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Notes

Photophysical Characterization of Conformational Rearrangements for Amphiphilic 6-Arm Star Block Copolymers in Selective Solvent Mixtures

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Introduction

Block copolymers are well-known to form supermolecular self-assembled structures, or micelles, in a selective solvent that is thermodynamically good for one block and poor for the other.[1,2] The architecture of polymer micelles depends on temperature, concentration, solvent, and the molecular weight of the copolymer.[3] These materials are of interest because of their fundamental structure−property relationships,[4,5] e.g., rheology and interaction with neighboring molecules, and applications as solubilizers, e.g., solubilizer of pyrene in water[4] and in drug delivery.[6] At concentrations above the critical micelle concentration, linear block copolymers adopt an architecture in which the poorly solvated block minimizes its volume in the center of micelle with the core being surrounded by a shell of swollen chains. The multimolecular structure is not static, however; the polymer molecules are in dynamic equilibrium. For example, by changing the polarity of the solvent, inverse structures could be formed, or the micelle could be destroyed. Furthermore, linear block copolymer micelles are often polydisperse, which means that the cores are not uniform in size and there may be a chemical heterogeneity between the inner block and the outer block.[7]

To prevent this kind of dynamic exchange, amphiphiles that are tethered to a multifunctional core, such as dendritic macromolecules[8,9] and heteroarm star copolymers,[10−12] have been synthesized and investigated as unimolecular micelles. Their structures closely resemble those of traditional micelles except for the tethering to the core, and the structures remain intact as solvent and concentration are varied. Voulgaris et al.[10] showed that the star copolymer micelles exhibit a smaller corona thickness in which chains are less stretched, and there is a lower aggregation number than for micelles of linear copolymers.

In our previous work,[13] we have used light scattering and ^{1}H NMR to show that 6- and 12-arm star copolymers form unimolecular micelles and respond to the polarity of solvents by selective expansion and collapse. In this paper, we examine this change in molecular geometry using pyrene fluorescence. We used pyrene-tagged PMMA as a hydrophobic inner block attached to a 6-arm initiator and PAA as a hydrophilic outer block, as shown in Figure 1. We also investigated the inverse architecture in which PAA is the inner block and pyrene-labeled PMMA is the outer block.

Pyrene has been widely used as a probe of structure and dynamics in macromolecular systems[14] because of its long excited-state lifetime and spectral sensitivity to the surrounding medium.[15] Excimer fluorescence measured by the excimer-to-monomer ratio (I_e/I_m) provides highly localized information because the excimer complex is only formed when aromatic rings closely approach each other within 4−5 Å.[16] In addition, the ratio of the first vibronic emission peak to the third emission peak (I_1/I_3) yields information about the polarity of the environment around the chromophore,[15,17] since polar solvents enhance the first peak. Thus, using pyrene, we can simultaneously study the distribution of pyrene within the micelle and the polarity of the micelle interior, which gives information on conformational rearrangement for amphiphilic star block copolymers in selective solvent mixtures.

Experimental Section

Materials. The 6-arm initiators were synthesized as described in a previous paper.[18] To prepare pyrene-labeled MMA, 1 g (3.6 mmol) of pyrenebutanol was suspended in ca. 10 mL of methylene chloride. After addition of 1 g (9 mmol) of triethylamine, 1 mL (9 mmol) of methacryloyl chloride was added dropwise. The reaction mixture was stirred overnight at room temperature, and after filtration the product was purified by flash chromatography using hexane/ethyl acetate (95:5).

To produce the 6-arm-PMMA(Py)-*b*-PAA, we utilized atom transfer radical polymerization (ATRP) in two consecutive polymerizations with CuBr/4,4′-di(5-nonyl)2,2′-bipyridine. A 6-arm PMMA(Py) was synthesized by bulk copolymerization of MMA with pyrene-tagged MMA. The molecular weight (M_n = 11 000 g/mol) and the amount of pyrene monomer incorporated in the copolymer (7.5%) were determined by ^{1}H NMR spectroscopy. Note that molecular characteristics listed in parentheses are for all six arms. In accordance with the controlled polymerization characteristics of ATRP, the polydispersity of this copolymer is low (1.15). Samples taken at a low conversion in the polymerization process possess the same composition as the final copolymer, confirming that both monomers are of similar reactivity and that the pyrene tags are distributed randomly in the copolymer. We used 6-arm PMMA(Py) for the subsequent polymerization of *tert*-butyl acrylate followed by the hydrolysis of the ester functionality

