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Dynamics of Poly(styrene-*b*-2-vinylpyridine) in Toluene

Ming Xie[†] **and Frank D. Blum***

Department of Chemistry and Materials Research Center, University of Missouri—Rolla, Rolla, Missouri 65409-0010

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ABSTRACT: Low molecular weight specifically labeled block copolymer poly(β-deuteriostyrene-*b*-2-vinylpyridine) (β-DSVP) and poly(α-deuteriostyrene) (α-DS) (7600 and 10000 g/mol with polydispersities of 1.15 and 1.7, respectively) have been prepared by anionic polymerization. Deuterium NMR relaxation times and self-diffusion coefficients of DSVP and DS were measured for the polymers in solution as a function of concentration. The relaxation times were interpreted through the use of the Hall−Helfand model for chain dynamics. In toluene, the dynamics of the styrene segments in block copolymers were different than in homopolystyrene. The effect of concentration on segmental motions was more pronounced for the low molecular weight block copolymers than it was for the homopolymer above 15 wt %. The results indicated that the short-range motions were similar for the homo- and copolymer while the long-range motions were different. Self-diffusion coefficients for the block copolymer also showed a sharp decrease at concentrations greater than 15 wt %. The changes in the relaxation behavior and self-diffusion coefficients were attributed to micellization of the block copolymer in toluene. The cmc value was estimated to be 11 wt % based on a pseudophase model.

Introduction

In the past two decades, block copolymer solutions have received considerable attention.[1−4] In analogy to widely used synthetic surfactants, block copolymers exhibiting an amphiphilic nature can self-assemble into organized structures in various solvents. This creates useful microenvironments under controlled conditions, which might be useful for a number of specific purposes. Numerous theoretical[5−10] treatments have been proposed to describe micelle formation by block copolymers. A picture has emerged of an outside corona region, surrounding an internal core.

Extensive studies have been made on the factors that influence the micellization process and the structure of micelles. Less has been done on their dynamics, especially segmental motion. Some limited theoretical work has suggested that block copolymers add and leave micelles as single-chain species.[11] More recent simulations suggest that multimolecular exchange occurs at higher concentrations.[12] Proton NMR has been a useful tool to follow the coil overlap process.[13,14] Additional work has been done on the measurement of the diffusion coefficients of the micelles by light scattering,[15−19] optical anisotropy,[20] or NMR.[21] More “local” dynamics of the chains have been probed with dielectric spectroscopy[22] and NMR.[23] In the latter study, Gao et al.[23] used deuterated styrene and observed a dependence on the position of the label in the chains relative to the ionic end. They interpreted their data in terms of a distribution of correlation times. It is along similar lines that this work is focused. Since the NMR relaxation properties of many nuclei in polymers are determined by the nature and frequency of the chain motions at their site, they can provide detailed insight at the molecular level. Several reviews[24,25] describe the various models developed for the interpretation of nuclear spin relaxation data for polymers in solution.

In previous work from our group,[26,27] the structure and dynamics of poly(styrene-*co*-2-vinylpyridine) (SVP) on silica swollen with different solvents were reported. The relaxation behavior was probed in toluene, carbon tetrachloride, and carbon tetrachloride/methanol mixtures. In toluene, a good solvent for polystyrene, the highly extended styrene segments show mobility which is enhanced relative to that in corresponding solutions of either the homopolymer or copolymer. The vinylpyridine segments were relatively immobile because of their interaction with the silica. In poorer solvent systems, the styrene segments were found to have more restrictive mobility as compared to their behavior in a solution with toluene. The presence of methanol also gave additional motional freedom to the bound-VP segments.

The goal of this study is to obtain insight into the local motions of the block copolymer poly(β-deuteriostyrene-*co*-2-vinylpyridine) (β-DSVP) and homopolymer poly(α-deuteriostyrene) (α-DS) dissolved in toluene. The aim is to extend our understanding of the block copolymer dynamics in solution. Recently, Oostergetel et al.[28] reported the cryotransmission electron microscopy of diblock copolymer poly(styrene-*co*-2-vinylpyridine) in toluene. The SVP block copolymer forms spherical micelles in toluene which can be visualized using phase contrast microscopy. In our work, a comparison of the deuterium NMR relaxation times of the block copolymer with the homopolymer solution was used to explore the association of the block copolymer and its micellar motion. The Hall−Helfand model[29] was used as the basis to quantify the dynamics of this system. Measurement of the self-diffusion coefficients with pulsed-gradient spin-echo (PGSE) NMR[30,31] provided additional information about micelle formation.

