

Emulsifier-Free Synthesis and Self-Assembly of an Amphiphilic Poly(styrene-*co*-acrylic acid) Copolymer

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ABSTRACT: A poly(styrene-*co*-acrylic acid) copolymer was synthesized by surfactant-free polymerization with the assistance of power ultrasound in water. Fourier transform infrared, NMR, and differential scanning calorimetry measurements revealed that the copolymer was random. Atomic force microscopy and laser light scattering were used to investigate the self-assembly of the copolymer, and it was found that the copolymer chains formed micelles or other self-assemble structures in solution. Atomic force microscopy also indicated that the self-assembled structures devel-

oped into nanospheres with a poly(acrylic acid)-rich or polystyrene-rich surface in a film, depending on the solvent used for the preparation of the film. In particular, a wheel-like structure could result in a film when the copolymer film was prepared in a moist environment; it resulted from heterogeneous aggregates of poly(acrylic acid) at the rim of water bubbles. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3718–3726, 2006

Key words: amphiphiles; copolymerization; self-assembly

INTRODUCTION

Amphiphilic copolymers have attracted much attention because of their fascinating self-assembly behavior and potential applications as macromolecular surfactants in the coating and print industries.¹ Block copolymers prepared via ionic polymerization under strictly anhydrous conditions are the main members of this family.² Amphiphilic copolymers with a blocky structure have been prepared with emulsion polymerization,³ which is conducted under mild conditions with surfactants to stabilize the emulsion. However, the presence of surfactants often brings some problems to their applications; for example, surfactants in an adhesive usually migrate at the interface, leading to a poor adhesion.³ It has also been reported that surfactants usually lead polymeric particles prepared via emulsion polymerization to have a broad particle size distribution.⁴ To overcome these drawbacks, reactive surfactants or polymer surfactants have been proposed.⁵

An ultrasound-assisted chemical reaction is a potential method for green chemistry.⁶ Ultrasonic cavitations

create an extremely high local temperature and pressure, as well as heating and cooling rates for a chemical reaction, allowing for the generation of radicals that initiate chemical reactions such as polymerization. Moreover, ultrasonic irradiation can lead to such an efficient mixing of the system that water and oil phases form an emulsion without any surfactants.⁷ Recently, we successfully prepared amphiphilic copolymers, using surfactant-free polymerization with the assistance of ultrasound.⁸ Yin and Chen⁹ also reported the polymerization of *n*-butyl acrylate and acrylamide with such a method.

Poly(styrene-*b*-acrylic acid) chains can form several supermolecular structures, such as rods, micelles, tubules, onions, spindles, and vesicles.¹⁰ The assemblies can be controlled by different factors, such as the absolute and relative block lengths, the presence of additives (ions, homopolymers, and surfactants), the nature and composition of the solvent, the temperature, and the polydispersity of the hydrophilic block.¹¹ This amphiphilic block copolymer is usually synthesized by the anionic block polymerization of styrene and butyl acrylate, followed by the hydrolysis of poly(butyl acrylate) blocks into poly(acrylic acid) (PAA).¹²

In this study, we prepared the amphiphilic copolymer poly(styrene-*co*-acrylic acid) (PS-*co*-PAA) with a surfactant-free emulsion polymerization with the assistance of ultrasound, and we investigated their self-assembly with laser light scattering (LLS) and atomic force microscopy (AFM).

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EXPERIMENTAL

Materials

Styrene and acrylic acid (Shanghai Chemical Reagents Co., Shanghai, China) were distilled under reduced pressure. 4,4'-Azobis(isobutyronitrile) (AIBN) from Shanghai Chemical Reagents was purified by recrystallization from alcohol. Tetrahydrofuran (THF) was distilled before use. Dimethyl sulfoxide- d_6 (DMSO- d_6 ; Beijing Chemical Industry Factory, Beijing, China), used as the solvent for NMR measurements, and aqueous ammonia (30%) were used as received.

Ultrasound-assisted polymerization

A 20-kHz ultrasonic generator with a power output range of 1–900 W in the dial reading (JY92-2D, Xinzhi, Ningbo, China) with a titanium horn (tapered, with diameter $\phi = 6$ mm) was used. The actual acoustic energy entering the reaction was measured by a calorimeter. The reaction temperature was controlled by a water bath surrounding the reaction vessel.

After a mixture of styrene, acrylic acid, and distilled water with a volume ratio of 1:1:2 was added to a vessel, the initiator AIBN with a concentration of 0.016 g/mL was introduced. The temperature of the water bath was kept at 50°C, and the ultrasonic output power was adjusted from 0.082 to 0.263 W/cm³. A white, viscous colloid resulted after polymerization. The product was washed with toluene several times to remove polystyrene (PS) and PAA homopolymers and residual styrene. Residual acrylic acid was washed out with distilled water. The product was collected with high-speed centrifugation and subsequent drying in a vacuum oven.

Characterization and instrumentation

Fourier transform infrared (FTIR) spectra were recorded with a Bruker spectrometer (KBr; EQUINOX55, Bruker, Germany). ¹H-NMR spectra were obtained on a Bruker spectrometer (Avance 300; 300 MHz) with DMSO- d_6 as the solvent. The viscosity was measured with an Ubbelohde viscometer. The glass-transition temperature (T_g) of the sample was measured by a differential scanning calorimetry (DSC; DSC-4, PerkinElmer, Norwalk, CT). The measurements were performed with a heating rate of 20°C/min from 25 to 200°C.

