallization such an effect is absent [4]. Gelation leads to a characteristic transition from exponential to stretched-exponential to powerlike behaviour of the correlation function of the scattered light in dynamic light scattering (DLS) [10, 11].

The investigated diblock copolymer exhibits peculiar behaviour [6, 7], the reason for which lies in the glassy state of the polystyrene chain parts at room temperature (for which *n*-decane is a nonsolvent): the structures formed in the copolymer solutions at room temperature are intimately related to those in the solid polymer, the polystyrene core of the micelles being in a frozen nonequilibrium. When the micellar solution is heated above the glass-transition temperature of the polystyrene cores, which is at about 60 °C in our case [12], the micelles can equilibrate and they decrease considerably in size. After subsequent cooling to room temperature, the high-temperature structure is again frozen in, and we again get frozen micelles, but now of smaller size. These effects have been investigated in detail in recent papers where mainly the hydrodynamic radius, the core radius and the micelle molar mass were measured by light and X-ray scattering under different experimental conditions [6, 7, 12].

In this paper, the investigation of the self-diffusion behaviour of the diblock copolymer micelles by PFG NMR is reported. The spectrometer used has a high sensitivity, therefore solutions with concentrations down to 0.22 g/100 ml could be measured. We have investigated the concentration dependence of the self-diffusivity of the ‘‘native’’ micelles as well as the micelles which formed after heat treatment of the solutions. At high concentrations, anomalous diffusion could be found. The results are compared with known results from earlier light scattering, X-ray scattering and viscosity measurements [6, 7].

Experimental

The diblock copolymer used was a polystyrene-*b*-poly(ethylene-*co*-polypropylene), a hydrogenated polystyrene-*b*-polyisoprene diblock copolymer, produced by Shell Chemical Company, with the trademark Kraton G 1701. The molar mass M_w was 1.05×10^5_g mol^{-1} with a polydispersity, M_w/M_n, of 1.28. The diblock copolymer contains 34 wt% polystyrene. The respective amounts of polymer and solvent were weighed into NMR sample tubes of 7.2-mm outer diameter with subsequent flame-sealing of the tubes. The samples were stored for several weeks at room temperature with occasional shaking for the promotion of dissolution and equilibration. After the first measurement of the solutions, the samples were heated to 80 °C for at least 1 day and were measured again at room temperature. Protonated *n*-decane and for four highly concentrated samples also deuterated *n*-decane (Chemotrade, Leipzig, Germany) were used as solvents.

The self-diffusion coefficients were measured using PFG NMR using the FEGRIS 400 home-built spectrometer operating at a resonance frequency of 400 MHz for protons. PFG NMR as a general scattering experiment measures the intermediate incoherent dynamic structure factor $S_{\mathrm{inc}}(q,t)$ of the positions of the protons in the sample [13]. $S_{\mathrm{inc}}(q,t)$ is equal to the ratio of the spin echo amplitude with applied field gradient pulses to the spin echo amplitude without applied field gradient pulses. For normal, free diffusion, we have

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

with D denoting the self-diffusion coefficient. $q = \gamma\delta g$ is a general scattering vector [14, 15]. Here γ stands for the gyromagnetic ratio of the proton, δ for the width and g for the magnitude of the field gradient pulses. $t = t' + \tau$ is the distance between the leading edges of the field gradient pulses and is equal to the diffusion or observation time (in the case $t \gg \delta/3$ which is always fulfilled in our experiments). The stimulated echo pulse sequence was applied: $\pi/2$-τ-$\pi/2$-t'-$\pi/2$-τ-echo with the two field gradient pulses applied after the first and the third radio frequency $\pi/2$ pulses. The self-diffusivity, D, is related to the mean squared displacement $\langle r^2 \rangle$ of the proton-bearing molecular species in the sample by the Einstein relation

$$\langle r^2 \rangle = 6Dt \tag{2}$$

in case of normal diffusion. If the diffusion is anomalous or restricted, which implies a time exponent in Eq. (2) smaller than 1 and in the case of completely restricted diffusion a time exponent equal to 0 (i.e. $\langle r^2 \rangle$ is independent of the diffusion time), then an apparent self-diffusivity, D_{app}, is measured in the experiment which decreases with increasing diffusion time. In the case of completely restricted diffusion D_{app}, is proportional to t^{-1}. Details of PFG NMR can be found in Refs. [14, 15], and especially for colloidal solutions in Ref. [4].