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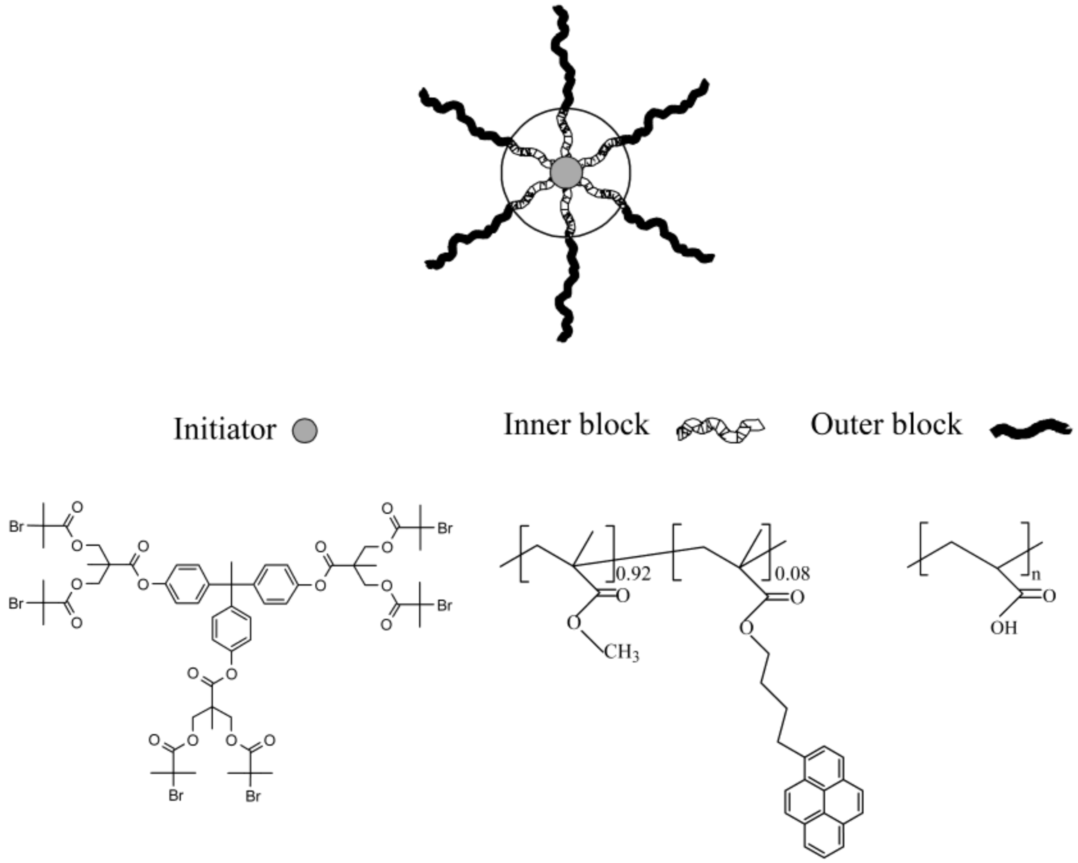

Figure 1. Scheme for the 6-arm-PMMA-*b*-PAA with pyrene probe attached within the PMMA block. The inverse architecture was also examined.

with trifluoroacetic acid. This reaction was monitored by the disappearance of the *tert*-butyl ester signal in the ^{1}H NMR spectrum. We were thus able to obtain starlike block copolymers with a PAA hydrophilic block (36 000 g/mol) and PMMA hydrophobic block with a polydispersity of 1.3. The inverse architecture with PAA (6000 g/mol) as the inner block and PMMA (30 000 g/mol) and pyrene labels (6.5%) as the outer block was also synthesized, and the polydispersity was 1.27.

Fluorescence Measurement. To examine the behavior of micelles in selective solvent mixtures, we prepared 1×10^{-4} M (per 6-arm star) solutions using mixtures of chloroform and methanol. The fluorescence emission spectra were taken on an Edinburgh FS900CDT fluorometer with a 450 W steady-state xenon arc lamp and front-face excitation. The excitation wavelength was at 343 nm, corresponding to the ^1L_a band of the pyrene ring, and the spectra were collected from 360 to 700 nm. Generally, there are two kinds of emission bands. The five monomer bands are characteristic of the pyrene vibronic structure: three distinct peaks (376, 396, 418 nm) and two shoulders (381, 386 nm).[15] In addition, the excimer emission appears as a broad, structureless band around 480 nm. Two spectral parameters are of interest: the excimer (around 480 nm) to monomer (376 nm) intensity ratio (I_e/I_m) and the ratio of intensities of the first (376 nm) and third (386 nm) monomer bands (I_1/I_3).