AFM measurements

A copolymer was dissolved in water, THF, aqueous ammonia, or their mixtures. A droplet (20 μ L) of the solution was deposited onto newly cleaved mica. A dried film was prepared after spin casting at a speed of 1300 rpm for 8 s and then at a speed of 4000 rpm for

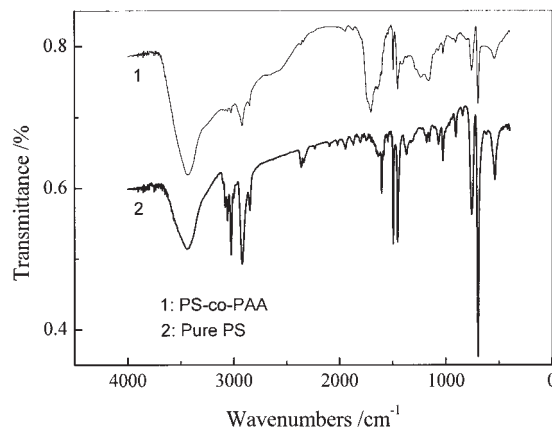


Figure 1 FTIR spectra of the prepared copolymer and pure PS.

30 s. The height and phase images of the copolymer film on mica were measured with AFM (IIIa, Nanoscope; Digital Instruments, USA) in the tapping mode with silicon TESP (tapping mode etched silicon probe) cantilevers. The scanning rate ranged from 0.5 to 1.0 Hz, and 512 pixel \times 512 pixel images were recorded.

LLS

A commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi- τ digital time correlator (ALV5000) and a cylindrical 22-mW Uniphase He-Ne laser (initial wavelength = 632 nm) as the light source was used. The hydrodynamic radius ($\langle R_h \rangle$) and its distribution [$f(\langle R_h \rangle)$] were measured in dynamic LLS.^{13,14} The dn/dc (specific refractive index increment) value of PS-*co*-PAA in THF at 25°C was measured to be 0.149 mL/g with a precise and novel differential refractometer at a wavelength of 632 nm.¹⁵

RESULTS AND DISCUSSION

Figure 1 presents the FTIR spectra of the prepared copolymer and pure PS. In curve 1, the peaks at 1702 and 3432 cm^{-1} correspond to hydroxyl and carboxyl groups of acrylic acid, and the peaks at 1601, 1493, 1453, and 700 cm^{-1} were contributed by the PS segment. ¹H-NMR spectra show $\delta = 12.0$ ppm for $-\text{COOH}$ and $\delta = 7.2$ and 6.7 ppm for $-\text{C}_6\text{H}_5$, as shown in Figure 2. Both FTIR and NMR results support the idea that the product is a copolymer of acrylic acid and styrene. The T_g values of pure PS and PAA are 100 and 105°C, respectively. DSC measurements show that the copolymer has two T_g values, 60 and 139°C, as shown in Figure 3. For the acrylic acid rich phase, the PS segments dilutes the H bonds, and this results in a low T_g (60°C); in the PS-rich phase, the presence of a few H bonds among PAA may give rise to a high T_g (139°C). This indicates that the copolymer

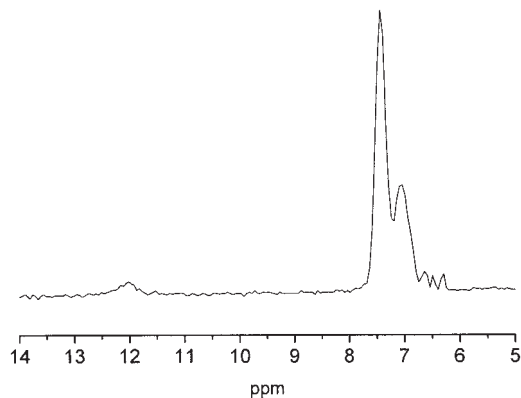


Figure 2 $^1\text{H-NMR}$ of the prepared copolymer.

is random.^{16–18} Figure 4 shows that the viscosity of the copolymer much depends on the ultrasonic power density. At a low ultrasonic power density, the intrinsic viscosity is about 93 mL/g. An increase in the power density results in a sharp decrease in the viscosity. When the ultrasonic power density is greater than 0.2 W/cm^3 , the viscosity tends to be a constant of $\sim 51 \text{ mL/g}$. This fact indicates that the copolymer prepared at a low ultrasonic power density has a high average molar mass, whereas a high ultrasonic power density leads to a copolymer with a lower average molar mass.

The static light scattering experimental results reveal the weight-average molecular weight (M_w) and the radius of gyration ($\langle R_g \rangle$) values of the copolymers. For the copolymer prepared at 0.121 W/cm^3 , M_w is 1.342×10^6 , and $\langle R_g \rangle$ is approximately 109.46 nm; for the copolymer prepared at 0.23 W/cm^3 , M_w is 9.333×10^5 , and $\langle R_g \rangle$ is approximately 96.83 nm. Figure 5 shows $f(\langle R_h \rangle)$ of the copolymer in THF measured by LLS. $\langle R_h \rangle$ of the copolymer obtained at a low ultrasonic power density shows three peaks. The peaks at about $\langle R_h \rangle \sim 220 \text{ nm}$ correspond to the micelle spheres

