Novel Approach to Synthesizing Hydrophobically Associating Copolymer Using Template Copolymerization: The Synthesis and Behaviors of Acrylamide and 4-(ω-Propenoyloxyethoxy) Benzoic Acid Copolymer

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Hydrophobically associating copolymers of acrylamide (AM) with a small amount of 4-(ω-propenoyloxyethoxy) benzoic acid (PEBA, <2.5%) were synthesized by template copolymerization in the presence of poly-(allylammonium chloride) (PAAC) as a template in an aqueous medium. These template copolymers exhibited remarkable thickening properties due to the effective hydrophobic association, which were similar to those copolymers with a multiblock structure obtained by the micellar process. The pH of the reaction medium and the molecular weight of the template strongly influenced the thickening properties of the products. In the experimental range, the higher the PEBA content, the larger the thickening capacity of these hydrophobic copolymers. The aggregate behaviors of these copolymers were studied by fluorescence, transmission electron microscopy (TEM), and light scattering techniques. The apparent critical interpolymer aggregate concentration (cac) of the copolymer solution was about 0.5 g/dL. As the concentration of the copolymer became higher than the cac, the aggregates changed their morphology from small hollow spheres to big flower-shaped aggregates. All the above results indicated that the template copolymerization gave access to a very simple and powerful means for the preparation of hydrophobically associating copolymers and other functional polymer materials.

1. Introduction

Hydrophobically associating copolymers consisting of a water-soluble polymer and a small number of hydrophobic groups have recently become the subject of extensive research.[1−10] In aqueous solution, above a certain polymer concentration, intermolecular hydrophobic interactions lead to the formation of polymolecular association. As a result, these copolymers exhibit thickening properties far higher than those of the homopolymers with the same molecular weight. These polymers have many potential applications in such diverse fields as enhanced oil recovery,[11,12] mobility control agents,[13,14] formulation thickeners of coatings,[15,16] and frictional drag reduction.[17,18]
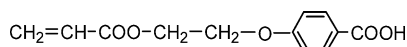
In general, the water-soluble hydrophobically associating copolymers were prepared by a free-radical polymerization process in an aqueous solution. However, hydrophobic monomers are insoluble in water. A variety of techniques have been suggested to overcome this problem: (i) a "micellar" process in the presence of a surfactant, (ii) a "homogeneous" process in a miscible cosolvent, and (iii) a "heterogeneous" process without additive to solubilize the insoluble monomer. Candau et al.[19] investigated the influence of the three methods on the properties of acrylamide and ethylphenlacrylamide copolymers. The properties in dilute and semidilute solutions indicated that copolymers obtained by micellar copolymerization exhibited improved thickening properties, while the other two behaved like homopolyacrylamide and hydrophobic interactions did not occur significantly. These differences were directly related to the copolymer microstructure, that is, to a random or blocky distribution of the hydrophobic units. It is well-known that the initial monomer segregation affected the distribution of hydro-phobe in the copolymer. In contrast to the homogeneous and heterogeneous processes, in the micellar process, hydrophobic monomer was solubilized within surfactant micelles, while hydrophilic monomer was dissolved in the aqueous solution bulk. In the process of polymerization, when the growing macroradical headgroup encountered a monomer swollen micelle, it added several hydrophobic molecules inside the micelle to form a short hydrophobic block and then added more hydrophilic molecules in the aqueous phase to form a long hydrophilic block. As the reaction continued, the above steps were repeated again and again so the products were multiblock.

Up to now, the micellar process has been the most effective method for synthesizing hydrophobically associating copolymers. However, this process requires a large amount of surfactant, which accretes potential difficulties in the commercial application of the products.

On the other hand, one of the most effective methods that could be applied to obtain copolymers with multiblock structure is template copolymerization. Several authors have done many works[20−24] to explain the template copolymerization process. It was found that the template copolymer exhibited a longer sequence distribution of monomers than that of traditional copolymers. In our previous papers,[25,26] template copolymerization of acrylamide and acrylic acid using poly(allylammonium chloride) (PAAC) as the matrix was introduced and the influence of the template on the reaction kinetics and the microstructure of the products was studied. Due to the presence of the template, the sequence length of acrylamide and acrylic acid in the copolymer chains was much longer than that of traditional copolymers obtained without a template; in other words, the microstructure of the products exhibited multiblocklike characteristics.

