Preparation of Hairy Particles by Grafting PEG onto the Poly(styrene-*co*-maleic anhydride) Surface and PEG Effect on SiO₂ Nanoparticles Adsorption

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ABSTRACT: Hairy particles were prepared by immobilization of poly(ethylene glycol) (PEG) on the surface of poly(styrene-*co*-maleic anhydride) (poly(S-*co*-MA)) spheres. It was found that the carbonyl groups on the poly(S-*co*-MA) surface can be conveniently esterified with the hydroxyl groups of PEG. Chemical and morphological changes were analyzed by FT-IR, TEM, and water contact angle. Results revealed that, with the immobilization of PEG, the morphology of poly(S-*co*-MA) turned from a smooth surface to a hairy-like structure and the hydrophilicity of the polymer particles improved. In addition, berry-like polymer/silica particles can be obtained by using the hairy particles as template. The PEG hairy chains show steric repulsion during the deposition of silica nanoparticles by *in situ* sol-gel process. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 3650–3655, 2013

INTRODUCTION

Recently, the synthesis of dual-size hierarchical particles (such as raspberry-like) has emerged to a frontier in colloid research. The hierarchical particles are important for self-cleaning coating, biotechnology, and surface-enhanced Raman scattering. Synthetic strategies toward raspberry particles include: (1) adsorption of oppositely charged particles on larger colloids,[1–4] (2) covalent grafting of small particles to larger ones,[5–7] and (3) miniemulsion,[8–10] emulsion-free,[11] or pickering polymerization[12,13] using nanoparticles as stabilizers. The most attractive method to prepare berry-like particles is generating nanoparticles on the surface of hard-templates, such as polymer latex or silica particles.

In previous studies, the physical interactions (such as electrostatic interaction,[2] hydrogen bond,[14,15] and acid–base interaction[16–18]) or chemical interactions between the microspheres and nanoparticles[5–7] have been discussed in detail. In our previous study,[19] monodispersed carboxyl-functionalized polystyrene (PS) particles were used as cores and nanosized silica particles were then assembled at the surface of PS particles to construct the raspberry-like particles. It has been observed that the poly(-acrylic acid) (PAA) hydrophilic chains were the key factor in the formation of raspberry-like structure. The formation mecha-

nism of the berry-like PS/SiO₂ particles was contributed to the weak acid–base interaction between the carboxyl groups, amine catalyst, and hydrolyzed tetraethoxysilane (TEOS) molecular (—COO⁻/—N⁺/—SiO⁻).[20] Cheng[21] employed polyamine-based core–shell polymer spheres as a template to prepare berry-like PS/SiO₂ particles. The poly[2-(diethylamino)ethyl methacrylate] hairy shell was designed to catalyze the silica precursor deposition on the template surface. However, the role of the hydrophilic chains is still unclear.

It has been proved that the weak acid–base interaction was crucial to determine the *in situ* nuclei and growth of silica particles on the carboxyl-functionalized PS spheres.[20] But, the steric-effect of hydrophilic polymer chains on the surface of template spheres was insufficiency. To verify the role of hydrophilic polymer chains, surface-bound polymer chains are a suitable candidate to meet these criteria. Here, poly(ethylene glycol) (PEG) was selected as the hairy chain. PEG is composed of —CH₂CH₂O— repeating units with a hydroxyl group at each end of the chain. PEG is a hydrophilic polymer and is frequently used to prevent protein adsorption and cell adhesion. The mechanism of the repellent effects of PEG-modified surfaces is unclear. The two most common theories explaining its resistance are based on the steric repulsion and water barrier effects resulting from the structuring of water in the environment surrounding PEG chains.[22–24] The

Additional Supporting Information may be found in the online version of this article.

magnitude of repulsive force depends on the surface density and chain length of the PEG. So, it is attractive to introduce the PEG chains on the surface of inorganic particles or polymer latex.

There are several methods to graft PEG or its derivatives, such as cold plasma,[25] esterification with acid anhydride group[26] or with carboxyl groups,[27] photopolymerization of PEG monoacrylate on PMAA films,[28,29] or by living polymerization.[30,31] To prepare hairy-like polymer particles, it is effective to copolymerize vinyl monomers with maleic anhydride (MA) to gain prefunctionalization on the particles' surface. These anhydride groups can easily undergo a ring opening reaction with nucleophilic reagents which contain hydroxyl or amine groups.