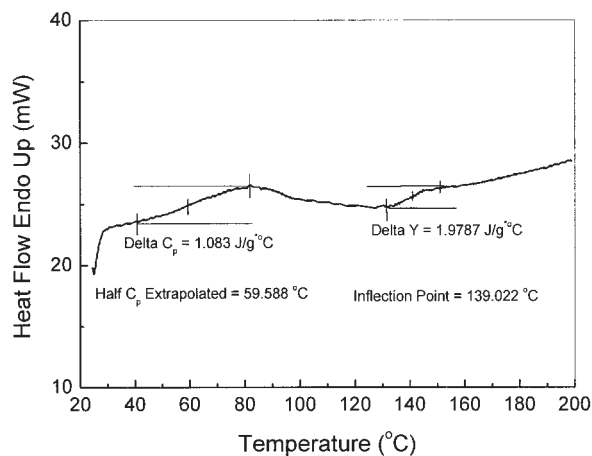


Figure 3 DSC thermogram of the prepared copolymer.

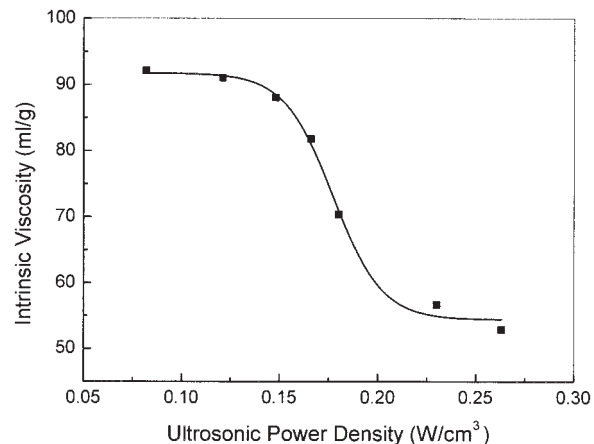


Figure 4 Effect of ultrasonic power on the intrinsic viscosity of the copolymer under fixed reaction conditions (styrene/acrylic acid/water = 1:1:2, reaction time = 30 min, reaction temperature = 50°C , initiator AIBN concentration = 0.016 g/mL).

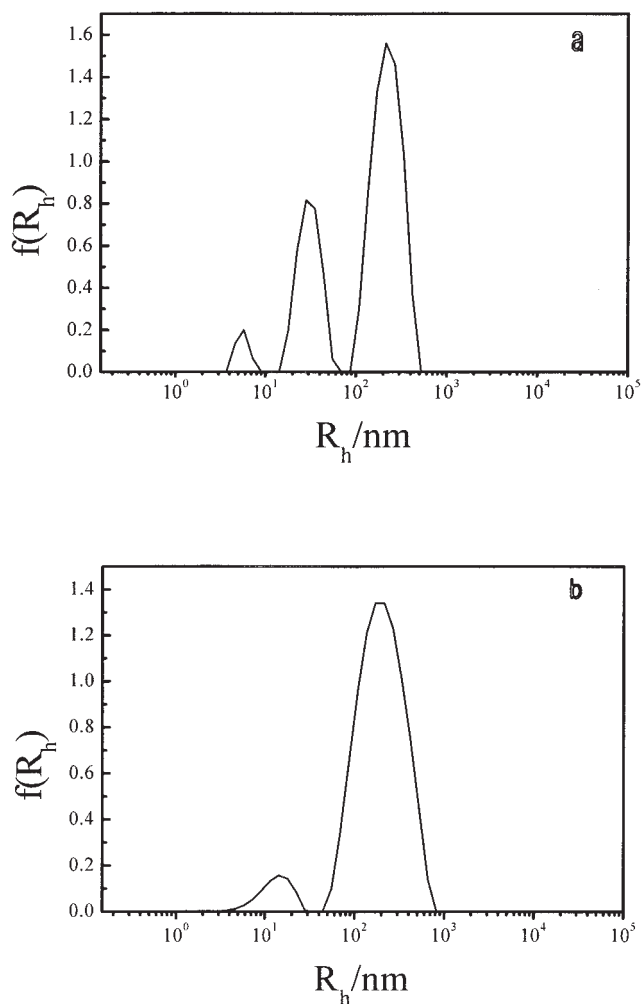


Figure 5 $f(\langle R_h \rangle)$ of (a) the copolymer prepared at an ultrasonic power density of 0.112 W/cm^3 and (b) the copolymer prepared at an ultrasonic power density of 0.23 W/cm^3 (concentration = $1.0 \times 10^{-4} \text{ g/mL}$).