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Synthesizing Hydrophobically Associating Copolymer

J. Phys. Chem. B, Vol. 109, No. 47, 2005 **22251**

$$CH_2=CH-COO-CH_2-CH_2-O-\langle\bigcirc\rangle-COOH$$

Figure 1. Structure of hydrophobic monomer.

TABLE 1: Structural Parameters of the Copolymers

sample	PEBA/PAAC	PEBA content × 100	$M_w \times 10^{-6}$
PAM	0	0	7.23
HP	0	0.75	7.30
MP	0	0.75	6.83
TP-1	1	0.15	5.95
TP-2	1	0.45	6.45
TP-3	1	0.75	5.17
TP-4	1	0.90	5.01
TP-5	2	0.75	5.87
TP-6	0.5	0.75	5.36
TP-7	1	1.5	5.32

Motivated by the outcomes, we synthesized hydrophobically associating copolymers by template copolymerization. The template used here was PAAC. The hydrophobic monomer used was 4-(ω-propenoyloxyethoxy) benzoic acid (PEBA). The structure of the hydrophobic monomer is illustrated in Figure 1. The carboxyl group ensured the monomer PEBA had strong interaction with the template PAAC through electrostatic interaction.

2. Experimental Section

Materials. Acrylamide (AM) from Jiangxi Changjiu Biochemical Engineering Corporation with a purity higher than 98.5% was used as received. The template poly(allylammonium chloride) (PAAC, M_w 8000, 12 000, 30 000) and the hydrophobic monomer 4-(ω-propenoyloxyethoxy) benzoic acid (PEBA, mp 137−139 °C) were synthesized in our laboratory.[27] 2,2′-Azo-bi-(2-amidinopropane) dichloride (AIBA) was used as an initiator.

Polymer Synthesis. Template copolymers of AM and PEBA were synthesized in the presence of PAAC as a template and AIBA as an initiator. If not explained specifically, the molar ratio of PAAC to the hydrophobic monomer PEBA was 1. The experimental parameters were kept constant: the overall concentration of monomers (8 wt %), the temperature (45 °C), the pH of the reaction medium (if not explained specifically, the pH was about 6.9), and the concentration of initiator (AIBA at 0.2 wt % related to the total monomer feed). The polymerization reactions were conducted to exceed 90% (about 15 h). The separation of the resulting copolymers from the template was performed as described in a previous paper.[26]

For reference, homopolyacrylamide (PAM) and copolymer in the absence of template were prepared under identical experimental conditions. The experiment with the micellar process was conducted under the same conditions but with sodium dodecyl sulfate (SDS) as the surfactant and a concentration of 4.8% (g/v). The product was precipitated in acetone to remove surfactant.

The polymer and copolymer samples prepared were presented in Table 1. Copolymer samples obtained by the homogeneous process, the micellar process, and the template process are distinguished by having HP for homogeneous, MP for micellar, and TP for template. The molecular weight of the template used here was 12 000.

Characterization. The molecular weights of the copolymers were determined in a capillary viscometer (Ubbelohde) at 25 °C and with 0.5 M NaCl solution.[28]

Viscosity measurements were conducted with an NDJ-1 rotational viscometer at 25 °C and a shear rate of 6 min^{-1}. Polymer solutions were prepared by dissolution of the samples in deionized water at room temperature in the concentration range 0.1−1.5 g/dL and stood for 24 h before measurement.

Steady-state fluorescence measurements were carried out with a Hitachi F-4500 apparatus at room temperature. The slit widths for both the excitation and emission were kept at 2.5 nm. Pyrene was used as a probe. Florescence emission spectra of pyrene were measured with excitation at 340 nm. The intensity ratio of the third and first vibronic peaks (I_3/I_1) of the emission spectrum of pyrene was a good indicator of the polarity of the probe microenvironment.

Sample preparation for transmission electron microscopy (TEM) measurement was as follows: one drop of copolymer solution was put onto a carbon-coated copper grid and was stained with uranyl acetate.

