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Molecular Exchange in PEO−PB Micelles in Water

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Introduction

Micelles generally have a limited lifetime due to the continuous redistribution of the component molecules, and knowledge of the time scales associated with this exchange process is essential for describing the structures in molecular detail.[1] A wide range of techniques (including fluorescence nonradiative energy transfer probing,[2−5] sedimentation,[6] gel permeation chromatography,[7] pulsed field gradient NMR,[8] temperature jump differential scanning calorimetry,[9] etc.) have been used in the numerous studies that have been performed on the kinetics and mechanisms of the component exchange of block copolymer micelles.[10] These studies generally have dealt with combinations of polymer pairs and solvents that offer marginal amphiphilicity and result in micelle dynamics that are limited to an experimentally favorable range of times (i.e., seconds to hours). The aim of the study reported here is to assess copolymer exchange rates in micelles formed in water by poly(ethylene oxide)−polybutadiene (PEO−PB) diblock copolymers. These copolymers provide examples of exchange behavior for highly amphiphilic systems since the Flory−Huggins interaction parameter between the hydrophobic monomer and the solvent has been estimated to be ∼3.5 at room temperature.[11] Given the slow rate of exchange for this system, we opted to use the combined techniques of deuterium labeling and time-resolved small-angle neutron scattering (SANS).

One unique, polymer-related aspect of block copolymer micelle kinetics is the arrested molecular exchange, which has been documented with many examples in the literature. In nearly all cases, these examples involve block copolymer micelles with a glassy core composed of such materials as polystyrene[3,6,12−15] and poly(methyl methacrylate) (PMMA)[16,17] and have been considered as a reflection of the glassy character of the core-forming blocks. Recently, Wegner and co-workers have presented an alternative interpretation regarding the origin of such behavior; on the basis of fluorescence experiments which probed the frozen micelles with a solvent-swollen PMMA core, they suggested that the hindrance of molecular exchange is due primarily to the strong incompatibility rather than the kinetic effect.[17] Examples are known with a strictly nonglassy polyisoprene core but restricted to high molecular weights of the polymer.[18] In the present study, the material chosen for the hydrophobic core is low molecular weight 1,2-polybutadiene (1,2-PB), which has a glass transition temperature at −12 °C[19] and an entanglement molecular weight of 2.0 kg/mol.[20] Therefore, unwanted coupling between the micellar kinetics and the glassy or entanglement dynamics of the core domain does not complicate our experiments.

Table 1. Molecular Characteristics of the Block Copolymers

sample ID	M_n[c] (kg/mol)	N_{PEO}[d]	N_{PB}[e]	f_{EO}[f]	PDI[g]	micelle structure[h]
OB1[a]	8.87	145.3	72.7	0.662	1.13	sphere
OB8[a]	5.39	66.2	72.9	0.483	1.07	cylinder
OB10[b]	5.38	67.2	68.8	0.494	1.10	cylinder
OB13[b]	8.17	132.2	68.8	0.658	1.09	sphere

[a] Diblock copolymers of poly(ethylene oxide) (PEO) and normal poly(1,2-butadiene) (PB). [b] Diblock copolymers between PEO and deuterium-labeled PB. Deuterium content per C_4 repeat unit of the PB block was determined to be 3.92 by ^{1}H NMR spectroscopy. [c] Number-average molecular weight determined from reaction stoichiometry and ^{1}H NMR spectrum. [d] Number of repeat units on the PEO block. [e] Number of repeat units of the PB block. Here N_{PEO} and N_{PB} were calculated on the basis of the same monomer size. The specific volume of amorphous PEO of $v_{EO} = 65$ Å^3 per EO segment at 20 °C (estimated from published data[17]) was taken as the reference monomer volume, and the corresponding monomer molecular weights for the hydrogenated and deuterated (D_4) PB are 34.0 and 37.2 g/mol, respectively. [f] Volume fraction of PEO. [g] Polydispersity index determined from gel permeation chromatography (GPC). [h] Identified with cryogenic temperature transmission electron microscopy (cryo-TEM).