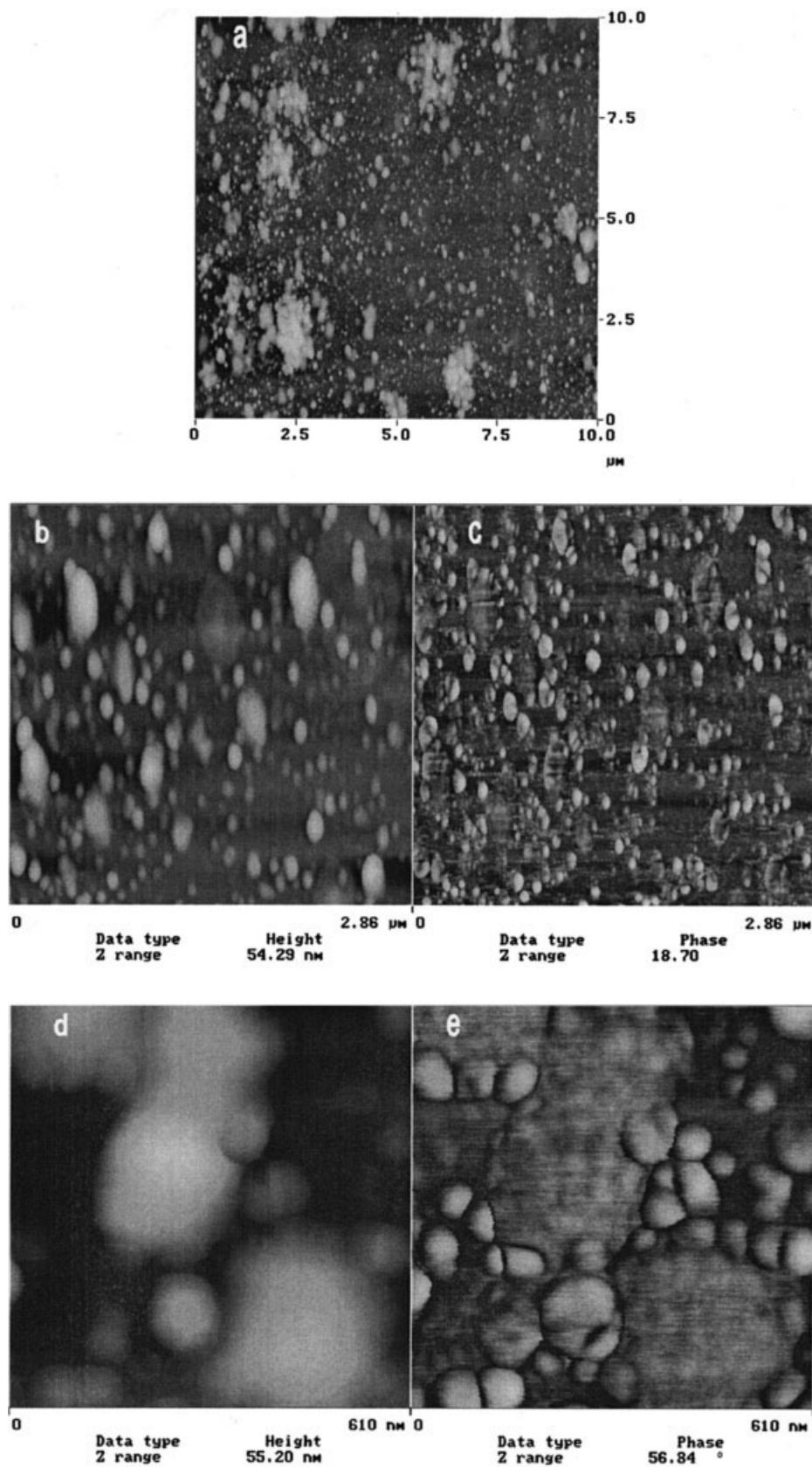


Figure 6 Typical AFM images of the copolymer film: (a,b,d) height images and (c,e) phase images. The copolymer was synthesized at an ultrasonic power density of 0.112 W/cm^3 . The film was prepared by the deposition of $20 \mu\text{L}$ of a THF solution of the copolymer (0.1 mg/mL) onto the surface of newly cleaved mica, following spin coating at a speed of 1000 rpm for 9 s and at a speed of 5000 rpm for 30 s.

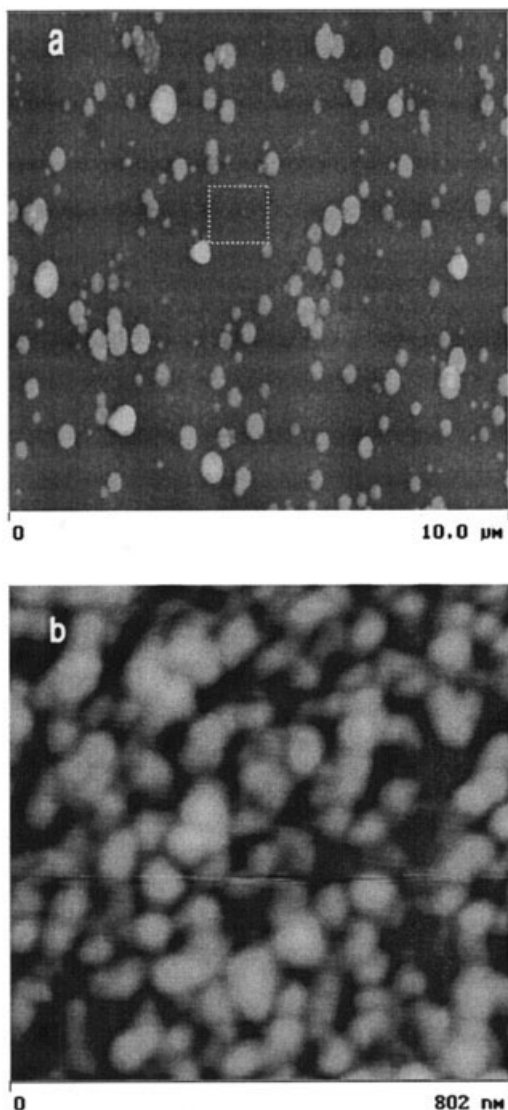


Figure 7 Typical AFM images of the film of the copolymer synthesized at an ultrasonic power density of 0.23 W/cm^3 : (a) height image and (b) enlargement of a selected area. The film was prepared by the deposition of $20 \mu\text{L}$ of a THF solution of the copolymer (0.1 mg/mL) onto the surface of newly cleaved mica, following spin coating at a speed of 1000 rpm for 9 s and at a speed of 5000 rpm for 30 s .