Experimental Section

A Grignard-type reaction was used to prepare the labeled monomers, α-deuteriostyrene and β-deuteriostyrene. The choice of α- or β-deuterated material was based upon the availability of the starting bromo compounds. In the procedure, α-bromostyrene or β-bromostyrene, obtained from Aldrich Chemical Co. (Milwaukee,WI), was added dropwise to a Mg metal/tetrahydrofuran (THF) mixture in the dark to form the Grignard complex. D_2O was then added carefully to hydrolyze the Grignard solution. The products were obtained after vacuum distillation. Care was taken to maintain the

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* To whom correspondence should be sent.

[†] Current address: Composite Materials and Structures Center, Michigan State University, East Lansing, MI 48824-1326.

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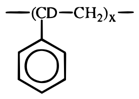
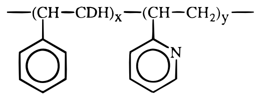
Table 1. Molecular Weights of Polymers from GPC

	wt % styrene	wt % 2-vinylpyridine	M_w (kg/mol)	M_w/M_n
DS-4	100		10.0	1.15
DSVP-B1	77	23	9.8	1.76
DSVP-B2	71	29	7.6	1.74

temperature below 70 °C, even during distillation. The yields of the products were 70−80%, and the level of deuteration was typically 80−90% as determined by deuterium and proton NMR.

Both α-DS and *β*-DSVP were prepared by anionic polymerization. Solvents (cyclohexane and tetrahydrofuran) first were refluxed with sodium metal under a nitrogen atmosphere to remove moisture and peroxides. The purified solvents were distilled from the ketyl solution before use. Monomers (α-deuteriostyrene, *β*-deuteriostyrene, and 2-vinylpyridine) were stored over finely ground calcium hydride. The styrene monomers were initially double vacuum distilled from calcium hydride and then distilled again over lithium aluminum hydride the use. 2-Vinylpyridine was double vacuum distilled from calcium hydride prior to use. All of the operations were done under a nitrogen atmosphere. The synthesis of poly(α-deuteriostyrene) was conducted in a solution of cyclohexane using *sec*-butyllithium as the initiator. Typical conditions for polystyrene were 30 wt % monomer at 0 °C in cyclohexane for 1 h. Poly(*β*-deuteriostyrene-*co*-2-vinylpyridine) was made in THF because of the insolubility of 2-vinylpyridine in cyclohexane. The reaction was initiated with a few drops of *β*-deuteriostyrene at room temperature. The sample was then cooled to −78 °C and the remaining *β*-deuteriostyrene was added dropwise, followed by 2-vinylpyridine. The structures of resulting polymers are shown along with their designations:


α-DS


ß-VPDS

The molecular weights, polydispersities, and compositions of polymers determined by GPC are listed in Table 1. Polystyrene standards were used to calibrate the molecular weights for both homopolymer and block copolymers.

Solutions of several different concentrations for NMR studies were prepared by adding distilled toluene directly to weighed polymers in 5-mm NMR tubes. The tubes were sealed and no attempt was made to remove dissolved oxygen because of the shortness of the relaxation times. Deuterium NMR T_1 and T_2 measurements were performed on a Varian VXR-200/S spectrometer at 30.7 MHz for deuterons at a temperature of 25 °C. The T_1 values were measured by inversion−recovery (180°−τ−90 °) and T_2's by the Carr−Purcell−Meiboom−Gill (CPMG) method. A pulse delay of at least 5 × T_1 was used to allow the deuterons to achieve equilibrium magnetization after each data acquisition. In all cases, the decay curves could be characterized by a single-exponential relaxation time. The relaxation times were calculated from signal heights using a log−linear least-squares fit. The accuracy of the measured relaxation times was approximately 5% as estimated from three runs on the same sample. The precision for a single T_1 measurement was typically about 3%, for T_2 measurements it was estimated to be 5%.

Self-diffusion coefficients were measured using the pulsed-field-gradient spin-echo (PGSE) technique (90°−Δ−180−Δ−echo sequence with two field-gradient pulses of duration δ during the Δ periods)[30,31] on a JEOL FX-100 spectrometer equipped with a LEO-J (Tecmag, Houston, TX) acquisition unit. A minor spectrometer modification was made to allow the Tecmag unit to control the homospoil accessory on the FX-100. The samples for diffusion were prepared in toluene-d_8. The field gradient strength, G, was determined to be 5.10−5.40 G/cm based on a calibration on a 1:1 H_2O/D_2O sample for which the proton self-diffusion coefficient, D, was taken to be equal to 2.03×10^{-9} (m²/s) at 25 °C.[32] The time between the initial and refocusing pulses, D, was about 40−65 ms. The amplitude, A, of a given NMR resonance was given by[30,31]