The diameter distribution of copolymer aggregates in solution was measured by small angle laser light scattering on a Malvern new Zeta Nano-ZS system.

3. Results and Discussion

3.1. Polymerization Process. The hydrophobic monomer PEBA used here was ionizable and partly soluble in aqueous medium. In this template copolymerization system, PEBA formed complexes with template PAAC through strong intermolecular electrostatic interaction and the complexes were soluble in water when the pH was higher than 6.5. Under the same conditions, the neutral monomer AM was without interaction with PAAC. The polymerization process could be illustrated by the following schematic representation.

SCHEME 1: Schematic Representation of Template Copolymerization (Type I)
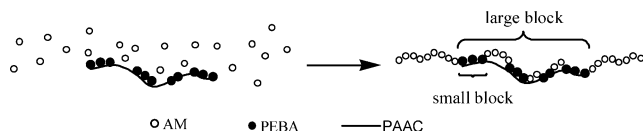
In the template copolymerization process, when a growing macroradical headgroup in the solution bulk encountered PEBA that adsorbed on template PAAC, it would initiate PEBA to polymerize along the PAAC chain to form a short hydrophobic block and then initiate AM in the solution bulk to form a hydrophilic block. These steps were repeated many times, so the structure of the products was multiblock. However, just like the products obtained by the micellar process, the exact sequence distribution was unable to be detected by NMR or IR due to the amount of hydrophobic monomers being too small. As illustrated in Scheme 1, the blocks formed by several hydrophobic monomers linked to each other directly as small blocks, while the blocks formed by several small blocks together with some AM molecules was large blocks (the block length may be equivalent to that of the template molecule). Scheme 1 only illustrated the case that one template copolymer chain contains one large block. In practice, the number of large blocks contained in one template copolymer chain was from 1 to 7 on average as the contents of hydrophobic monomer changed from 0.15 to 1.5%. The hydrophobic property of template products was related to the length of small blocks as well as to the length of large blocks. The length of small blocks was dependent on the pH of the reaction medium and the ratio of hydrophobic monomer to template. The length of large blocks was dependent on the molecular weight of the template. Under proper conditions, products with high hydrophobic property could be obtained through the template process.
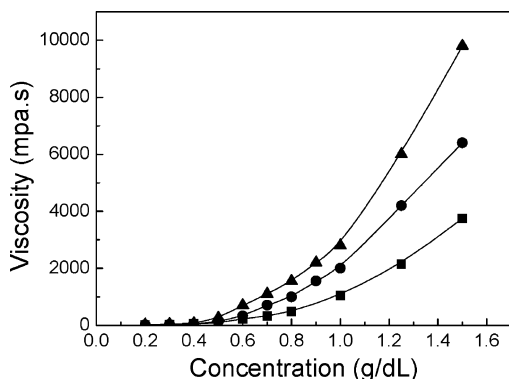
Figure 2. Viscosity as a function of copolymer concentration for samples prepared by different processes: TP-3 (▲); MP (●); HP (■).
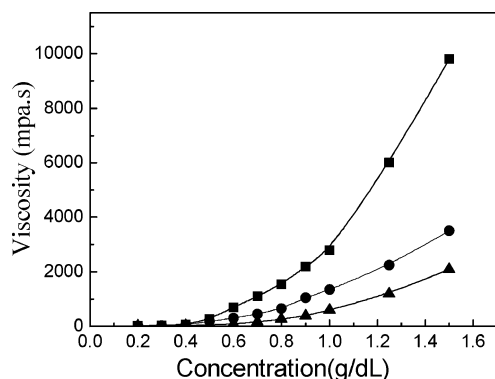

Figure 3. Viscosity as a function of copolymer concentration at different pH values: pH = 6.9 (■); pH = 8.05 (●); pH = 9.18(▲).

Figure 2 shows the relationships of viscosity and copolymer concentration for copolymers obtained by template copolymerization, micellar copolymerization, and homogeneous copolymerization, respectively. The concentration of hydrophobic monomer in feed was kept constant at 0.75 mol % (relative to AM). Comparing the viscosity thickening capacities, it was found that the template copolymer was the most efficient one. As is well-known, the viscosity thickening properties for hydrophobic copolymer are closely related to the microstructure of hydrophobic monomer units in copolymer chains. This result indicated that the template copolymer similar to the micellar copolymer exhibited a multiblock characteristic, which made it easy to form hydrophobic association. Under the experimental conditions, it seems that the thickening capacity of template copolymers was higher than that of micellar copolymers.

