

## Studies on Micellization of a Polystyrene-*b*-poly(acrylic acid) Copolymer in Aqueous Media by Pyrene Fluorescence

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**Abstract:** Pyrene probe and TEM have been employed to investigate the behavior of a polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) copolymer in aqueous solution. A significant annealing temperature effect on the  $I_1/I_3$  ratio of pyrene was observed and was interpreted in terms of the morphological change of micellar cores. Annealing at a temperature higher than the glass transition temperature ( $T_g$ ) of PS leads to densification of the hydrophobic core.

**Keywords:** Polystyrene-*b*-poly(acrylic acid), micelle, fluorescence, pyrene.

The aggregation of amphiphilic block copolymers is a crucial phenomenon that controls various applications, and has been extensively treated in the literature<sup>1-3</sup>. Pyrene is a widely used fluorescence probe for the relative intensities of the vibrational fine structure (five bands) of its fluorescence spectra have been found to be sensitive to the polarity of its environment, the so-called Ham effect<sup>4</sup>. We report the studies of the aggregation properties of a PS-*b*-PAA copolymer using pyrene as fluorescence probe.

### Experimental

The block copolymer polystyrene-*b*-poly(*tert*-butyl acrylate) (PS-*b*-PtBA) was obtained from Polymer Source Inc. PS block:  $M_n=66900$ ,  $PI=1.03$  (Polydispersity Index); PtBA block:  $M_n=120000$ ,  $PI=1.05$ . The hydrolysis of the PS-*b*-PtBA can be performed efficiently in a very mild condition. <sup>1</sup>H-NMR and IR spectra indicate that the block copolymer of PS-*b*-PtBA can be completely hydrolyzed<sup>5</sup>. Pyrene (99% purity) was purchased from Aldrich and was further recrystallized three times from ethanol. Water was deionized and distilled twice before use.

Aqueous solutions of the block copolymer PS-*b*-PAA were prepared in water. Calculated amounts of pyrene were added to aqueous solutions of the block copolymer contained in small ampules. The pyrene concentration was  $1.67 \times 10^{-7}$  mol/L in all samples. The ampules were sealed at temperature below ambient. The solutions were annealed at 90°C and 105°C for 48 h to achieve equilibrium, respectively.

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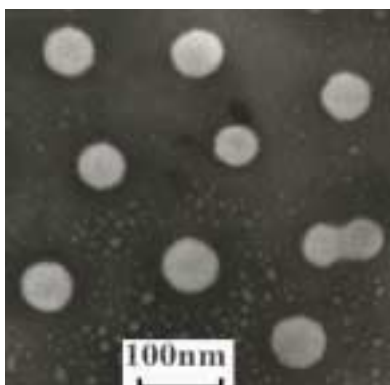
Transmission Electron Microscopy (TEM) was performed on a Phillips EM 400 microscope operating at an acceleration voltage of 80 kV. Samples were deposited from dilute solutions of water onto copper EM grids. Water was allowed to evaporate from the grids at atmospheric pressure and room temperature. Finally, the PAA domain of the samples on the grids was stained by phospho-tungstic acid. The size of the aggregates was measured directly from prints of the microscope negatives.

A SPEX FL 212 Spectrofluorometer was used. The spectra were recorded in the front face geometry in 1.0 nm steps, integrating counts for 0.1 s at an excitation wavelength of 335 nm. The slit widths were 1.7 nm for all measurements. Each spectrum was obtained by averaging three scans. The experiments were conducted at 25°C.

### Results and Discussion

TEM picture is presented in **Figure 1**, which illustrate the morphologies of the micelles formed by our block copolymer in water. The block copolymer concentration was *ca.*  $1.0 \times 10^{-5}$  g/mL.