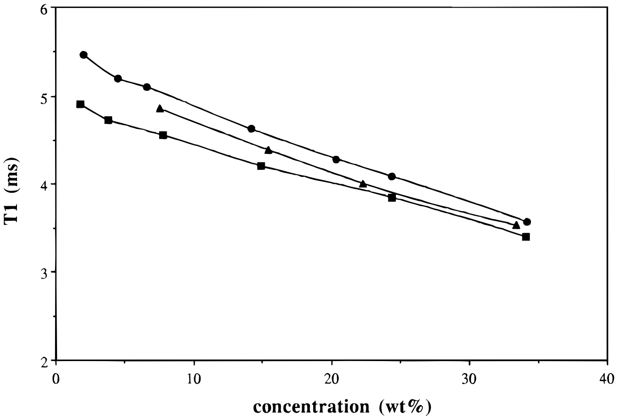


Figure 1. Longitudinal (T_1) relaxation times for DS and DSVP at 25 °C in toluene: (●) DS-4; (▲) DSVP-B2; (■) DSVP-B1. The curves are connected to aid the eye.

$$A = A_0 \exp(-\gamma^2 G^2 \beta D) \qquad (1)$$

with

$$\beta = \delta^2(\Delta - \delta/3)$$

where δ is the time of field gradient pulse, G is the field gradient strength, and γ is the magnetogyric ratio. A semi logarithmic fit of A vs β values gave straight lines with a slope which yielded D. Typically, the accuracy of these measurements was estimated to be within 10%.

Results

In order to understand the dynamics in the block copolymer (DSVP) solutions, we have chosen to compare their relaxation times to those of the homopolymer (DS) solutions. The homopolymer (DS-4) and block copolymer (DSVP) were deuterated at different positions on the polymer backbone. ^{13}C NMR relaxation measurements[32] have shown that the α-CH on the polystyrene backbone have T_1 relaxation times twice as long as that of *β*-CH_2. This was indicative of the same motional behavior at the α- and *β*-positions. Therefore, the position of the deuterium labels should not affect the results reported. In addition, all data showed relaxation behavior which could be fit well to a single exponential decay. This, coupled with the fact that only a single resonance was observed, suggests that polymers in different microenvironments (e.g., micelle and free solution) exchanged rapidly on the deuterium NMR timescale.

Shown in Figures 1 and 2 are the deuterium NMR relaxation time values for α-DS and block *β*-DSVP at 25 °C as a function of concentration. As expected, the longitudinal relaxation times, T_1, for both homopolymer and block copolymer decreased as the concentration increased. This decrease was gradual. The changes in the transverse relaxation times, T_2, with concentration were quite different. For the homopolymer, the T_2 values showed a gradual decrease with increasing concentration. The rate of change with concentration was slightly higher than that of T_1. For the block copolymers, there was a marked decrease for the T_2 values after approximately 15%. T_2 was more sensitive than T_1 to concentration, especially for the block copolymer system.

NMR self-diffusion measurements were also used to probe the block copolymer's behavior. The self-diffusion

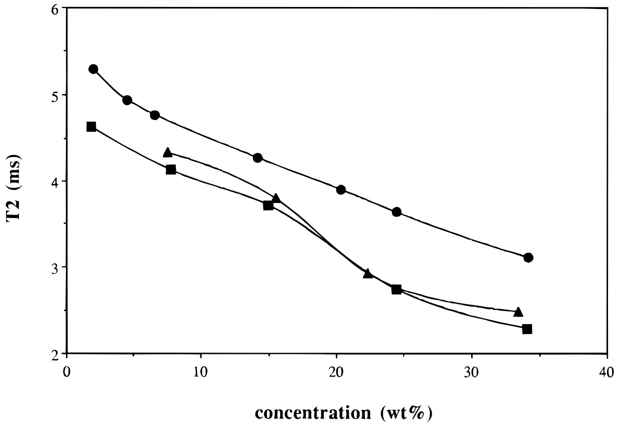


Figure 2. Transverse (T_2) relaxation times for DS and DSVP at 25 °C in toluene: (●) DS-4; (▲) DSVP-B2; (■) DSVP-B1. The curves are connected to aid the eye.

coefficients of homopolymer DS and block copolymer DSVP as a function of concentration at 25 °C are shown in Figure 3. The diffusion decay curves were successfully fitted to a single exponential, implying the fast exchange between microenvironments over the course of the experiment. A plot of $1/D$ vs concentration was used to highlight the self-diffusion coefficient change with concentration. For the DS homopolymer, the self-diffusion coefficients show only a relatively small change over entire range. For the block copolymer, a dramatic increase in $1/D$ after 15% was found. The concentration range for the large change in diffusion coefficient was in good agreement with the large change in T_2's for the block copolymer.