Experimental Section

In this work, we examine the two basic micellar geometries, spherical and cylindrical, by utilizing two pairs of nearly monodisperse diblock copolymers, OB1/OB13 and OB8/OB10. Relevant properties of the four copolymers are listed in Table 1. OB10 and OB13 are composed of deuterium-substituted polybutadiene. The polymers were synthesized by a published two-step anionic procedure,[21] and the pertinent molecular characteristics along with the resultant micelle morphologies identified by cryo-TEM (not shown) are listed in Table 1.

One percent (by weight) solutions of the pure block copolymers were prepared by adding heavy water (D_2O, 99.9% D, Cambridge Isotope) directly into the weighed amount of dry bulk polymer. Solutions containing 1.0 wt % of the copolymer pairs (i.e., OB1/OB13 or OB8/OB10) were prepared in two different ways: mixing of the two polymers before (*premixing*) or after (*postmixing*) hydration. In the former case, the weighed mixtures of the two block copolymers were first homogeneously dispersed in chloroform, dried, annealed in a vacuum oven at 50−60 °C for several hours, and then dissolved with an appropriate amount of D_2O at room temperature. The *postmixed* samples were prepared, for example, simply by mixing a premade 1.0 wt % OB1 solution with a premade 1.0 wt % OB13 solution, or likewise between OB8 and OB10. SANS experiments were carried out on the NG-7 30 m instrument of the Cold Neutron Research Facility at the National Institute of Standards and Technology (NIST). A sample-to-detector distance of 7 m with a monochromated neutron wavelength (λ) of 6 Å and a wavelength spread (λ/λ) of 0.11 was used to cover scattering wave vectors 0.007 Å^{-1} < q < 0.085 Å^{-1}. Here the scattering wave vector (q) is defined as $q = (4\pi\lambda)\sin(\theta/2)$, where θ is the scattering angle. All measurements were taken at 20 °C. The resulting data were corrected for background electronic noise, nonuniform detector efficiency, solvent plus empty cell scattering, and sample transmission. The scattering intensities for the dissolved polymers were then scaled to absolute values on the basis of direct beam flux measurements.[22]

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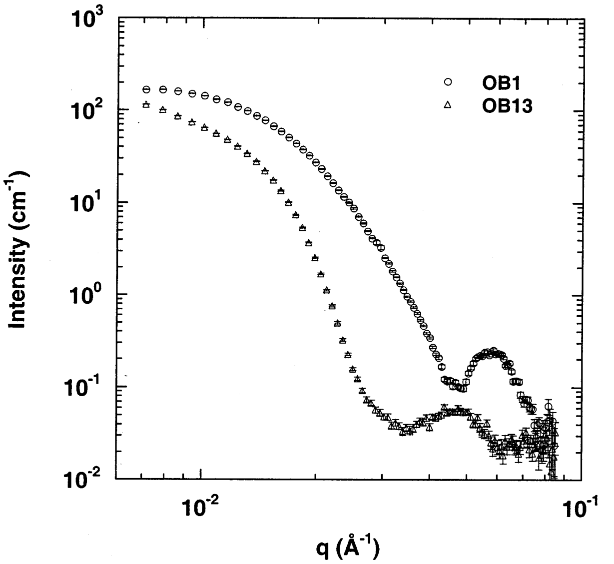

Figure 1. SANS patterns measured at 20 °C from 1.0 wt % spherical micelles of OB1 (circles) and OB13 (triangles) in D_2O.