3.2. Influence Factors on the Template Copolymerization.
3.2.1. pH Value. The ionization degree of both the hydrophobic monomer PEBA and the template PAAC depended on the pH of the medium. As a consequence, the pH of the medium determined the interaction between PEBA and PAAC. Under strong acid or strong basic conditions, the interaction between PEBA and PAAC disappeared due to the fact that one of them was nonionized and the effect of the template on the copolymer process disappeared too.

Figure 3 illustrates the pH effect on the solution viscosity behavior as a function of copolymer concentration. The solution viscosity increased rapidly as the copolymer concentration elevated to a certain value. The most efficient thickening capacity was obtained at pH 6.9. In the pH range, both PEBA and PAAC were ionized, but as the pH increased, the ionic density of the template PAAC decreased which led to a decrease in the quantity of preadsorbed hydrophobic monomer on the template and a decrease in the length of the small block, so the thickening capacity decreased.
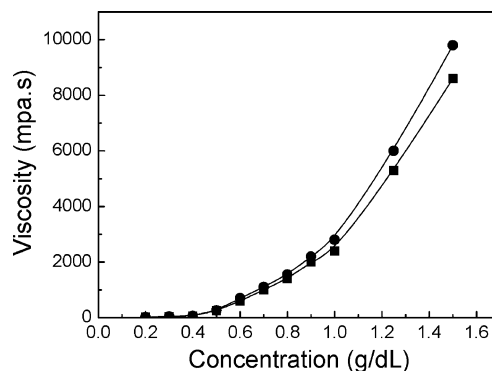

Figure 4. Viscosity as a function of copolymer concentration (TP-3): before template separation (■); after template separation (●).
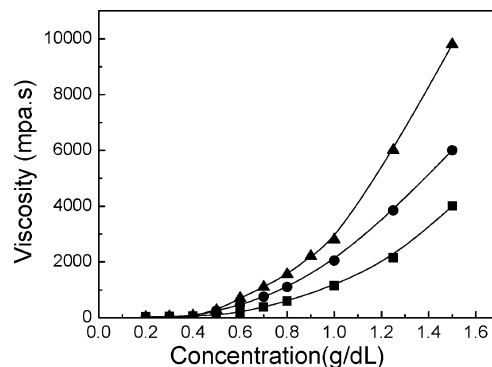

Figure 5. Viscosity as a function of copolymer concentration for copolymers with different ratios of PEBA/PAAC: TP-5 (■); TP-6 (●); TP-3 (▲).
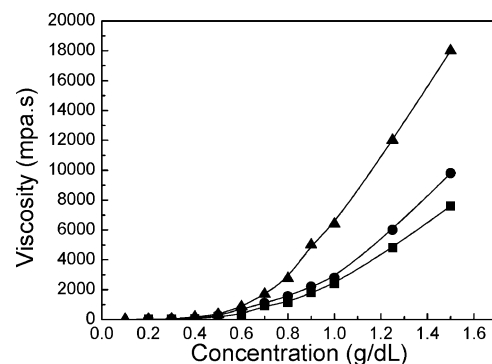

Figure 6. Viscosity as a function of copolymer concentration for different molecular weights of PAAC: 8000 (■); 12 000 (●); 30 000 (▲).

Figure 4 represents the relationships between viscosity and template copolymer concentrations before and after template separation, respectively. As illustrated, the viscosity of the copolymer solution after template separation was a little higher than that of the unseparated ones, which indicated that the increase in the viscosity with copolymer concentration was mainly due to the hydrophobic interaction between PEBA units.