As experimental parameters we used a fixed $\tau = 3$ ms, g was varied between 0 and 25 T/m in one experiment, and δ (between 0.3 and 1.85 ms) and t (between 13 and 603 ms) were chosen such that the measurable echo attenuation was a maximum at the largest possible field gradient at a given signal-to-noise ratio. Since the echo attenuations were slightly nonexponential, caused by a distribution of self-diffusivities, the echo attenuations were fitted with a stretched exponential, a Kohlrausch–Williams–Watts (KWW) function,

$$S_{\mathrm{inc}}(q,t) = \exp\left[-(q^2 tD)^{\beta}\right] \ , \tag{3}$$

with the two fit parameters D and β, where $\beta \leq 1$ characterizes the width of the distribution, and $\beta = 1$ means exponential behaviour. This mathematically simple fit is favourable in those cases where the content of low molecular traces with a high diffusivity is not negligible, since the initial slope of a stretched exponential (at $q^2 t \to 0$) is infinite. We calculated an averaged self-diffusivity, $\bar{D}$, with the relation

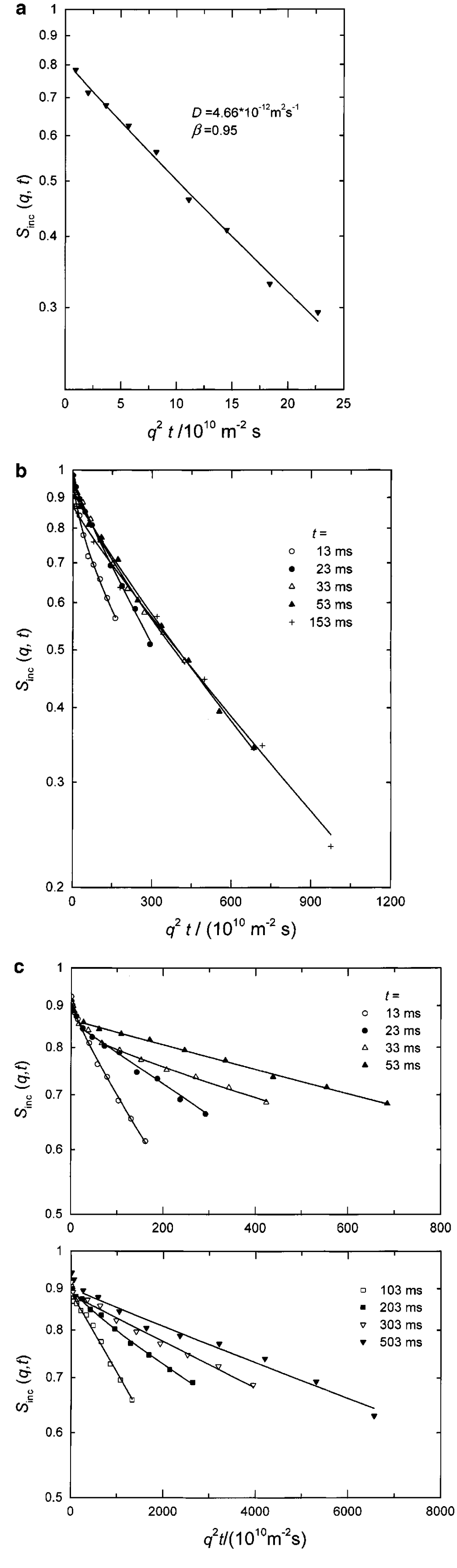
$$\bar{D} = D\beta/\Gamma(1/\beta) \ , \tag{4}$$

where Γ denotes the Gamma function. In the following we denote this averaged measured self-diffusivity simply by D.