We also observed a slight turbidity for solutions with concentrations from 7% to 15% at 25 °C. The solutions with concentrations below 5% and above 20% were transparent. Similar phenomena have been observed by other studies of block copolymer solutions as well.[34-36] It was suggested [36] that the system had phase-separated, resulting in the turbidity. We suspect that a small amount of phase separated material was in equilibrium with isotropic solution. Transparency in the solutions at higher concentrations was believed as evidence of the existence of micelles in the block copolymer solutions.[36] In order to observe the potential influence of phase separation, the self-diffusion coefficients of DSVP-B1 were also measured at 50 °C, where none of the samples exhibited turbidity. The results are also shown in Figure 3. No significant change was observed in the 7−15% range when temperature was raised.

Discussion

NMR relaxation experiments can yield a wealth of information on both solvent and solute dynamics. Some relaxation theories[33-37] have been modified to describe quantitatively the motional characteristics of polymer chains. The general expression for the deuterium quadrupolar relaxation in liquids is well-known:[49]

$$1/T_1 = (3\pi^2/20)(e^2qQ/h)^2[J(\omega) + 4J(2\omega)] \quad (2)$$

and

$$1/T_2 = (3\pi^2/40)(e^2qQ/h)^2[3J(0) + 5J(\omega) + 2J(2\omega)] \quad (3)$$

where e^2qQ/h is the quadrupole coupling constant, ω is the Larmor frequency, and $J(\omega)$ is the spectral density.

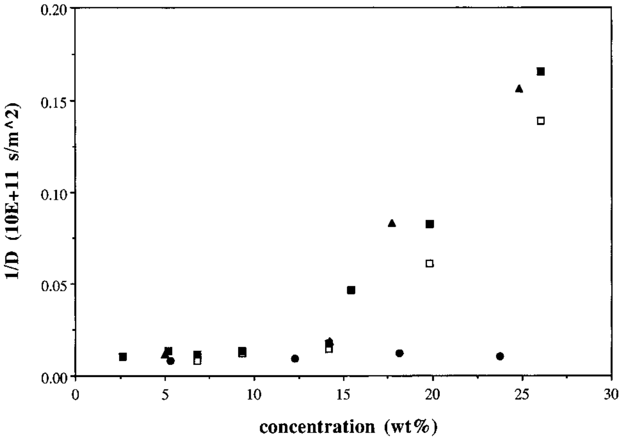


Figure 3. $1/D$ coefficients as a function of concentration for (●) DS-4, (▲) DSVP-B1, and (■) DSVP-B1 at 25 °C, plus (□) DSVP-B1 at 50 °C.

The quadrupole coupling constant has been determined to be 165 kHz based on the solid-state deuterium spectrum of bulk polystyrene-*d*. The spectral density is a frequency-domain function corresponding to an autocorrelation function, $G(t)$

$$J(\omega) = \int_{-\infty}^{\infty} G(t)\mathrm{e}^{-\mathrm{i}\omega\tau}\,\mathrm{d}t \quad (4)$$

in this case, $G(t)$ represents the correlation of the C−D bond vector axis at times 0 and t.

According to the Hall−Helfand (HH)[29] model, many of the rapid relaxation processes in polymers which can be probed by NMR are related to conformational transitions of the chain backbone from one rotational isomeric state to another. Hall and Hellfand classified them according to the displacement of the polymer tails into three types. The correlation function used has the form

$$G(t) = (t/\lambda_1)I_0 \exp(-t/\lambda_0) \exp(-t/\lambda_1) \quad (5)$$

and the spectral density is given by[38]

$$J(\omega) = 2A(\omega)\{[\lambda_0(\lambda_0 + 2\lambda_1) - \omega^2]^2 + [2(\lambda_0 + \lambda_1)\omega^2\}^{-0.25} \quad (6)$$

where

$$A(\omega) = \cos\{0.5 \tan^{-1}[(2(\lambda_0 + \lambda_1)\omega)/(\lambda_0(\lambda_0 + \lambda_1) - \omega^2)]\} \quad (7)$$

λ_0 and λ_1 are two fitting parameters, λ_0 is the single-bond conformational transition rate, λ_1 is the cooperative conformational transition rate which involves several bonds, and I_0 is a modified Bessel function of order zero.