3.2.2. Ratio of Hydrophobic Monomer to Template. Figure 5 illustrates the influence of the molar ratio of PEBA to PAAC on the solution viscosity as a function of copolymer concentration. In all cases, the molar ratio of the hydrophobic monomer PEBA to AM was kept constant. When the PEBA/PAAC ratio was equal to 1(TP-3), the thickening capacity was the best, which was well consistent with the type I template copolymerization mechanism. In this case, due to the strong interaction between PEBA and PAAC, most PEBA molecules were adsorbed preferentially on PAAC chains and reacted preferably
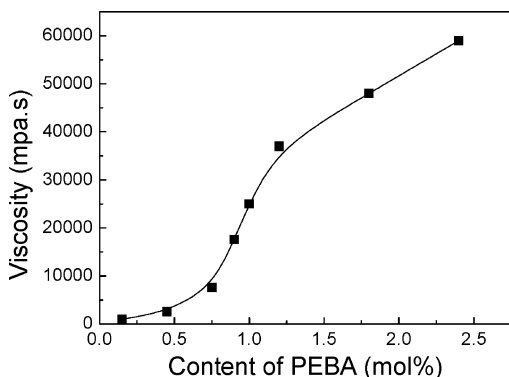
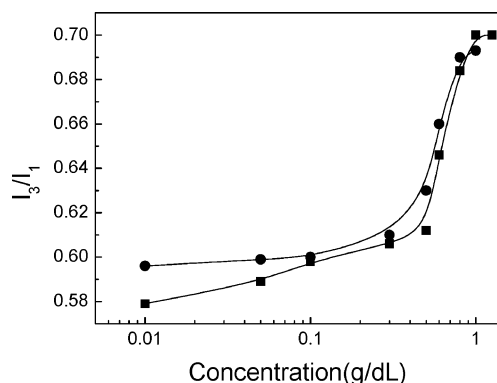**Figure 7.** Effect of PEBA content on the solution viscosity at the copolymer concentration 1.5 g/dL.

Figure 8. I_3/I_1 of pyrene emission as a function of copolymer concentration for TP-3 (■) and TP-7 (●) in deionized water.

according to the template mechanism. When the ratio was higher than 1(TP-5), the number of free PEBA molecules dissolved in the solution bulk increased, which led to a decrease in the number of large blocks along the molecular chains and also the thickening capacity. When the ratio was lower than 1(TP-6), most of the PEBA molecules were preadsorbed on the PAAC chains, but the length of the small block was decreased and the hydrophobic monomer inclined to random distribution so the thickening capacity decreased.

3.2.3. Molecular Weight of the Template. Figure 6 illustrates the effect of the molecular weight of PAAC on the thickening capacity. The molar ratio of PEBA to AM was 0.75%, and as the molecular weight of the template increased, the thickening capacity increased significantly. As the concentration and the molar ratio of hydrophobic monomer to template were fixed, the increase in the molecular weight of PAAC led to the increase

in the length of the large block. This behavior was an indication that the average size of the hydrophobic blocks seems to be more effective than their block number. A similar result about the effect of microstructure on the thickening capacity was also observed in the micellar copolymerization process.[29–31]

3.3. Effect of PEBA Content on Thickening Property. Figure 7 illustrates the effect of copolymer composition on the viscosity of the template copolymer solution at a concentration of 1.5 g/dL. It was found that, with increasing PEBA content in the copolymer, the viscosity increased slowly at first, increased rapidly when the content reached 0.75%, and then increased gradually until the precipitation of PEBA occurred in solution as the content was higher than 2.5%.

In this range, no viscosity decrease was found. It is worth noting that the ionic hydrophobic PEBA exhibited more efficient viscosity enhancement and higher permissible content than the corresponding nonionic hydrophobic monomer decarboxylic PEBA.[32] The reason is that the hydrophobic monomer PEBA is ionizable. The charge repulsion among PEBA units leads to the copolymer chains being in more extended states than those of the decarboxylic PEBA copolymers, which induces PEBA copolymers to have a higher viscosity than that of the decarboxylic PEBA ones at the same concentration.

3.4. Apparent Critical Aggregate Concentration (cac). Figure 8 depicts the dependence of I_3/I_1 values of pyrene steady-state fluorescence spectra on copolymer concentration in aqueous solution. The I_3/I_1 values remained almost constant when the concentration was lower than 0.5 g/dL. As the concentration was increased, the I_3/I_1 values began to increase significantly. The abrupt increase of the I_3/I_1 values indicated that the pyrene molecules removed from water bulk to the highly hydrophobic microdomains resulted from the formation of strongly hydrophobic association. The results indicated that strong hydrophobic interaction occurred in the copolymer concentration above 0.5 g/dL (cac), which also could be deduced on the plots of viscosity versus concentration.