formed by copolymer chains. In Figure 5(a), there are two other peaks with $\langle R_h \rangle$ values of 5.6 and 30 nm , which should be the single chains of the amphiphilic copolymer. The two peaks indicate a wide molecular weight distribution of the copolymer prepared at a low ultrasonic power density. In Figure 5(b), there appear only two peaks of $\langle R_h \rangle$. Similar to those of Figure 5(a), the peaks at about 200 nm correspond to the formed micelles. The $\langle R_h \rangle$ value of about 14 nm corresponds to the single chains of the copolymer. The one peak of single chains reveals that the molecular weight distribution of the copolymer prepared at a high ultrasonic power density becomes narrower than

that of the copolymer prepared at a low ultrasonic power density. Figure 5(b) also shows that many copolymer single chains form micelles. THF is a good solvent for both PS segments and PAA segments and leads to the association. Figure 5 also shows that the copolymer chains form aggregates with a wide distribution. This can be better viewed by AFM.

Figure 6 shows typical AFM images of the copolymer prepared at 0.121 W/cm^3 . The copolymer forms aggregates varying in size and shape. The bigger ones with an elliptical shape are about 400 nm long and 200 nm wide, whereas the smaller spheres are about $20\text{--}95 \text{ nm}$ in diameter. The scale is consistent with the LLS experiment. A similar elliptical shape of micelles or vesicles was also reported in LLS and transmission electron microscopy experiments for both amphiphilic A-B-C-A block copolymers¹⁹ and mixtures of a non-ionic alkylglucoside and an anionic surfactant in water.²⁰ In addition, it has been reported that elongated micelles are stabilized in a different manner than spherical or disklike micelles.²¹ In this study, the elliptical shape may be a result of the inhomogeneous surface chemical properties of the basic copolymer particles. Comparing the AFM height image in Figure 6(b) and the phase image in Figure 6(c), we know that the bigger aggregates in the height image have a weak phase signal, whereas the smaller spheres exhibit a stronger phase signal. For the phase image created by the hysteresis force between the tip and sample, it is clear that the surface has different chemical structures for the bigger aggregates and smaller spheres.²² In the phase image, the PS-rich segment is dark, whereas the

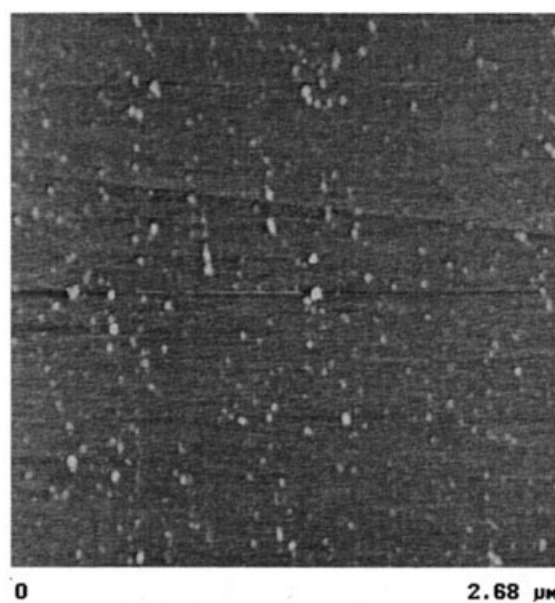


Figure 8 Typical AFM image of the film of the copolymer synthesized at an ultrasonic power density of 0.23 W/cm^3 with a concentration of 0.01 mg/mL in THF. The film was prepared by the same spin-coating method used for Figure 7.