As shown in Figures 1 and 2, the block copolymers of similar molecular weight and concentration have shorter relaxation times (both T_1 and T_2) than those of the homopolymer over all observed concentration range. However, it is interesting to note that the experimental T_2 measurements showed a pronounced decrease after 15% only for block copolymer solutions. The decrease of T_1 values for both homo- and copolymer was similar. In this regime, shorter relaxation times are indicative of more restricted motions. The T_1/T_2 ratio can be used as an indicator. For NMR fast isotropic motion, the T_1/T_2 ratio would be 1. This is often seen in small molecule solutions. For polymers, dominated by anisotropic local

Table 2. Relaxation Time Ratios and HH Parameters for DS and DSVP at 25 °C in Toluene

	concn (wt %)	T_1/T_2	λ_0[a]	λ_1[a]	λ_1/λ_0
DS-4	1.99	1.03	10.23	16.3	1.6
	4.50	1.05	7.48	21.1	2.8
	6.59	1.07	6.30	23.8	3.8
	14.18	1.08	5.62	20.9	3.7
	20.35	1.10	5.07	18.9	3.7
	26.07	1.11	4.78	16.9	3.5
	34.16	1.15	3.97	14.5	3.6
DSVP-B1	1.79	1.06	6.99	19.7	2.8
	3.83	1.12	4.46	25.9	5.8
	7.74	1.10	4.89	22.4	4.6
	14.91	1.13	4.19	20.6	4.8
	24.40	1.41	1.56	21.4	13.7
	34.09	1.48	1.29	16.1	12.5
DSVP-B2	7.52	1.12	4.34	27.9	6.4
	15.46	1.16	3.70	24.2	6.5
	22.30	1.37	1.70	23.4	13.8
	33.41	1.42	1.51	17.6	11.7

[a] In units of 10^8 s^{-1}.

segmental motions, the ratio is often much greater than 1.[25] Of course, this is dependent upon molecular weights, concentrations, solvents, and temperatures. Previous work[26] on high molecular weight polystyrene (ca. 265 000 g/mol) has shown T_1/T_2 ratio as high as 1.5 at 20 wt % in toluene. However, the T_1/T_2 ratios for polymers could also be close to 1 when the molecular weights and concentrations are very low. It is evident from Table 2 that the ratios for DS polymer solutions from 6% to 15% are less than 1.10. For the DSVP samples in the same concentration range, the ratios range from 1.10 to 1.16. This small difference was indicative of a slightly more restricted mobility for the block copolymer. In the higher concentration range (greater than 15%), the ratios for DS polymer solutions were still around 1.1, but for the DSVP samples, the ratios were higher, 1.4. This difference suggested that there was a more significant difference in the motion of the two systems. It should also be noted that the reason for this difference was chiefly because of the difference in T_2, not T_1. Thus, it is fair to conclude that the fast local motions to which T_1's are sensitive were similar for the homo- and copolymer. However, the longer range motions, to which T_2's are sensitive, were different for the copolymer due to a reduced contribution from the overall rotational tumbling of the polymer molecules because of their association with the micelle.

The results of fitting the data to the HH model are presented in Table 2. In a macromolecular solution, a single-bond conformational transition will be slow because of the large, swinging motion of the attached polymer tail and the frictional resistance which the tails present to the transition. This is represented by λ_0. The fast motion, representative of pair transitions, is represented by λ_1. This cooperative conformational transition is a special dynamics aspect of conformational transitions in large chain molecules. These motions will have greatly reduced frictional resistance. Thus λ_1/λ_0 represents the ratio of the fast motion rate and slow motion rate in a given system. This ratio is more sensitive to the differences in motional rates than the T_1/T_2 ratio. In our system, as shown in Table 2, the λ_1/λ_0 ratios for the block copolymers were greater than the ratios for the homopolymers at all concentrations, especially at higher concentrations. The λ_1/λ_0 ratios for the block copolymers at higher concentrations are 2–4 times greater than those of the homopolymers or copolymers at lower concentrations. It is clear that there was a motional hindrance in the block copolymer solutions which was much greater at higher concentrations.

From the NMR point of view, polymer segmental motion is dependent only on the microviscosity of the immediate environment of the chain segments.[25] In solutions of homopolymers, we expect that the average composition of the polymer environment is similar to that of the solution as a whole except in a very dilute solution. However, for block copolymers in certain solvents, the formation of micelles makes the local chemical composition very different from the bulk solution.[39,40]

Previous studies[34,35] have used the high-resolution NMR spectra and NMR relaxation measurements to investigate the micellar solutions of block copolymers. Those studies showed a distinct difference in NMR relaxation times or chemical shifts between the homopolymer solutions and the micellar solutions of block copolymers. We also expect a difference in relaxation behavior before and after micellization in the block copolymer solutions. Based on our NMR relaxation studies and turbidity observations, we tentatively conclude that the block copolymer SVP has a tendency to associate and to form micelles in toluene; there is significant evidence of it when the concentrations were greater than 15%. This seems to be a relatively high concentration for these effects, but this is probably because of the low molecular weight and the polydispersity of the polymers. A complication of the block copolymer micelles is that they are comprised of chains which are much more polydisperse than low molecular weight amphiphiles, e.g., conventional surfactants. Block copolymers form "mixed" micelles in solution. Recently, it has been shown[41,42] that polydispersity can have a major effect on the critical micelle concentration (cmc) in block copolymers. The theoretical calculation of Munch and Gast[10] on diblock copolymer solutions also demonstrated the effect of the copolymer−solvent compatibility, the ratios of soluble block and insoluble block, and the solubility of the head group etc. on the cmc. All of these factors make a well-defined sharp cmc unlikely.