3.5. Aggregation Behavior. The morphology and hydrodynamic size of aggregates for hydrophobic copolymer (TP-7) were studied by transmission electron microscopy (TEM) and the light scattering technique. The TEM images for the copolymers TP-7 at different concentrations were shown in Figure 9. It is very interesting that in the dilute copolymer solutions (<cac) the copolymer existed in the form of hollow sphere aggregates (Figure 9A and B). As the concentration was increased to a value higher than the cac, the hollow sphere aggregates changed to swollen micelle aggregates with flower-shaped structures (Figure 9C–E). The size distribution of the
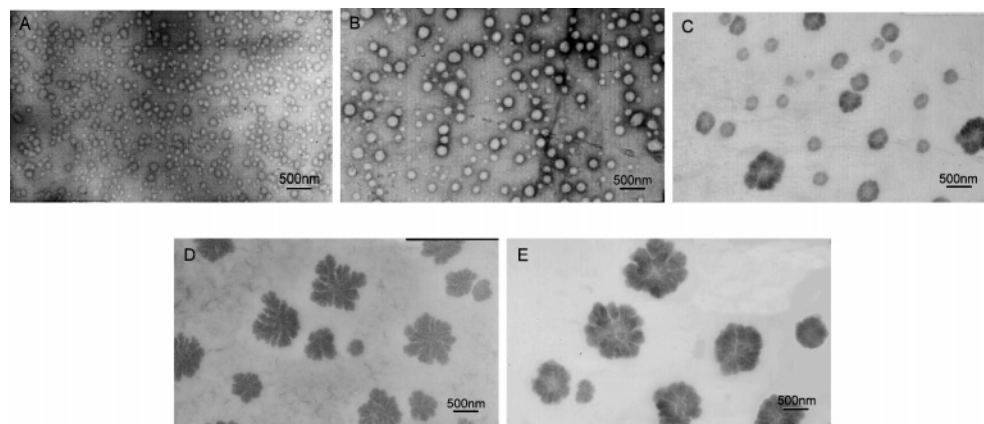