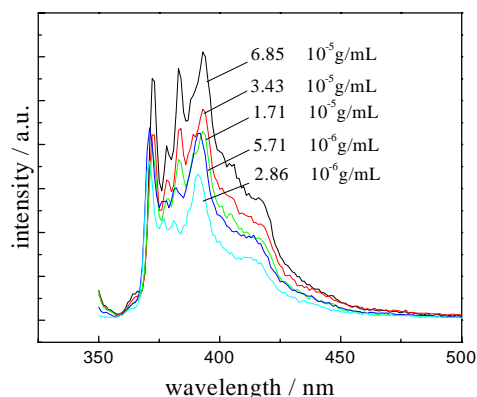
**Figure 1** TEM picture of micelles from the block copolymer PS-b-PAA



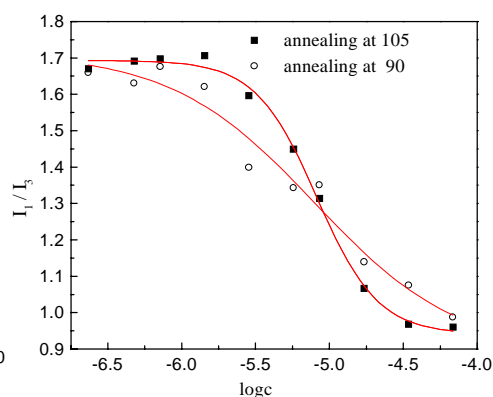
The aggregates are readily observable by TEM because of the high  $T_g$  of polystyrene, and their sizes are measurable from the prints. Our results indicated that the PS-b-PAA copolymer underwent self-assembly forming spherical micelles. As shown in **Figure 1**, it could be clearly distinguished from the TEM images of the samples stained by phospho-tungstic acid that the micelles formed in water were regular with PS block forming the cores, which were not stained and show white color as shown in **Figure 1**.

In the present study, the pyrene probe was used to monitor the formation of micelles with increasing concentration of PS-b-PAA copolymer. Pyrene may report the micropolarity of its experiencing environment through the ratio  $I_1/I_3$ , the intensities, respectively, of the first and third bands in the pyrene fluorescence spectra. This ratio varies from 1.9 in water to 0.95 in a PS film<sup>6</sup>. Fluorescence spectra of the block copolymer samples of various concentrations are shown in **Figure 2**. The spectrum is

**Figure 2** Fluorescence spectra of pyrene in aqueous PS-b-PAA solutions with various concentration



**Figure 3** Plots of  $I_1/I_3$  ratio of pyrene fluorescence spectra as a function of polymer concentration



typical of pyrene fluorescence. **Figure 3** is the plot of the  $I_1/I_3$  intensity ratio of pyrene spectra as a function of concentration of PS-b-PAA copolymer aqueous solutions. The magnitude of the  $I_1/I_3$  ratios of pyrene spectra can be classified as having values characteristic of three regions. In region 1, at low polymer concentration (less than  $2.0 \times 10^{-6}$  g/mL), the values of  $I_1/I_3$  ratio are those expected if the probe resides mainly in the aqueous phase or in a highly polar environment. Thus, the polymer structure is evidently unable to bind to or accommodate a hydrophobic probe in this region. In region 2, at still higher concentration (*ca.*  $0.2 \times 10^{-5}$  ~  $2.0 \times 10^{-5}$  g/mL), the  $I_1/I_3$  ratio decreases sharply as the polymer concentration increases. The sharp decrease is attributed to the formation of micelles composed of a hydrophobic core into which pyrene partitions preferentially. This change reflects the onset of micelle formation and the partitioning of the pyrene between the aqueous and micellar phases. The probe pyrene is being drawn into a hydrophobic environment. One approach to the determination of cmc is to take the  $I_1/I_3$  ratios and fit the  $I_1/I_3$  ratio vs  $\log c$  plot to a sigmoidal curve. The fitted equations are as follows :

$$I_1/I_3 = 0.820/[1+\exp(\log c+5.099)/0.485] + 0.888 \quad (\text{annealing at } 90^\circ\text{C})$$

$$I_1/I_3 = 0.852/[1+\exp(\log c+5.086)/0.207] + 0.941 \quad (\text{annealing at } 105^\circ\text{C})$$

By minimizing the second derivatives, the cmc values of  $7.96 \times 10^{-6}$  g/mL and  $8.20 \times 10^{-6}$  g/mL for  $90^\circ\text{C}$  and  $105^\circ\text{C}$  annealing were obtained, respectively. In region 3, at still higher polymer concentration ( $>2.0 \times 10^{-5}$  g/mL), we find that the  $I_1/I_3$  intensity ratio is 0.96 and comparable to that for pyrene in film PS. Almost all of the pyrene molecules are partitioned into the hydrophobic polystyrene cores.