The typical experimental error of D is ±20% at low concentrations ($c < 0.5$ g/100 ml); it decreases to ±10% at intermediate concentrations and increases again to ±30% at the highest concentration. All measurements were carried out at room temperature.

Results and discussion

We were able to measure the echo attenuation in the diblock copolymer solutions down to a concentration of



►

Fig. 1 Echo attenuations for the diblock copolymer solutions of **a** $c = 0.22$ g/100 ml in protonated *n*-decane, **b** $c = 2.58$ g/100 ml and **c** $c = 3.01$ g/ml in deuterated *n*-decane, for the diffusion times indicated in the figure. The fast decay of the protonated *n*-decane was omitted. The restricted diffusion manifests itself in the time dependence of the slopes, i.e. in the time dependence of the measured apparent self-diffusivities. A "biphasic" behaviour as in crystallizing star polymer solutions, cf. Ref. [4] is not observed

0.22 g/100 ml with sufficient accuracy owing to the high sensitivity of our spectrometer. Examples of the echo attenuations are shown in Fig. 1. The fast echo decay of the *n*-decane could be easily subtracted in the NMR signal because the self-diffusivity of *n*-decane is 2 orders of magnitude or more faster than that of the diblock copolymer micelles (it is not shown in the curves in Fig. 1). On the other hand, we were able to measure very highly concentrated solutions (i.e. highly viscous solutions) with self-diffusivities below 10^{-14} m^2 s^{-1} due to the large field gradient pulses which can be applied with our spectrometer. An example is shown in Fig. 1c in which the anomalous diffusion becomes visible: the slope and hence the self-diffusivity decrease with increasing observation time, *t*. In the native samples, the KWW β was always between 0.85 and 0.95, indicating only a slight distribution of D and, hence, of the hydrodynamic radii, R_H, of the micelles. In a previous paper an $M_\mathrm{w}/M_\mathrm{n}$ value of the apparent micellar molar masses in the low concentrated native solutions of approximately 2 was reported from light scattering measurements [6]. This value is rather large, but the hydrodynamic radius which is effective in diffusion experiments scales with $R_\mathrm{H} \sim M^{1/3}$ only. Unfortunately, the experimental scatter in the heat-treated samples was rather large; this was also the case for the β values. We see the reason in the dissolution of low molecular traces stemming from the glassy frozen polystyrene core or from some degradation products. The scatter of β between different heat-treated samples points to possible inhomogeneity of the initial solid diblock copolymer.

We have depicted the concentration dependence of the self-diffusivity of the diblock copolymer solutions in Fig. 2 for native and heat-treated solutions. We observe after a flat region at low concentrations a rather fast slowing down of the self-diffusivity starting at about $c = 1$ g/100 ml. The self-diffusivity goes to zero at a concentration of about 2.5 g/100 ml. This behaviour is typical for colloidal solutions, not for solutions of linear polymers [16] or star polymers of low arm number [17, 18]. Those solutions show a steeper initial slope at low concentrations and a weaker slowing down at high concentrations. We have fitted the concentration dependence of D with a VFT-like equation [19], known as the Mooney equation [20], which was successful in fitting the concentration dependence of the self-diffusivity of 128-arm stars [4]