Further support for micellization was found from NMR self-diffusion measurements. The mobility of a molecule in a solution depends on the degree of interaction with other species in the system. If two or more molecules form a new kinetic entity, this will affect the microdynamic properties of the solution. Thus comparison of translational diffusion of the copolymers and homopolymer in the same solvent at similar concentrations will constitute one additional way to obtain information on association phenomena. Molecules associated with the aggregate will diffuse more slowly, and a decreased diffusion coefficient indicates association into an aggregate structure.

There are three basic models of micellization known as the pseudophase or two-site model, the single-step equilibrium model, and the multistep equilibrium model.[43] Up to now, the pseudophase model has been used frequently in surfactant NMR studies, such as aqueous sodium octanoate solutions.[44,45] Although only the multistep equilibrium model is able to account for the polydispersity of aggregate size, it was demonstrated that the concentration dependence of NMR chemical shifts for surfactant solutions can be reproduced equally well using either a single-equilibrium model or a multiple-equilibrium model.[46]

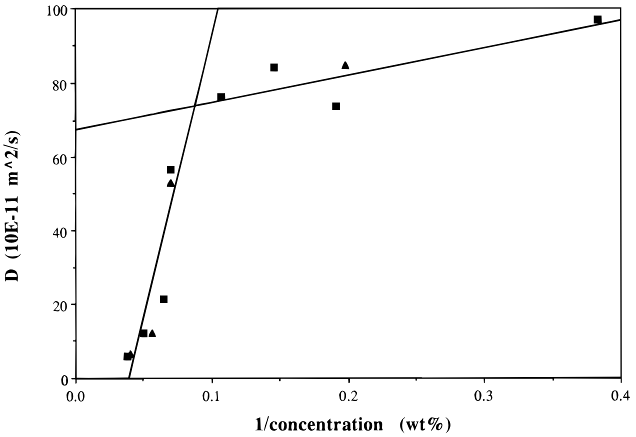


Figure 4. Relationship between diffusion coefficients and concentrations based on pseudophase model: (▲) DSVP-B2; (■) DSVP-B1.

In the present paper, we consider the simplest possible model, namely the pseudophase model and apply it to the block copolymer solution. In the pseudophase model,[47] there are only two different environments for the surfactant, one corresponding to a free surfactant molecule and one to a surfactant molecule occurring in a micellar aggregate. There is no aggregation below the cmc whereas the monomer concentration remains constant and equals the cmc upon micellization. Species in the two different environments are believed to be in fast exchange. Then observed self-diffusion coefficients are population-weighted averages of the diffusion coefficients of the nonassociated species and of the micelles:

$$D = D_f P_f + D_m P_m \tag{8}$$

where D and P represent the self-diffusion coefficients and fractional populations, respectively. The subscripts f and m refer to those molecules which are free and in the micelle, respectively. For the pseudophase model

$$D = D_f \,\text{cmc}/C + D_m (C - \text{cmc})/C \tag{9}$$

or

$$D = D_m + (D_f - D_m)\,\text{cmc}/C \tag{10}$$

where C is the total concentration of polymer in solution. The model described should give two straight lines intersecting at the cmc if D is plotted against $1/C$. Figure 4 shows such a plot of our data. The association of block copolymer in toluene occurred roughly around 11−12% at 25 °C. The accuracy of our estimate based on the pseudophase model is limited by several factors. The polydispersity of our block copolymer sample will be a significant one. The possible formation of small complexes below the cmc may also be inferred from Figure 4 as the self-diffusion coefficient starts to decrease well below the cmc. Usually, the explanation for the deviation is to assume the formation of small complexes at concentrations lower than the cmc is attained.[47] Premicellar phenomena are well known and have been observed in other surfactant systems.[48,49] We observed the major change in diffusion coefficient and NMR relaxation measurements when the system was going from the solution state to the micelle formation.

Table 3. Modified log χ^2 Distribution Results for DSVP-B1 in Toluene[a] and for Precursors and Ionomers in CCl$_4$[b]

DSVP-B1[a]				nonionic precursor[b]		ionomer[b]	
concn (wt %)	τ_0 (ns)	P	temp (°C)	τ_0 (ns)	P	τ_0 (ns)	P
1.79	0.66	45	21	7.4	21	117.4	12
3.83	0.73	41	30	6.0	22	59.0	13
7.74	0.75	45	40	4.8	23	49.5	13
14.91	0.85	45	50	2.3	25	32.4	13
24.40	1.30	36	60	1.4	29	15.0	14
34.09	1.67	34	70	1.1	30	4.5	17

[a] This work, 25 °C. [b] For the backbone aliphatic deuteron; corrected (see text) from ref 32 at 9.1% (w/w) in CCl$_4$.