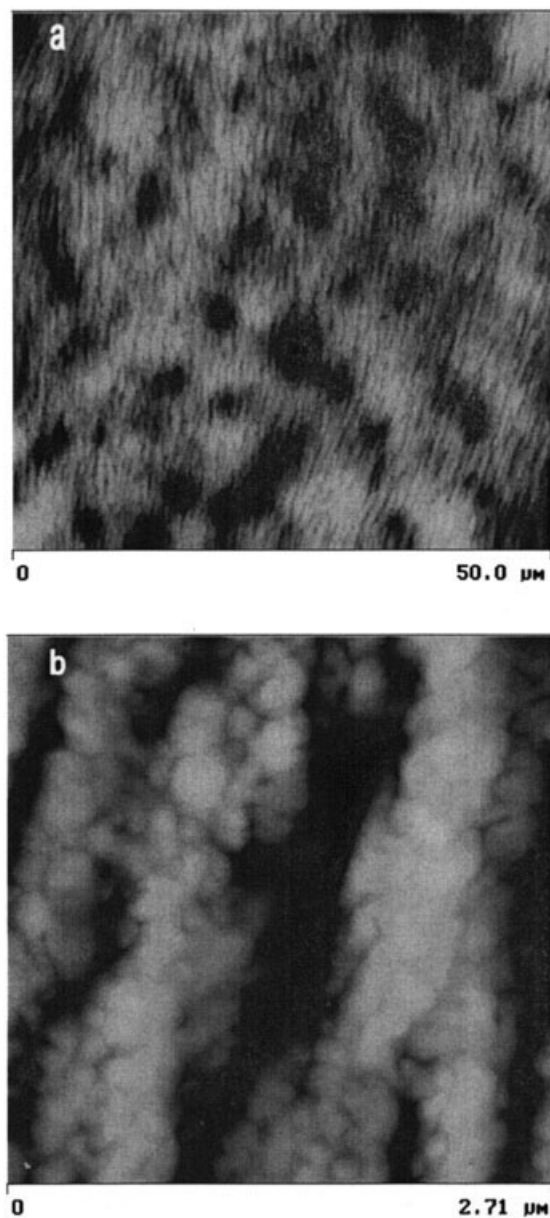


Figure 9 (a) Typical AFM image of the film of the copolymer prepared at an ultrasonic power density of 0.23 W/cm^3 on newly cleaved mica prepared by the spin coating (1300 rpm for 8 s and 4000 rpm for 30 s) of 20 mL of its THF solution with a concentration of 8.58 mg/mL and (b) an enlargement of the AFM image.

PAA-rich region is light.²³ The intrachain hydrogen bond of the PAA segment in the copolymer results in a collapse of the copolymer chain into a sphere with the PAA-rich segment as the inner core and the PS-rich segment as the exterior shell. For micelles, the self-assembly of the copolymer may result in the formation of a big sphere with a PS-rich inner core and a PAA-rich exterior surface. The different surface chemistry is the reason for the phase image diversity. Figure 6(d,e) shows enlarged images of the sample, and the difference of the height image and phase image

can be seen more clearly. From the phase image, it can also be found that the bigger aggregates consist of some smaller spheres.

Figure 7 shows typical AFM images of the copolymer prepared at 0.23 W/cm^3 . The sample was prepared by the deposition of $20 \mu\text{L}$ of a THF solution of the copolymer (0.1 mg/mL) onto newly cleaved mica and sequence spin coating at 800 rpm for 10 s and at 4000 rpm for 30 s. The sample also consisted of two

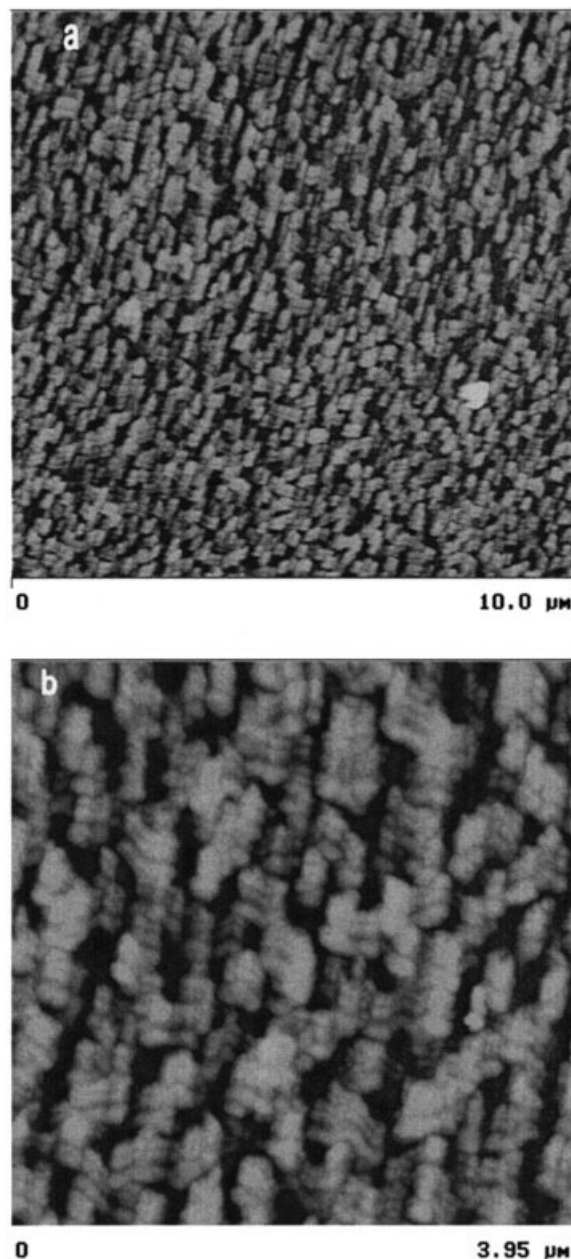


Figure 10 (a) Typical AFM image of the film of the copolymer prepared at an ultrasonic power density of 0.23 W/cm^3 on newly cleaved mica prepared by the spin coating (1300 rpm for 8 s and 4000 rpm for 30 s) 20 mL of its aqueous ammonia solution with a concentration of 9.14 mg/mL and (b) an enlargement of the AFM image.