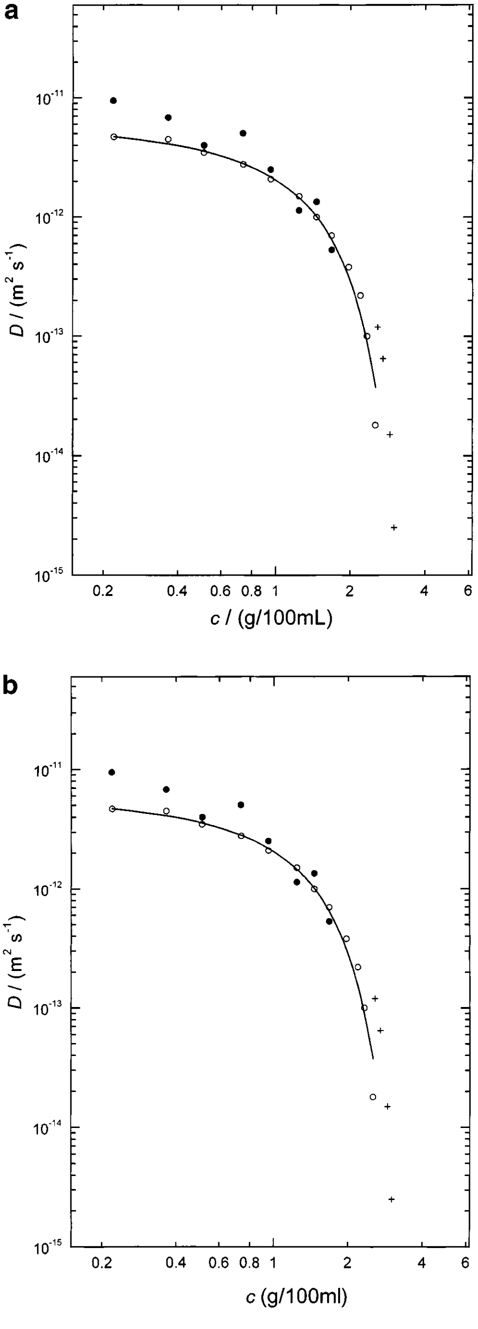


Fig. 2 Concentration dependence of the self-diffusivities of the micelles in the native solution (○) and the heat-treated solution (●). The *line* is a fit with Eq. (5). $D_o = 5.6 \times 10^{-12}$ m^2 s^{-1}, $A = 3.0$ and $c^* = 4.04$ g/100 ml have been obtained. The *crosses* (+) show data for native solutions in deuterated *n*-decane

$$\ln(D/D_o) = -A/(c^*/c - 1) \ . \tag{5}$$

The fit is also shown in Fig. 2: it works very well. We obtained $c^* = 4.04$ g/100 ml and $A = 3.0$ in good agreement with the data for the 128-arm stars where $A = 2.7$ and $D_o = 5.6 \times 10^{-12}$ m^2 s^{-1} (for the native samples) was found. This value is in accord with the results from DLS measurements published earlier [6, 7]: there $D_o = 3.5 \times 10^{-12}$ m^2 s^{-1} was found. The difference can be explained by the different averaging behaviour of PFG NMR and DLS. While PFG NMR weights the faster diffusing species in the sample more strongly, DLS weights the larger and, hence, the more slowly diffusing species in the sample more strongly. This effect becomes more pronounced at larger polydispersity of the samples. For the hydrodynamic radii, R_H, of the micelles we obtain 70 nm from DLS and 45 nm from PFG NMR with the Stokes–Einstein equation using the viscosity $\eta = 0.854$ mPas for *n*-decane at room temperature. No reasonable fit was possible with the data of the heat-treated samples, but $D_o = 1.0 \times 10^{-11}$ m^2 s^{-1} can be extracted from the data. We find $R_H = 25$ nm with this D_o value, the heat treatment leading to smaller micelles, again in remarkable agreement with the earlier light scattering measurements [12].

The self-diffusivity of the diblock copolymer solution slows down greatly at a concentration of about 1 g/100 ml. At this concentration, the viscosity of the solution shows a marked upward curvature, and also in light scattering measurements an increasing interaction between the micelles becomes visible [6, 7].