In this study, PEG with different molecular weight was immobilized on poly(styrene-co-maleic anhydride) (poly(S-co-MA)) surface by the esterification reaction with acid anhydride groups. After immobilizing PEG on the particle's surface, the virgin and modified spheres were compared with respect to their hydrophilicity. And then the steric-effect of PEG chains on the deposition of silica nanoparticles was studied by introducing the poly(S-co-MA)-g-PEG into the hydrolysis reaction of TEOS.

MATERIAL AND METHODS

Materials
The styrene (Shanghai Chemical Reagents, Shanghai, China) was purified by through a basic alumina column to remove the inhibitor before use. Potassium persulfate was recrystallized before use. MA, PEG 400 (PEG-400), PEG 1000 (PEG-1000), anhydrous ethanol, p-toluenesulfonic acid, TEOS, and diethanolamine (DEA) were purchased from Shanghai Chemical Reagent (China) and used as received. Dodecyltrichlorosilane (96%) was supplied by Alfa Aesar Chemical Reagents and used as received.

Preparation of Poly(S-co-MA) Spheres
Poly(S-co-MA) spheres were prepared by radical copolymerization of MA and styrene. The standard recipes for emulsifier-free polymerization of styrene with MA are listed in Table I. All the ingredients were added to a 250 mL three-neck reaction flask equipped with a mechanical stirrer, a condenser and a gas inlet. After the mixture was deoxygenated by bubbling N_2 gas at room temperature for 30 min, the flask was placed in a 70°C water-bath and stirred mechanically at 300 rpm for 24 h. The Poly(S-co-MA) spheres were collected by centrifugation and then washed with ethanol for three times. The final product was dried in vacuo at 40°C for 24 h.

Table I. Recipes for the Emulsifier-Free Polymerization of Styrene with MA

Materials	Sample amounts		
	SMA-1	SMA-2	SMA-3
Styrene (g)	9.5	9.0	8.5
MA (g)	0.5	1.0	1.5
KPS (mg)	75	75	75
Water (mL)	100	100	100

Preparation of Poly(S-co-MA)-g-PEG
Fifty milligram of poly(S-co-MA) powder was dispersed into 10 mL ethanol by ultrasound. Then, 2.5 g PEG and 0.1 g p-toluenesulfonic acid were added directly. The esterification was operated at 80°C for 2 h. After reaction, the synthesized poly(S-co-MA)-g-PEG particles were collected by centrifugation and washed with ethanol three times. The synthesis recipes of poly(S-co-MA)-g-PEG are listed in Table II.

Preparation of Berry-Like Particulate Films for Hydrophobic Surfaces
Fifty milligram of poly(S-co-MA)-g-PEG particles was dispersed into 0.1 mL of TEOS, 40.0 mL of ethanol and 5.0 mL water under stirring, then 0.5 g DEA were dripped to catalyze the hydrolysis of TEOS. The hydrolysis reaction was carried out at 30°C for 4 h. Polymer/silica composite particles were directly obtained by centrifugation. Then, the composite particles were dispersed in ethanol. A glass substrate was placed on the spin coater (KW-4A, SIYOUYEN Electronics Technology, Shanghai, China), and allowed to spin. For all coating experiments 0.5 mL of dispersed solution was used. Finally, the particulate films were chemically modified by being dipped in 1 wt % dodecyltrichlorosilane in hexane for 30 min.

Characterization
FT-IR spectra were recorded on a VECTOR22 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were recorded on an English ESCALAB MKIIinstument with Li Kα radiation (1486.6 eV) as the excitation source under high vacuum (5×10^{-9} Pa). All the samples were dried under an infrared lamp and ground into powder before examination. The morphology of particles was observed by TEM (Hitachi H-7650) and FESEM (JEOL JSM-6700). The number average diameter (D_n) and weight average diameter (D_w) were measured from the TEM images (no less than 50 particles) and calculated using the following set of equations:

$$D_n = \sum n_i D_i / \sum n_i \qquad (1)$$

$$D_w = \sum n_i D_i^4 / \sum n_i D_i^3 \qquad (2)$$

$$\mathrm{PDI} = D_w / D_n \qquad (3)$$

where n_i is the number of polymer particles with diameter D_i and PDI is the polydispersity.