Figure 9. TEM micrographs of aggregates for TP-7 at different copolymer concentrations: (A) 0.1 g/dL; (B) 0.2 g/dL; (C) 0.5 g/dL; (D) 0.8 g/dL; (E) 1 g/dL.
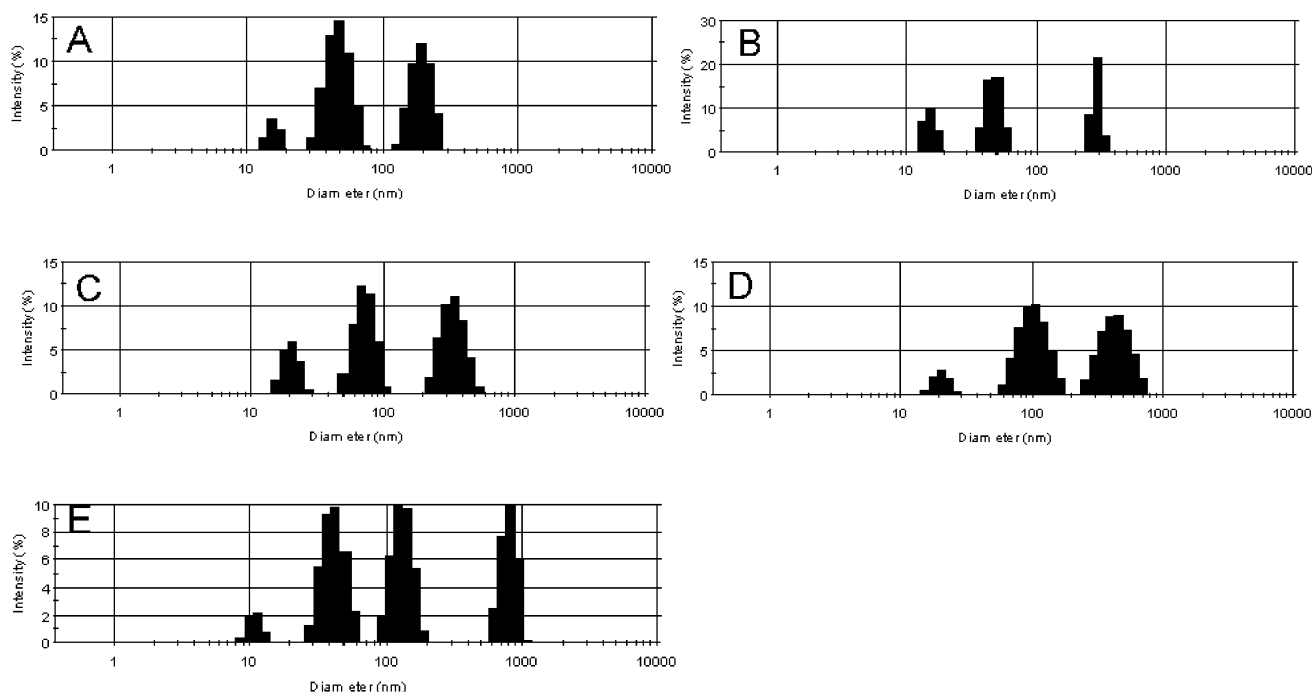
Figure 10. Diameter distribution for TP-7 at different copolymer concentrations: (A) 0.1 g/dL; (B) 0.2 g/dL; (C) 0.5 g/dL; (D) 0.8 g/dL; (E) 1 g/dL.
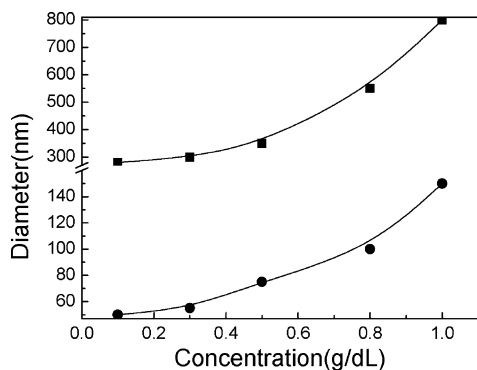

Figure 11. Plot of R_H of peak 1 (■) and peak 2 (●) as a function of copolymer concentration.

aggregates at different copolymer concentrations was measured by the light scattering technique (SALS). As illustrated in Figure 10, the aggregates were all multipopulations. As the concentration was increased, the diameter increased too. The results coincided with those of the TEM. The average diameter (R_H) values from the right-hand peaks 1 and 2 were plotted as a function of copolymer concentration. As shown in Figure 11, a pronounced increase of R_H was observed when the concentration was higher than 0.5 g/dL. The results indicated that, in dilute solutions (<0.5 g/dL), the small aggregates (formed mainly by intrachain association) were prominent; as the concentration increased, the big aggregates (formed mainly by interchain association) were prominent.

4. Conclusions

Hydrophobically associating copolymers consisting of AM and a small amount of PEBA were synthesized by template copoymerization in the presence of PAAC as a template. In this system, the products were multiblock due to the template effect. Viscosity versus copolymer concentration data indicated that template copolymers similar to the micellar copolymers exhibited remarkable thickening properties. The thickening properties were dominated by the molar ratio of PEBA to PAAC, the molecular weight of PAAC, and the pH of the reaction medium. Steady-state fluorescence spectra of pyrene revealed that the apparent critical interpolymer aggregate concentration of the copolymer solution was 0.5 g/dL. The microstructure of the aggregates studied by TEM indicated that the aggregates changed their morphology from small hollow spheres to big flower-shaped aggregates as the copolymer concentration increased. Light scattering data indicated that the aggregates were multipopulation, and the diameter of the aggregates increasing from 100 nm to 1 μm as the copolymer concentration increased. All of the above results clearly indicated that the template copolymerization gave good access to a very simple and powerful means for the preparation of hydrophobically associating copolymers and other functional polymer materials.

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Synthesizing Hydrophobically Associating Copolymer

J. Phys. Chem. B, Vol. 109, No. 47, 2005 **22255**

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