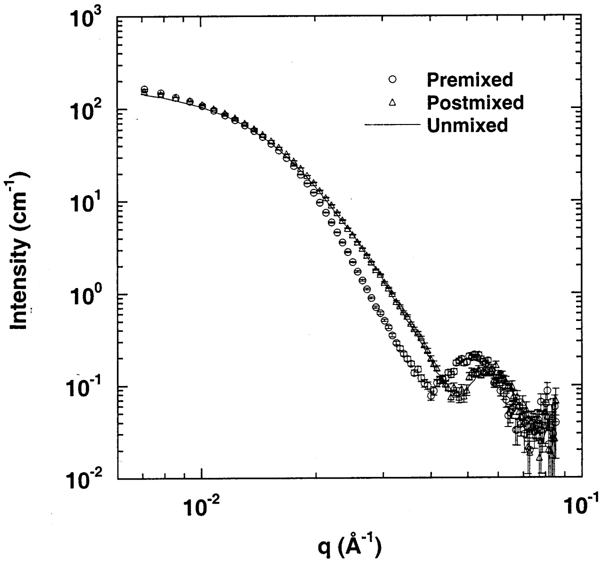

Figure 2. SANS data obtained at 20 °C from 1.0 wt % premixed (circles) and postmixed (triangles) OB1/OB13 (1:1) solutions in D_2O. The solid curve represents the anticipated SANS profile for no component exchange upon postmixing and was calculated by taking an average between the OB1 and OB13 intensities in Figure 1.

Results and Discussion

In our earlier work,[23] the detailed structures of the deuterated micelles of OB13 (spherical) and OB10 (cylindrical) have been determined using contrast variation SANS, resulting in micelle radii (R_{mic}) of 29 and 21 nm, respectively. It should be noted that the q range of our present investigation is connected to the structural features on a length scale of the order of $\sim 1/R_{\mathrm{mic}}$, and the form of the scattering intensity from the dilute (i.e., 1.0 wt %) micelle solutions is dominated by the oscillatory behavior arising from the cross-sectional intramicellar form factors.

Figure 1 illustrates the SANS profiles individually obtained for 1.0 wt % solutions of the spherical micelles of OB1 and OB13. In Figure 2, we compare the scattering patterns between 1.0% premixed and postmixed OB1/OB13 (1:1) solutions. The SANS measurements were performed 8 days after the preparation of the postmixed sample. We note that the data measured from the premixed micelles correspond to the contrast condition in the postmixed case at infinite time (I_∞). Also, a realistic postmixed intensity profile at initial time (I_0) can be calculated simply by taking an arithmetic mean between the individual OB1 and OB13 intensities (Figure 1) due to the fact that the structure factor has a negligible influence on the intensity distribution for the q range studied. As displayed in Figure 2, the two curves from the premixed and postmixed samples are unquestionably distinct, and it should be noted that, from a sensitivity point of view, this experimental probe is properly suited to our purpose of investigating the quantitative details of the exchange kinetics in the sense that the statistical uncertainties of the individual postmixed data points are typically less than a few percent of the intensity differences, $|I_\infty - I_0|$, at intermediate q. Remarkably, we found that the construction of the unmixed (i.e., zero time) scattering (shown as a solid curve in Figure 2) virtually reproduces the SANS data obtained from the 8 day old postmixed OB1/OB13 solution. On the basis of the measured uncertainties in the postmixed data, we anticipate that exchange of at least a hundredth of the original component population would have to occur for it to be detected in our experiments. Together with our prior cryo-TEM experimentation with these materials, it is not unreasonable to expect that the intermicellar equilibration time can be of the order of many years.[24,25] Figures 3 and 4 indicate that cylindrical micelles of OB8 and OB10 are also in an amphiphically frozen state, similar to the situation for the spherical micelles of OB1 and OB13.