The surface wettability of the particulate films was expressed in terms of the contact angles (CAs) of water on a film surface. The static CA and sliding angles were measured with Contact Angle Meter SL200B (Solon Tech., Shanghai, China). Doubly distilled water was used in this analysis.

Table II. Recipes for Surface Esterification Reactions

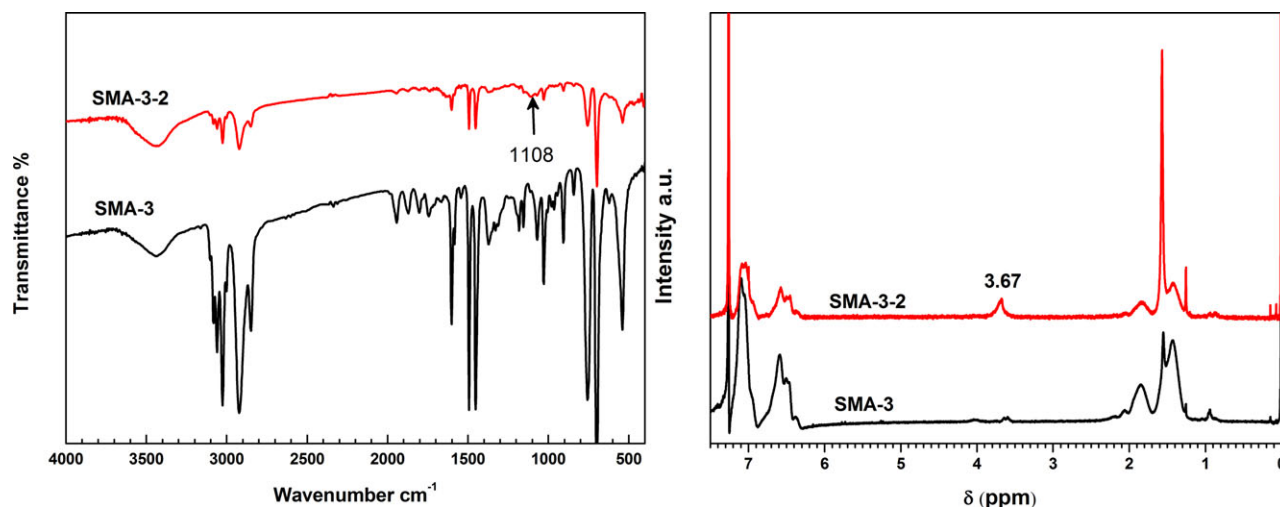| Runs	P(S-co-MA) (mg)	Ethanol (mL)	PEG (g)
SMA-3-1	50	10	2.5 (PEG400)
SMA-3-2	50	10	5.0 (PEG400)
SMA-3-3	50	10	2.5 (PEG1000)

Figure 1. FT-IR and ^{1}H-NMR spectra of Poly(S-*co*-MA) (SMA-3) and Poly(S-*co*-MA)-g-PEG (SMA-3-2). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

RESULTS AND DISCUSSION

Hairy spheres are successfully prepared through esterification reaction between PEG and acid anhydride groups on poly(S-*co*-MA) surface. The FTIR, NMR, and XPS of hairy spheres were recorded and the results are given in Figures 1 and 2. After immobilizing PEG on the particle's surface, the diameter of hairy spheres is larger than the virgin spheres. In addition, the water CA measurement indicates that the hydrophilicity of polymer spheres increase after modified by PEG. Morphologies of hairy spheres and results for CA measurement are given in Figure 3 and Table III.

Berry-like polymer/silica particles can be obtained by using the hairy particles as template. The PEG hairy chains show steric-repulsion to block the nucleation and growth of silica nanoparticles during *in situ* sol-gel process.