Finally, we compare our segmental motional results with those of Gao and Eisenberg[23] on ionomers. The fitting of their NMR data based on the log χ^2 distribution yielded information about micellization. They concluded that mobility of ^{2}H-labeled styrene segments close to the micellar cores was reduced. We obtain similar results in terms of segmental motion from HH model fitting. However, a more meaningful comparison can be made if both data sets are compared using the same model. In order to do this, the log χ^2 distribution used by these authors must be modified since the mean correlation time from the original distribution τ_0^{org} [50] was not the true mean correlation time, but a scaling factor.[51] This can be related to the true mean, τ_0, with a simple manipulation. The relationship has been determined to be[51]

$$\tau_0 = \tau_0^{\text{org}} \frac{(P^{\text{org}}/(P^{\text{org}} - \ln(b^{\text{org}})))^{P^{\text{org}}} - 1}{b^{\text{org}} - 1} \tag{11}$$

where P^{org} and b^{org} are the fitted parameters from the original data. Table 3 lists the corrected log χ^2 distribution results (b = 1000) for DSVP-B1 and the data from ref 23 (from their Table 5).

In some cases, the correction for τ_0 can be large. As shown in Table 5, the original distribution yielded unusually fast correlation times for (PS)$_{92}$-*b*-(PS-d_8)$_{4.5}$-*b*-(PS)$_{17}$-*b*-(PANa)$_{15}$ block ionomer micellar solutions. Originally, the comparison showed that the block ionomer's correlation time was only twice as long as that of the nonionic precursor. In our DSVP-B1 system, we found that the difference in correlation times before and after micellization was about a factor of 2. The styrene segmental motions in ionomer micelles are expected to be much more restrictive than those of our block copolymer micelles due to their dense ionic cores which are close to the labeled segments. The modified and corrected log χ^2 distribution gave a much more reasonable difference in τ_0 between the nonionic precursor and the block ionomerm, this difference being between 4 and 10 times slower for the ionomer. Our finding of an even stronger slow down further confirmed Eisenberg's concept of significantly reduced mobility near the micellar cores in ref 23. Both their study and ours showed that the correlation times increase and the P values decrease significantly upon micellization, indicative of the slower motions in micellar solutions. A comparison of their material and ours is reasonable to make at roughly 10% polymer and between 20 and 30 °C. In this range, we find that our system is about 1 order of magnitude faster than their nonionic system, but 2 orders faster than the ionomer. This is reasonable considering we have a lower molecular weight polymer in a thermodynamically better solvent for styrene.

Conclusions

Information on the dynamics and micellization of block copolymer (SVP) solutions can be obtained from relaxation time and self-diffusion measurements of specifically labeled polymers. The block copolymer in toluene has been shown to behave differently from homopolystyrene in the same solvent. The styrene segments on the block copolymers exhibit more restricted mobility as compared to the homopolymer. For the relatively low molecular weight block copolymer, the dependence of segmental motion on concentration is notable. Based on the HH model analysis of the relaxation behavior, styrene segmental motions of the block copolymers above 15% polymer are not only more restricted, compared to the homopolymer at the same conditions, but also much slower than that of block copolymer below 15% concentration. NMR self-diffusion coefficient measurements were also consistent with the relaxation results. The self-diffusion coefficients vary only moderately below 15%, but above 15%, a rapid decrease of self-diffusion coefficient with increasing concentration is observed. We believe that these results are consistent with the formation of block copolymer micelles. The cmc value, based on the pseudophase model, was estimated to be around 11%.