**Table 1**  $I_1/I_3$  ratio for the PS-b-PAA samples at different concentration and annealing temperature

Concentration (g/mL) $\times 10^6$	68.5	34.3	17.1	8.57	5.71	2.86	1.43	0.71	0.48	0.24
$I_1/I_3$ (90°C)	0.9872	1.0755	1.1397	1.3507	1.3425	1.3988	1.6205	1.6736	1.6799	1.6591
$I_1/I_3$ (105°C)	0.9601	0.9679	1.0664	1.3138	1.4497	1.5965	1.7062	1.6980	1.6914	1.6904

The  $I_1/I_3$  ratio has been measured for the PS-*b*-PAA copolymer samples annealing at 90°C and 105°C as a function of concentration, respectively. As shown in **Table 1** and **Figure 3**, a significant effect of annealing temperature on the  $I_1/I_3$  ratio was observed. As shown in **Figure 3**, it is obvious that the  $I_1/I_3$  ratio drops more steeply and the transition region becomes narrower for the samples annealed at 105°C than at 90°C. Actually, in transition region below the calculated cmc, the  $I_1/I_3$  ratio of pyrene for 90°C annealing decreases earlier than that for 105°C annealing. On the contrary, above the cmc, the  $I_1/I_3$  ratio of pyrene for 105°C annealing decreases faster than that for 90°C annealing. These results provide compelling evidences for the annealing temperature effect on  $I_1/I_3$  ratio. Fluorescence intensity in a micellar solution with solubilized pyrene is a sum of contributions from pyrene molecules in cores, shells, and aqueous phase. Here we may ascribe this temperature effect to two factors. The first one is the equilibrium of partitioning of pyrene molecules between the aqueous and micellar phases. Below the cmc, the concentration of the polymer aggregates is very low and the partition equilibrium is the major effect on the values of  $I_1/I_3$  ratio. For the annealing temperature above the PS glass transition temperature (*ca.* 100°C), the PS block of pre-micellar aggregates can form more compact micellar cores in aqueous solution than for annealing temperature below the PS glass transition temperature. As a result, below the cmc, the aggregates *via* 90°C annealing is looser than the aggregates *via* 105°C annealing, so more pyrene molecules partition into aggregates annealed at 90°C than those into the aggregates annealed at 105°C. Thus, below the cmc the  $I_1/I_3$  ratio of pyrene for 90°C annealing decreases earlier than that for 105°C annealing. Secondly, in region far above the cmc, almost all of the pyrene molecules are located inside the micelles and the  $I_1/I_3$  ratio of pyrene is affected predominantly by the polarity of the microenvironment. After 105°C annealing, PS-*b*-PAA diblock copolymer forms micelles with more hydrophobic cores. The first vibrational band of pyrene is symmetry forbidden and its intensity depends on interactions with the microenvironment. As a result, above the cmc, the  $I_1/I_3$  ratio of pyrene for 105°C annealing decreases faster than that for 90°C annealing. For all of these reasons, the variation of  $I_1/I_3$  with the polymer concentration can be explained quantitatively in terms of the partitioning of pyrene molecules and the hydrophobicity of the polymer micelle phase.

### Acknowledgment

We wish to express our great thanks to the National Natural Science Foundation of China (Grant No.29574165, 29928003, 29874019), Key Science and the Natural Science Foundation of Tianjin (013604011).

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Received 18 March, 2002