Characterization of Poly(S-*co*-MA) and Poly(S-*co*-MA)-g-PEG Particles

FT-IR spectra of the sample poly(S-*co*-MA) (SMA-3) and poly(S-*co*-MA)-g-PEG (SMA-3-1) are shown in Figure 1. Absorption peaks at 3027, 1601, 1493, 1453, 756, and 699 cm^{-1} correspond to the phenyl group, the peaks at 2923 and 2850 cm^{-1} can be attributed to the methylene and methenyl groups. The characteristic peaks at 1743 cm^{-1} (C=O) are assigned to the carboxyl group, which was originated from the hydrolysis of carbonyl group of MA during polymerization (as shown in Table I). It is also seen that the intensity of the absorption bands due to the C=O of carbonyl groups decreases after esterification. The characteristic peak at 1108 cm^{-1} corresponding to the symmetric stretch vibration of ether indicated that PEG had already grafted onto the surface of poly(S-*co*-MA) sphere. The ^{1}H-NMR spectrum of sample SMA-3-2 shows the δ corresponding to CH_2CH_2O of PEG at 3.67 ppm. The peaks at 6.4–7.3 ppm are contributed to aromatic proton and peak at 3.60 ppm belongs to maleic anhydride proton. The NMR demonstrates that the poly(S-*co*-MA)-g-PEG sphere is successfully prepared by esterification.

XPS is employed to determine the surface composition of poly(S-*co*-MA) spheres. The typical information depth of XPS is $\sim$ 5 nm. Figure 2 shows the XPS survey spectra of SMA-1, SMA-2, and SMA-3. All spectra reveal the presence of only carbon (284.6 eV) and oxygen (532.3 eV). The relative atomic concentration of oxygen is 1.93% for SMA-1, 2.38% for SMA-2, and 3.16% for SMA-3, respectively. The data are in accord with the calculated values (see Supporting Information Table SI) and implied that the maleric anhydride copolymerized with the styrene. After grafting with PEG, the relative atomic concentration of oxygen increased from 3.16% (SMA-3) to 6.95% (SMA-3-2), due to the contribution of oxygen on the PEG chain, indicating that the PEG is successfully grafted onto the poly(S-*co*-MA) surface.

The particle size and size distributions were determined from the TEM images (see Supporting Information Figure S1), no
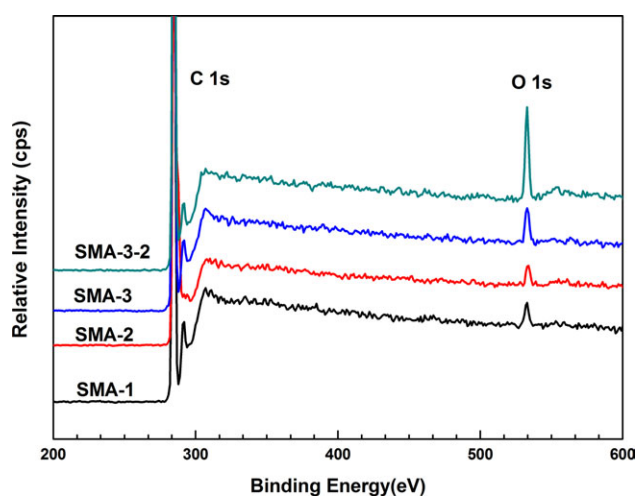