Hard-sphere colloids start to crystallize at a volume fraction, ϕ_{cr}, of 0.494, and crystallization is complete at $\phi_m = 0.545$ [21]. If crystallization can be circumvented, for example by a slight polydispersity in the sizes of the hard-sphere colloidal particles, the colloidal glass transition occurs at $\phi_g = 0.58$. Crystallization has been found in solutions of multiarm star polymers as well [4, 5]. In star polymer solutions as well as micellar solutions one is encountered with difficulties to calculate the volume fraction, ϕ, because both species have no exactly defined radius. We have used the quantity c/c^* as a measure for the volume fraction in the investigations of the star solutions. The fit parameter c^* of Eq. (5) was taken for the concentration at which $\phi = 1$. This fitted c^* was near to, but not exactly equal to, c^*_{RH} calculated from the hydrodynamic radius and molar mass according to $c^*_{RH} = 3M/4\pi N_A R_H^3$, where M denotes the molar mass of the micelle and N_A the Avogadro constant. We cannot calculate an exact c^*_{RH} for our native solutions because of a lack of exact data. R_H differs between PFG NMR (45 nm) and DLS (71 nm) measurements and M differs between small-angle X-ray scattering (SAXS) experiments (33×10^6) and static light scattering (SLS) experiments (66×10^6). Using the "best" values for our purpose, R_H from DLS (71 nm) and M from SAXS (33×10^6) we obtain $c^*_{RH} = 3.7$ g/100 ml. This is in satisfactory accord with the fitted c^* of 4.04 g/100 ml, but this agreement is fortuitous. To define a volume fraction, we use, as in our star polymer investigations [4], the quantity c/c^* with the fitted $c^* = 4.04$ g/100 ml.

We have depicted the dependence of the self-diffusivity of our diblock copolymer solution together with two solutions of star polymers from the previous investigation [4] for comparison in Fig. 3. A D/D_o versus c/c^* representation was chosen. The data for the micelles are in complete accord with the star solutions except at very high concentrations. Crystallization starts at $c/c^* = 0.55$ in the monodisperse star solutions. D has decreased to 0.03 D_o at this concentration, and D drops to zero in the crystalline state. No indication of crystallization is seen in the slightly polydisperse micellar solution and D could be extrapolated to 0.003 D_o at $c/c^* = 0.63$, the highest concentration which we were able to measure. The hypothetical crystallization concentration at which $D = 0.03D_o$ is $c = 2.22$ g/100 ml in our solution. Assuming an equal relative distance between the crystallization volume fraction, ϕ_{cr}, and the glass-transition volume fraction, ϕ_g, ($\phi_g = 1.174\phi_{cr}$ in hard-sphere colloids), we expect a colloidal glass transition at $c/c^* = 1.174 \times 0.55 = 0.646$, i.e. at $c = 2.61$ g/100 ml in our system. At this concentration, the long-range self-diffusivity is far below the experimental limit of our spectrometer and cannot be measured.

The echo attenuations shown in Fig. 1b for a solution of $c = 2.58$ g/100 ml (in deuterated *n*-decane) are proof against gelation. They remain essentially monoexponential, also for the concentrations between the (in our case hypothetical) crystallization concentration and the glass-transition concentration. They should become more and more nonexponential due to cluster formation at gelation [9]. Indications of stronger interactions between the micelles have been found in SLS studies for concentrations above about 1 g/100 ml. They were interpreted as associations between the corona chains of the micelles (concept of sticky contacts). If at all present, these interactions are weak and do not lead to real physical gelation. They must be very short-lived and therefore invisible in the PFG NMR measurements. However, one result is remarkable: when approaching the colloidal glass transition the self-diffusivity becomes more and more restricted within the time window of our experiments. Examples are shown in Fig. 1b and c. In Fig. 4 the root mean square displacements of the micelles in relation to the observation time for the four highest concentrations are presented, but in a solution of deuterated *n*-decane (so the solvent signal is invisible in the experiment). The diffusion remains restricted within a cage (in-cage diffusion) for short observation times, and free long-range diffusion is attained for long observation times. The transition time between in-cage and free long-range diffusion, i.e. the residence time within the cage, becomes dramatically longer with increasing concentration. The size of the cage can be estimated from the plateaus of the curves in Fig. 4 to be of the order of 120 nm and, hence, to be of the order of the micelle diameter. This result is qualitatively in accord