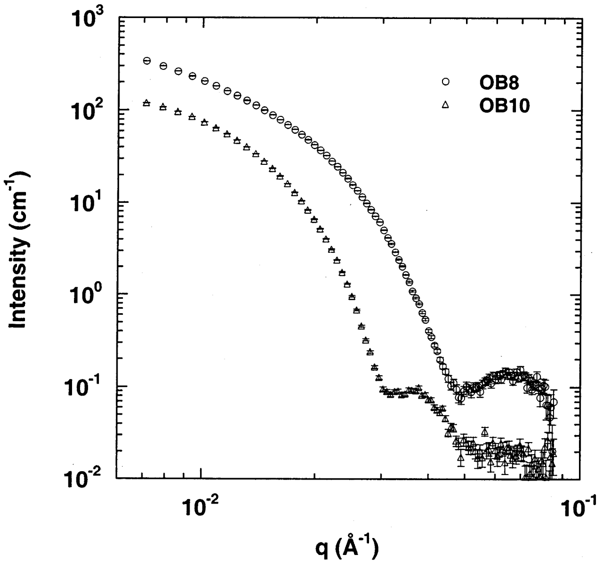

Figure 3. SANS patterns measured at 20 °C from 1.0 wt % cylindrical micelles of OB8 (circles) and OB10 (triangles) in D_2O.

Prior studies on the unimeric exchange kinetics suggested that the residence time of a single amphiphile in its micelles rises exponentially with the free energy of micellization,[26] and this, on the basis of published values for the standard free energies of micelle formation ($G_{\mathrm{mic}}(-CH_2-) \approx -1.15k_BT$ and $G_{\mathrm{mic}}(-CH_2-CH_2-O-) \approx +0.32k_BT$ at 25 °C, where k_B is the Boltzmann constant and T is temperature),[27] leads one to anticipate that the residence time, for instance, for OB1 with about 128 ethylene oxide and 184 methylene equivalent units

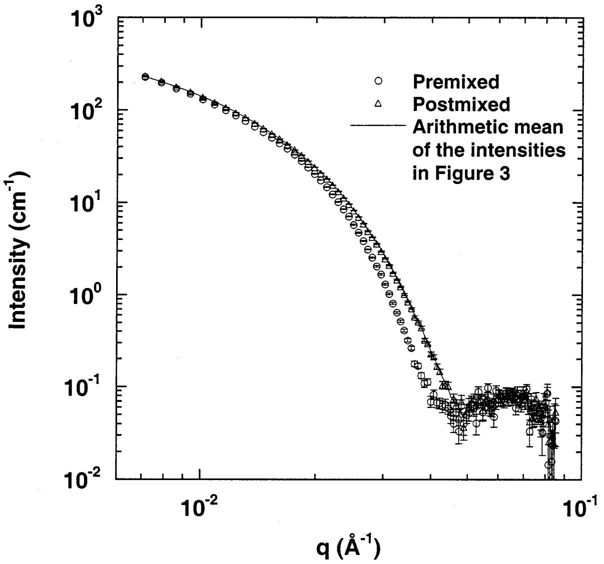

Figure 4. SANS data obtained at 20 °C from 1.0 wt % premixed (circles) and postmixed (triangles) OB8/OB10 (1:1) solutions in D_2O. The solid curve represents the expected SANS profile for no exchange upon postmixing.

may be unmeasurably large. Though other associative mechanisms (such as micelle fusion/fission[28−30] or even concerted cooperative exchange[4,26,30,31]) for redistribution of the amphiphilic molecule have in general been proposed, the results indicate that the level of amphiphilicity defies any of the mechanisms in our cases.

Concluding Remarks

We studied the kinetics of component exchange between micelles of poly(ethylene oxide)−polybutadiene (PEO−PB) block copolymers by using a combination of deuterium labeling and time-resolved SANS techniques. Measurements performed up to 8 days after the preparation of the samples indicate that the micelle structures initially formed upon dissolution are completely locked in due to the effect of strong amphiphilicity. Although the present investigation deals only with spherical and cylindrical micellar geometries, it is reasonable to anticipate that this effect is also operative in vesicular systems where the amphiphiles have relatively low hydrophilic contents; however, it would be much harder to quantify the vesicle dynamics. These concepts play an important role in understanding the unique properties of PEO−PB solutions we have documented (e.g., size/shape nonuniformity for vesicles[24] and nonliving polymer-like viscoelasticity for cylinders[32,33]).

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