Figure 2. XPS full-scan spectra of the poly(S-*co*-MA) and Poly(S-*co*-MA)-g-PEG spheres. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
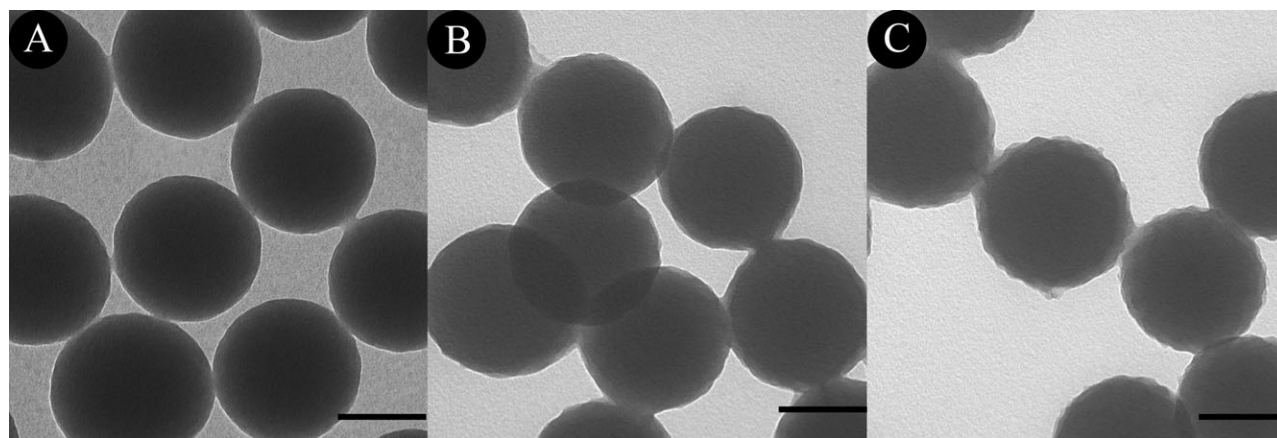
Figure 3. TEM images of poly(S-*co*-MA) before and after grafting with PEG. (A) SMA-3, (B) SMA-3-1, PEG = 2.5 g, (C) SMA-3-2, PEG = 5.0 g. The scale bar is 200 nm.

less than 50 particles were counted for every sample. The average particle sizes (D_n) is calculated according to eq. (1). The results are summarized in Table III. The result indicates that the particle sizes are all monodisperse.

The Morphology of PEG Grafting Poly(S-*co*-MA) Particles

Figure 3 shows a typical TEM image of the hairy particles (SMA-3-1 and SMA-3-2). The surface of particles changes from smooth to rough after grafting with PEG. We find that the average hairy particles diameters of SMA-3-1 (∼415 nm) and SMA-3-2 (∼420 nm) increase with the amount of PEG addition as shown in Table III. This result indicates that the graft ratio increases according amount of PEG during the esterification. The surface decorated by PEG is hydrophilic. In Table III, the water CAs decreased with increasing PEG content. The value of the CA of the SMA-3 was 95.7°. After grafting with PEG, the CA decreased to 77.9° (SMA-3-2). In previous literatures, the water CAs of PEG-400 modified surface varied between ∼50°[25] and ∼23°[26]. But, the decrease of CA between unmodified and modified surface was similar at about 20°.

The Formation of Berry-Like Polymer/Silica and Wettability of the Surface

In our previous study,[19] we found that hydrophilic polymer chains on the surface are the crucial factor for the formation of berry-like PS/SiO$_2$ particles. When the surface of latex templates is smooth, it tends to produce a core–shell structure. A hierarchical morphology is preferred when using hairy-like particle

as template. To further confirm our idea, we introduce polymer particles (SMA-3, and SMA-3-2) into the hydrolysis reactions of TEOS. PEG chains were used to replace PAA chains to discuss the steric-effect of polymer chains. Figure 4 shows a typical TEM image of polymer/silica with different morphologies. The core–shell particles were formed using SMA-3 as template and berry-like particles were obtained using SMA-3-2 as template. When SMA-3 was used as template, the anhydride groups can undergo hydrolysis and generate carboxyl groups. During the *in situ* sol-gel process of TEOS, the weak acid–base interaction between carboxyl groups, DEA, and hydrolyzed TEOS molecular can guide the nuclei and growth of silica particles. Finally, the core–shell structures can be obtained and the shell thickness was about 12 nm. When PEG chains were introduced on the surface of template spheres, few silica nanoparticles (diameter is no more than 10 nm) can be observed on the sphere's surface. This indicated that the PEG chains located at the particle's surface prevent the silica particles nuclei and growth during the *in situ* sol-gel reaction. At the same time, there are no weak interactions between PEG chains and silica particles (such as electrostatic interaction, hydrogen bond, acid–base interaction, etc.), and this will make the decrease of silica particles adsorbed on the surface.