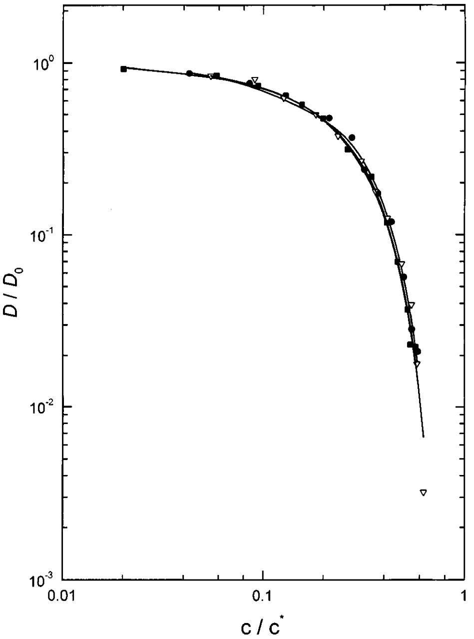


Fig. 3 Dependence of the reduced self-diffusivity, D/D_o, on the reduced concentration, c/c^*, for the micellar diblock copolymer solution (△), and for comparison purposes for two 128-arm star solutions with arm lengths $M_a = 7000$ (○) and $M_a = 28\,000$ (●), from Ref. [4]. The star solutions start to crystallize at $c/c^* = 0.55$, and the self-diffusivity goes to zero

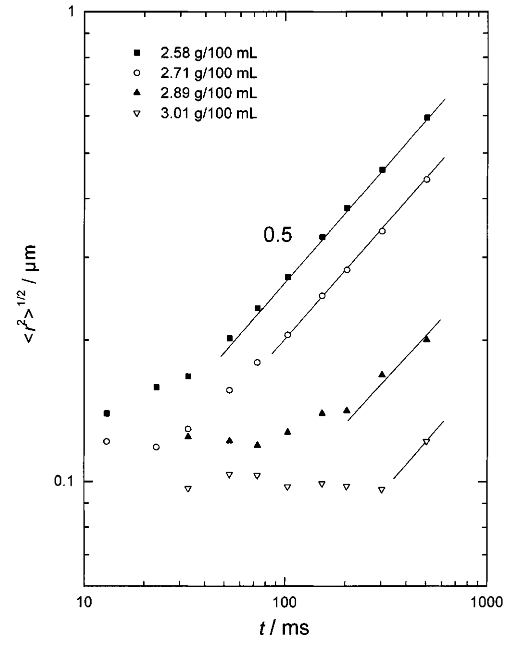


Fig. 4 Root mean squared displacements, $\langle r^2 \rangle^{0.5}$, of the micelles in deuterated *n*-decane in relation to the diffusion time, t, for the concentrations indicated. In-cage diffusion is observed for short times, whereas free long-range diffusion occurs at long times

with the star polymer solutions in the crystalline state which have, however, a smaller hydrodynamic diameter (between 28 and 62 nm) and a cage diameter about twice the diameter. The micelles are less soft in comparison with the multiarm stars because of their large solid core and the far more dense corona.