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References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Adv. Colloid Interface Sci.* **1976,** *6*, 201.
(2) Price, C. *Pure Appl. Chem.* **1983**, *55*, 1563.
(3) Brown, R. A.; Masters, A. J.; Price, C.; Yuan, X. F. In *Comprehensive Polymer Science*; Booth, C., Price, C., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 2, Chapter 6.
(4) Halperin, A.; Tirrell, T.; Lodge, P. *Adv. Polym. Sci.* **1991**, *31*, 100.
(5) Halperin, A. *Macromolecules* **1987**, *20*, 2943.
(6) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051.
(7) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.
(8) Gao, Z.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7353.
(9) Hunter, P. N.; Scheutjens, J. M. H. M.; Hatton, T. A. *Macromolecules* **1993**, *26*, 5592.
(10) Munch, M. R.; Gast, A. P. *Macromolecules* **1988**, *21*, 1360.
(11) Halperin, A.; Alexander, S. *Macromolecules* **1989**, *22*, 2403.
(12) Haliloglu, T.; Bahar, I.; Erma, B.; Mattice, W. L. *Solvents and Self-organization of Polymers*; Webber, S. E., Ed.; Kluwer Academic Publishers, in press.
(13) Bosse, F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 2846.
(14) Bosse, F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 2863.
(15) Xu, R.; Winnik, M. A.; Hallett, F. R.; Reiss, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 87.
(16) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *27*, 3287.
(17) Balsara, N. P.; Stepanek, P.; Lodge, T. P.; Tirrell, M. *Macromolecules* **1991**, *24*, 6227.
(18) Balsara, N. P.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1991**, *24*, 1975.
(19) Xu, R.; Winnik, M. A.; Reiss, G.; Chu, B.; Croucher, M. D. *Macromolecules* **1992**, *25*, 644.
(20) Saiz, E.; Floudas, G.; Fytas, G. *Macromolecules* **1991**, *24*, 5796.
(21) Kiraly, Z.; Cosgrove, T.; Vincent, B. *Langmuir* **1993**, *9*, 1258.
(22) Yao, M.-L.; Watanabe, H.; Adachi, K.; Kotaka, T. *Macromolecules* **1992**, *25*, 1699.
(23) Gao, Z.; Zhong, X.-F.; Eisenberg, A. *Macromolecules* **1994**, *27*, 794.
(24) Heatley, F. In *Dynamics of Chains in Solution by NMR Spectroscopy*; Booth, C., Price, C., Eds.; Comprehensive Polymer Science; Pergamon Press: New York, 1990; Vol. 1, Chapter 18, p 377.
(25) Heatley, F. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *13*, 47.
(26) Blum, F. D.; Sinha, B. R.; Schwab, F. C. *Macromolecules* **1990**, *23*, 3592.
(27) Sinha, B. R.; Blum, F. D.; Schwab, F. C. *Macromolecules* **1993**, *26*, 7053.
(28) Oostergetel, G. T.; Esselink, F. J.; Hadziioannou, G. *Langmuir* **1995**, *11*, 3721.
(29) Hall, C. K.; Helfand, E. *J. Chem. Phys.* **1982**, *77*, 3275.
(30) Stilbs, P. *Prog. NMR Spectrosc.* **1987**, *19*, 1.
(31) Blum, F. D. *Spectroscopy* **1986**, *1* (5), 32.
(32) Mills, R. J. *J. Phys. Chem.* **1973**, 77, 685.
(33) Allerhand, A.; Hailstone R. K. *J Chem. Phys.* **1972**, *56*, 3718.
(34) Spevacek, J. *Makromol. Chem., Rapid Commum.* **1982**, *3*, 697.
(35) Heatley, F.; Begum, A. *Makromol. Chem.* **1977**, *178*, 1205.
(36) Yang, Z.; Pickard, S.; Deng, N.-J.; Barlow, R. J.; Attwood, D.; Booth, C. *Macromolecules* **1994**, *27*, 2371.
(37) Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon Press: Oxford, 1961.
(38) Connolly, J. J.; Gordon, E.; Jones, A. A *Macromolecules* **1984**, *17*, 722.
(39) Krause, S.; Reismiller, P. A. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 663.
(40) Price, C.; Mcadam, J. D. G.; Lally, T. P.; Wood, D. *Polymer* **1974**, *15*, 228.
(41) Khougaz, K.; Gao, Z.; Eisenberg, A. *Macromolecules* **1994**, *27*, 6341.
(42) Linse, P. *Macromolecules* **1994**, *27*, 6404.
(43) Chachaty, C. *Prog. NMR Spectrosc.* **1987**, *19*, 183.
(44) Drakenberg, T.; Lindman, B. *J. Colloid Interface Sci.* **1973**, *44*, 184.
(45) Stilbs, P.; Lindman, B. *J. Phys. Chem.* **1981**, *85*, 2587.
(46) Muller, N. *J. Phys. Chem.* **1975**, *79*, 287.
(47) Lindman, B.; Brum, B. *J. Colloid Interface Sci.* **1973**, *42*, 388.
(48) Danielsson, I.; Stenius, P. *J. Colloid Interface Sci.* **1971**, *37*, 264.
(49) Danielsson, I. *Surface Active Subst., Proc. Int. Cong., 5th* **1969**, *2*, 869.
(50) Schaefer, J. *Macromolecules* **1973**, *6*, 882.
(51) O'Connor, R. D.; Blum, F. D. *Macromolecules* **1994**, *27*, 1654.

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