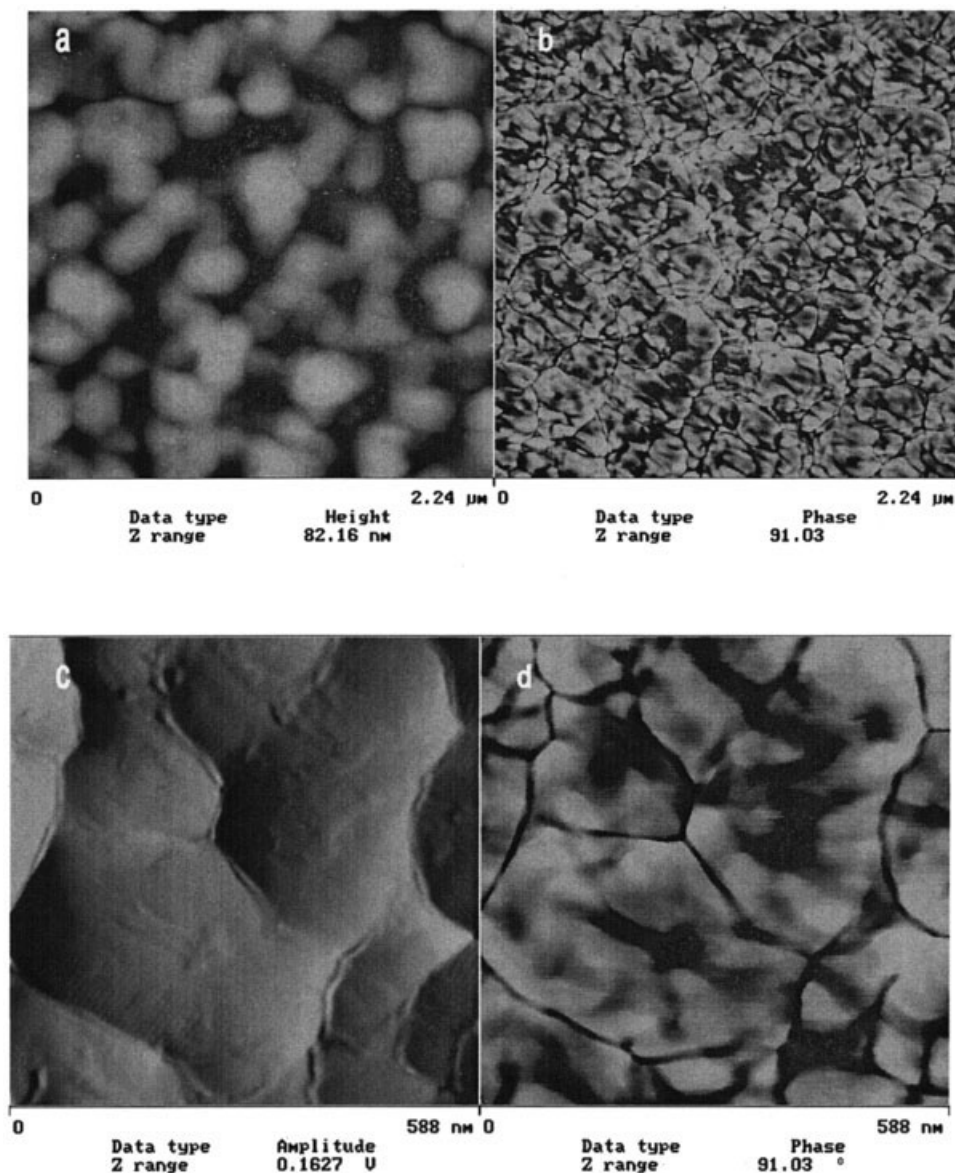


Figure 11 Typical AFM (a,c) height images and (b,d) phase images of the film of the copolymer prepared at an ultrasonic power density of 0.23 W/cm^3 . The film was prepared by the deposition of $20 \mu\text{L}$ of a THF/ $\text{NH}_3 \cdot \text{H}_2\text{O}$ (1:1 v/v) solution of the copolymer with a concentration of 4.57 mg/mL onto the surface of newly cleaved mica, following spin coating at a speed of 1000 rpm for 9 s and at a speed of 5000 rpm for 30 s .

kinds of spheres, the bigger one $300\text{--}450 \text{ nm}$ in size, and this indicated they were the micelles of the copolymer. Figure 7(b,c) presents enlarged AFM scanning images of the sample; the micelles also have an elliptical shape. The size of the smaller spheres is about $30\text{--}50 \text{ nm}$.

Figure 8 shows the AFM image of a sample prepared with $20 \mu\text{L}$ of a THF solution of the copolymer with a concentration of 0.01 mg/mL . No bigger spheres appear, and the size of the particles is about $40\text{--}70 \text{ nm}$. The result indicates that when the copolymer solution is very dilute, no micelles form, and the particle should be the globular structure of the copolymer single chain.

Figure 9 shows an alignment structure of the copolymer aggregates on mica from a THF solution of the copolymer. The sample was prepared via the spin coating (1300 rpm for 8 s and 4000 rpm for 30 s) of 20 mL of its THF solution with a concentration of 8.58 mg/mL . The self-assembly structure is constructed of many little spheres of $40\text{--}700 \text{ nm}$, as shown in Figure 9(b).

Figure 10 shows another kind of self-assembly structure of the copolymer prepared in aqueous ammonia. The sample was prepared by the spin coating (1300 rpm for 8 s and 4000 rpm for 30 s) of 20 mL of its aqueous ammonia solution with a concentration of 9.14 mg/mL . It has no alignment structure but many small particles aggregated together.