Results and Discussion

The results for 6-arm-PMMA(Py)-*b*-PAA and 6-arm-PAA-*b*-PMMA(Py) are quantified in Figure 2, where the change in I_e/I_m is plotted against the volume fraction of chloroform in the solvent mixtures. The 6-arm block copolymers were not soluble in the solvent mixtures that were bad solvents for the outer blocks since the molecular weights of the outer blocks for both systems are higher than those of the inner blocks in each case; therefore, the chloroform volume concentration in mixtures beyond 60% chloroform for 6-arm-PMMA(Py)-*b*-PAA and below 30% chloroform for 6-arm-PAA-*b*-PMMA(Py) were not investigated. The decrease of I_e/I_m with addition of chloroform indicates a decrease in the local concentration of pyrene, which corresponds to the expansion of PMMA. This phenomenon is consistent for both star block copolymers.

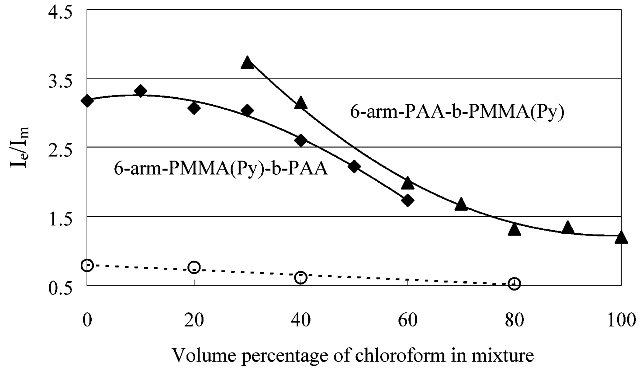

Figure 2. Excimer-to-monomer intensity ratio for 6-arm-PMMA(Py)-*b*-PAA (◆) and 6-arm-PAA-*b*-PMMA(Py) (▲) in chloroform/methanol mixtures with varying fractions of chloroform. Upon the addition of chloroform, the PMMA block expands, and consequently, the distance between pyrene groups increases, leading to the decrease of excimer fluorescence. The dotted line connecting the open circles indicates the I_e/I_m ratio for 1-pyrenebutyric acid.

Since the chloroform and methanol have different polarities in the chloroform/methanol mixture, we examined 1-pyrenebutyric acid over the range from 0 to 80% chloroform as a reference experiment in an attempt

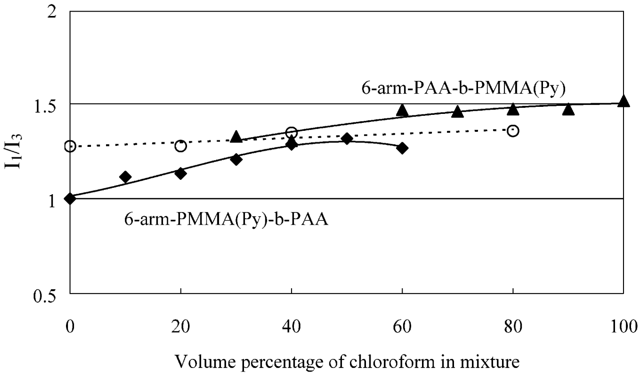

Figure 3. First-to-third peak intensity ratio for 6-arm-PMMA(Py)-*b*-PAA (◆) and 6-arm-PAA-*b*-PMMA(Py) (▲) as a function of volume percentage of chloroform in mixtures with methanol. As the volume percentage of chloroform increases, the I_1/I_3 ratio increases due to the PMMA block expansion. The dotted line connecting open circles shows the I_1/I_3 ratio for 1-pyrenebutyric acid, indicating that the solvent polarity effect on pyrene fluorescence is relatively small.

Table 1. Solubility Parameters for PMMA, Chloroform, and Methanol

	δ_d	δ_p	δ_h	δ_{total}
PMMA	18.6	10.5	7.5	22.6
chloroform	11.0	13.7	6.3	18.7
methanol	11.6	13.0	24.0	29.7