We have investigated four highly concentrated solutions of the diblock copolymer using deuterated *n*-decane to enhance the precision of the measurements of $S_{\mathrm{inc}}(q,t)$ at lower q^2t values. One remarkable result was the obviously different hydrodynamic radii of the micelles in deuterated and protonated solvent: the hydrodynamic radii in the deuterated solvent are slightly smaller than in the protonated solvent. The same isotope effect was found in aqueous solutions of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymers (Pluronics) [22]: the hydrodynamic radii of micelles in D_2O were found to be 10–20% smaller than in H_2O. To our knowledge, there are no detailed reports of these isotope effects of the solvent on micellization in the literature.

Using our largest possible field gradients, we measured the self-diffusivity in a sample with a concentration of 3.33 g/100 ml, i.e. at $c/c^* = 0.824$, which is near the glass-transition concentration. In Fig. 5, we have depicted the results: the self-diffusion is completely restricted, we observe only in-cage diffusion, and free long-range diffusion is not reached in the time window of the experiment (13–603 ms). We observe a broad distribution of (apparent) self-diffusivities, and the distribution width increases with increasing observation time. Since we measure the single-particle correlation function with PFG NMR, this result can only be interpreted as a result of inhomogeneities in the solution: the sizes of the cages are rather well distributed. These results seem to confirm new theories of the glass transition in which dynamic inhomogeneities play a central role [23]; however it is too early for a final discussion of this result, and further experiments are necessary.

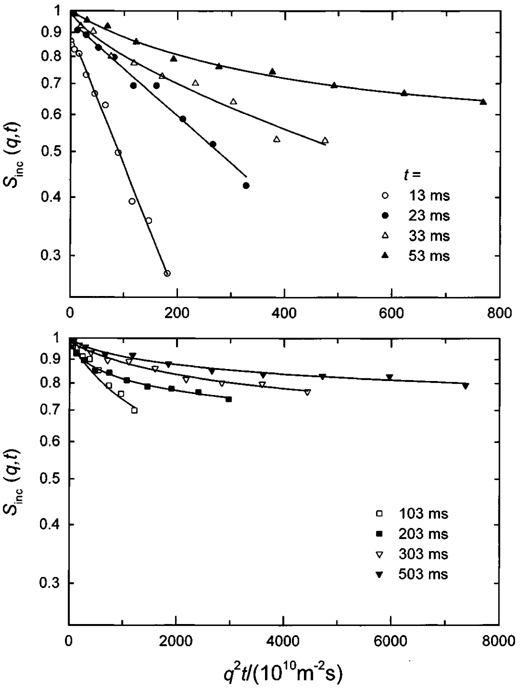


Fig. 5 Echo attenuations measured at different observation times, *t*, for a diblock copolymer solution at $c = 3.33$ g/100 ml, i.e. at $c/c^* = 0.72$. We observe, within experimental error, completely restricted diffusion and a distribution of apparent self-diffusivities which becomes broader with increasing observation time. Note the different scales on the abscissae of the two parts of this figure

Summary and conclusions

The self-diffusion of a polystyrene-*b*-poly(ethylene-*co*-propylene) diblock copolymer dissolved in a preferential solvent for the aliphatic block, *n*-decane, was investigated by PFG NMR. The diblock copolymer forms micelles in solution, the core of which consist of the polystyrene chain parts and the corona of the aliphatic chain parts. The micelle structure in the native solution is still determined by the state of the glassy polystyrene in the initial solid diblock copolymer. Equilibration of the micelles is achieved by heating the solution above the glass-transition temperature of the polystyrene cores. After cooling to room temperature, the equilibrium is again frozen in, but the size of the micelles has diminished.

The concentration dependence of the self-diffusivity of the native solutions shows typical colloidlike behaviour, and it could be described by a VFT-like equation. The result is in remarkable accord with the self-diffusivity of multiarm star polymers but with one difference: we find no indication of the crystallization of the micellar solution which is caused by the inherent slight polydispersity of the micellar sizes. The self-diffusivity could be measured up to concentrations where the colloidal glass transition is expected. In-cage diffusion at short observation times is found at these high concentrations. Indications of dynamic heterogeneity are found at the highest concentration investigated.

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