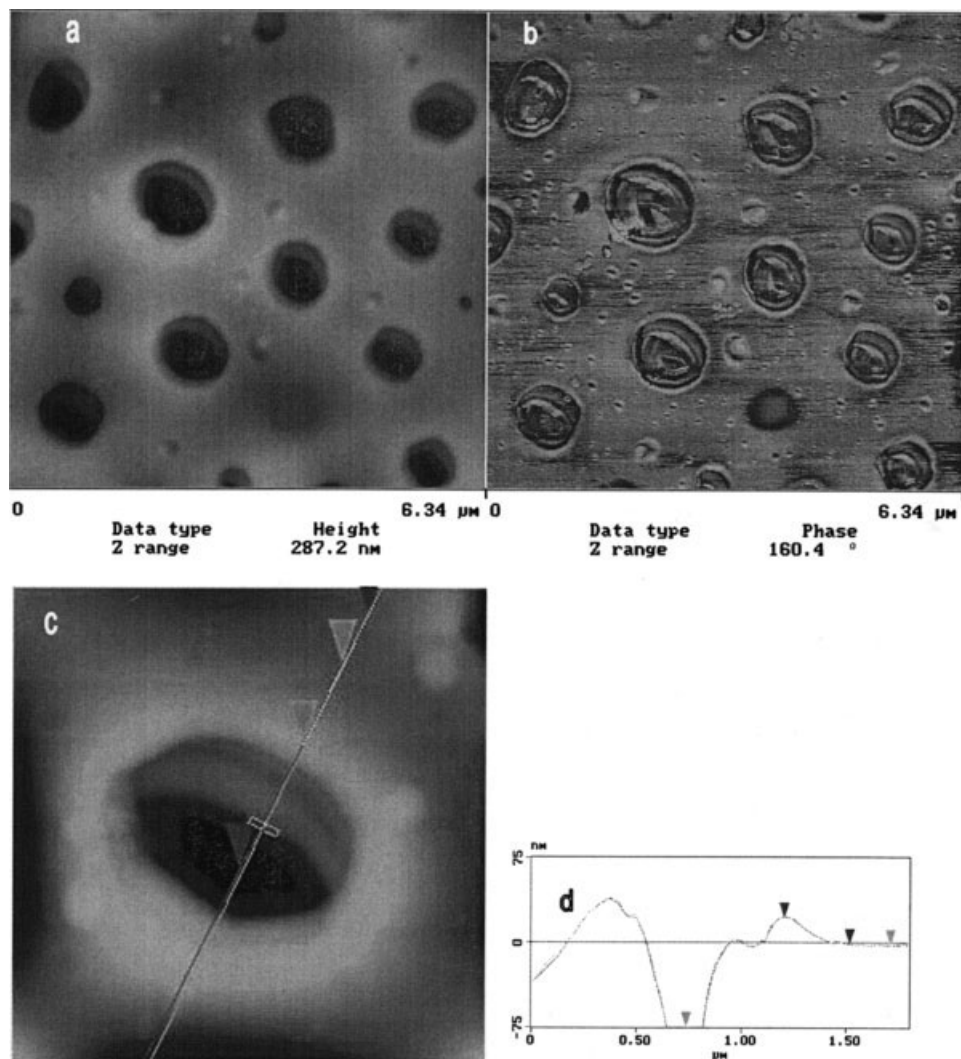


Figure 12 Typical AFM images of dewetting-induced wheel structures of the copolymer film: (a) height image, (b) phase image, (c) enlarged height image of one wheel, and (d) section line across the wheel. The film was prepared by the dewetting of a THF solution of the copolymer at humidity of 60%.

The self-assembly structures in both Figures 9 and 10 are constructed on the basis of nanospheres of the copolymer with different surface chemical properties. The mechanism requires further studies.

Figure 11 shows the morphologies of a copolymer sample prepared from solvents of aqueous ammonia and THF (1:1 v/v). The size of the spheres is about 300 nm. Figure 11(a,c) presents height images of the sample with different scales, whereas Figure 11(b,d) presents phase images of the same place in the film. The surface of the sphere has both dark and light regions, and this indicates the microphase separation of the surface. Because the solvent is a mixture of aqueous ammonia and THF, it provides a chance for both PS-rich regions and PAA-rich segments to appear at the surface, resulting in a heterogeneous surface of one sphere.

It has been reported that when a polymer solution is quickly evaporated at high humidity, some microme-

ter-size patterned structure such as a honeycomb, wheel, or network should be formed.²⁴ The driving force is believed to be the condensation of water droplets and consequently the formation of a template for the self-assembly of the polymer.²⁵ In this study, the THF solution of the copolymer was drop-coated onto the surface of mica at a humidity of 60%. After dewetting, the AFM image was measured and is shown in Figure 12. Some micrometer wheel structure is formed. Figure 12(b,c) shows the individual wheel structure with a section line across it. The thickness of the film is about 80 nm, and the height of the rim of the wheel is about 20 nm. The holes are formed after the evaporation of the water drop, so the hydrophilic segment of PAA should enrich the interface of the water and polymer solution. This results in a PAA-rich rim of the wheel. The phase image in Figure 12(b) verifies this, and the bright rim corresponds to the PAA-rich region, whereas the dark region is PS-rich.

CONCLUSIONS

The amphiphilic copolymer PS-*co*-PAA was directly synthesized in an aqueous emulsion free of an emulsifier with the assistance of ultrasound. Dynamic light scattering and AFM measurements showed that the size and distribution of the copolymer had a direct relationship with the ultrasonic power density, and micelles or a self-assembly structure of the copolymer formed in solution. With different solvents, the copolymer formed aggregates of different sizes on mica and could also self-assemble into some regular structure. When the copolymer was dewetted at high humidity, a self-assembly of a wheel structure formed with a PAA-rich rim.

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