to isolate the fluorescence parameters from the solvent polarity effect. As shown by the dotted line in Figure 2, I_e/I_m slightly decreases as the fraction of chloroform increases. The difference between the I_e/I_m ratio of 1-pyrenebutyric acid and those of the micelles is mainly due to the local concentration of pyrene. With the approximate hydrodynamic radius of 7 nm,[13] the calculated local concentration of pyrene in one micelle is 0.56 g/L in the case of 6-arm-PMMA(Py)-*b*-PAA, while the concentration of the 1-pyrenebutyric acid solution is 0.029 g/L. Thus, the highler local concentration of pyrene in the micelles leads to the higher I_e/I_m values. However, while the local concentration of pyrene differs by a factor of 20, the I_e/I_m value changes by only a factor of 5. For intermolecular excimer formation, the I_e/I_m ratio is proportional to pyrene local concentration, which was not consistent with this result. This is attributed to the estimated local concentration. Note that the hydrodynamic radius used for this calculation is for the same 6-arm star block copolymer with a similar molecular weight but does not contain the pyrene tags. With the pyrene tags, the hydrodynamic radius would be larger than 7 nm, possibly leading to a lower local concentration of pyrene in a micelle. Another possible factor for the difference is diffusion effects on excimer formation in the constrained geometry of PMMA in the presence of methanol.

Figure 3 shows the I_1/I_3 intensity ratios of two 6-arm star block copolymers and 1-pyrenebutyric acid in terms of volume percentage of chloroform in mixtures. The I_1/I_3 ratio of 1-pyrenebutyric acid shows a slight increase as the volume fraction of chloroform increases due to the solvent polarity. However, the change in this ratio is relatively small, ranging from 1.28 to 1.35, which is much less than the changes observed in the star block copolymers ($\Delta \sim 0.5$). This indicates that the effect of the solvent polarity is minimal, and the changes of fluorescence parameters are mainly caused by the geometry changes[19] of the star block copolymers in selective solvents. Table 1 shows the solubility parameters for PMMA, chloroform, and methanol.[20] The polar components in the solubility parameters of chloroform and methanol are similar, while that for PMMA has a smaller value. Therefore, the I_1/I_3 ratio of 1-pyrenebutyric acid, which feels the solvent polarity, shows only small changes over the range of chloroform in the mixture.

The 6-arm-PMMA(Py)-*b*-PAA shows an increase in the polarity to a final plateau value as the volume fraction of chloroform increases in Figure 3. Also, the 6-arm-PAA-*b*-PMMA(Py) shows an increased I_1/I_3 ratio with the addition of chloroform, which means that the polarity around pyrene chromophores increases. As the PMMA block expands, the polarity around the pyrene tags increases because the pyrene faces polar environment of PMMA rather than nonpolar pyrene. This result is again consistent with the extension of PMMA upon addition of chloroform. In the star block copolymers, the pyrene groups detect the polarity of the PMMA environment instead of the solvent polarity, especially in the case of 6-arm-PMMA(Py)-*b*-PAA because pyrene is more *shielded* from solvent when it is located in the core than when in the shell; therefore, the I_1/I_3 of 6-arm-PMMA-(Py)-*b*-PAA is smaller than that of 1-pyrenebutyric acid. In the 6-arm-PAA-*b*-PMMA(Py) system, when the PMMA block fully expands in 100% chloroform solvent, pyrene responds to the solvent polarity; therefore, the I_1/I_3 of 6-arm-PAA-*b*-PMMA(Py) might be expected to approach the value of 1-pyrenebutyric acid, which was not observed. This is attributed to the fact that there can be a subtle effect on the polarity due to the carboxylic acid functional group in 1-pyrenebutyric acid.

As shown in Figures 2 and 3, there are differences in the I_e/I_m and I_1/I_3 values of the two kinds of block copolymers in the middle range of chloroform fraction. These slight differences can be attributed to the different amount of pyrene incorporated in each 6-arm block copolymer, which leads to the different values of the I_e/I_m and I_1/I_3 ratios.

We have assumed here that the PMMA block expands or shrinks linearly. Gitsov et al.[21] proposed a different mechanism for their hydrophilic 4-arm poly(ethylene glycol) star polymers having hydrophobic dendritic blocks (with a pentaerithritol core), in which the inner block wraps around the outer block. However, this architecture is unlikely for our system because the molecular weights of the inner blocks are much smaller than those of the outer blocks for both systems.

Conclusions

We have shown that the structures formed from amphiphilic starlike copolymers depend on the solvent, and their conformations are observed using pyrene probe fluorescence. The decrease of excimer concentrationand the increase of polarity around pyrene with addition of chloroform in 6-arm-PMMA(Py)-*b*-PAA and 6-arm-PAA-*b*-PMMA(Py) indicate the expansion of PMMA. Although fluorophores were incorporated only into the PMMA block, we have demonstrated that this pyrene fluorescence is efficient for the detection of the conformation of the star block copolymers in the selective solvent mixtures.

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