The wettability of the surface was characterized by water CA using a 4 μL water droplet as the indicator. After a subsequent spin-coating the berry-like particles on glass substrate, a hierarchically structured surface was achieved. Before modification, the CA of core–shell and berry-like polymer/silica composite particles were 23.8° and 58.4°, respectively. The surface of core–shell polymer/silica particle covered with Si-OH groups, which turns the hydrophobic surface to hydrophilic. As the silica particles are embedded discontinuously in the berry-like particle's surface, the CA is decreased slightly from 81.7° (SMA-3-1) to 58.4°. To give the surface a hydrophobic property, the films were modified with dodecyltrichlorosilane. The CA was 131.2° for berry-like particles. As a comparison the CA on the core–shell particles was 134.7° (see Supporting Information Figure S2), conforming that core–shell structured surfaces contain more Si—OH than the berry-like particles. In our previous

Table III. Average Particle Size (D_n, D_w), PDI and CA of Poly(S-*co*-MA) and Hairy Poly(S-*co*-MA)-g-PEG Particles

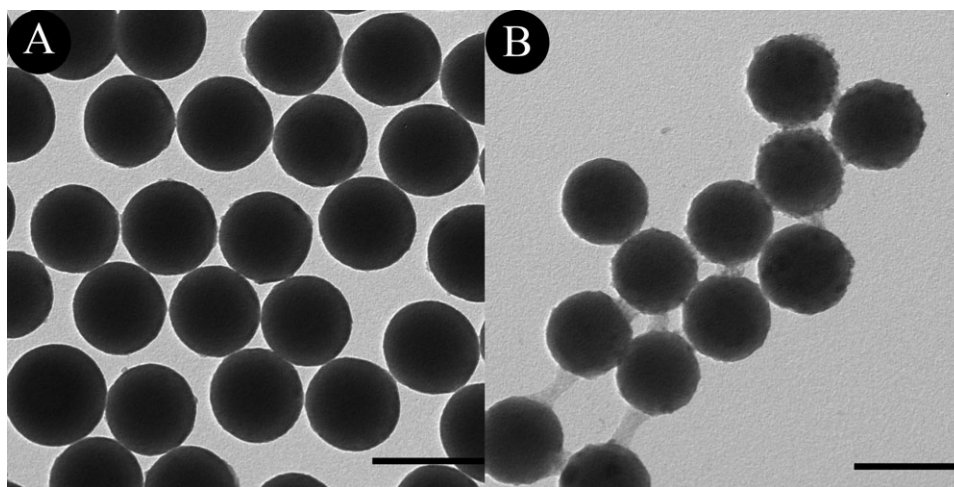| Runs	D_n (nm)	D_w (nm)	PDI	CA (°)
SMA-1	404.3 ± 5.3	404.5	1.001	87.2
SMA-2	345.4 ± 7.7	345.9	1.001	89.1
SMA-3	404.4 ± 11.3	405.3	1.002	95.7
SMA-3-1	413.6 ± 15.8	415.4	1.004	81.7
SMA-3-2	418.1 ± 15.3	420.2	1.005	77.9
SMA-3-3	405.2 ± 7.6	405.7	1.001	77.8

Figure 4. TEM images of composite particles prepared by sol-gel process. (A)P(S-*co*-MA)/SiO$_2$, (B) P(S-*co*-MA)-g-PEG/SiO$_2$. The scale bar is 500 nm.

work,[19,20] berry-like particles can be prepared based on PAA-functionalized PS particles as templates. The CA was over than 150°, which was due to the diameter of silica particles was large (varying from about 20–120 nm) and air can be trapped in the interstices of the rough surface. Here, the diameter of silica particles was less than 10 nm and the distribution of silica particles on the surface was rare. So, the final CA was about 130°. This phenomenon was contributed to tthat PEG chains showed a steric repulsion for the adsorption of silica particles.

CONCLUSION

Hairy particles were successfully prepared through esterification of anhydride groups on the surfaces of poly(S-*co*-MA) sphere with the hydroxyl end groups on PEG. The hydrophilicity of the surface was improved by PEG immobilization. The hairy morphology is more obvious with increase of grafting amount of PEG. The monodisperse poly(S-*co*-MA)-g-PEG particles ∼410 nm in diameter were used as cores and nanosized silica particles were then assembled at the surface of cores in the hydrolysis reaction to construct the berry-like particles. This study proves that the PEG chains exhibit steric-effect during the formation of berry-like particles. This is a useful method to build different dual-sized structured. Optimization of the method aimed at controllable hierarchic structures is in progress.

ACKNOWLEDGMENTS

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