

Polymer–Metal Composite Particles: Metal Particles on Poly(St-*co*-MAA) Microspheres

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ABSTRACT: Poly(styrene-*co*-methacrylic acid) P(St-*co*-MAA) microspheres with a monodisperse size distribution were prepared by emulsifier-free emulsion copolymerization of St and MAA. The effects of MAA content on the polymerization rate and the content of MAA in the copolymer were investigated by gravimetric and IR methods, respectively. The results of XPS measurement indicated the presence of a carboxyl functional group. By chemical metal deposition, nickel or palladium particles were formed and deposited on the surface of P(St-*co*-MAA) microspheres to form P(St-*co*-MAA)Ni or P(St-*co*-MAA)Pd composite particles. XRD measurement and TEM observation confirmed that nickel and palladium metal particles in a small size (20–40 nm) were distributed on surface of the copolymer microspheres. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1693–1698, 2000

Key words: P(St-*co*-MAA) microspheres; composite particles; chemical metal deposition

INTRODUCTION

Polymer–metal composite particles consisted of a polymer and metal particles either on the surface or in the interior (core) of the polymer microspheres. Dependent upon the type of metal, they exhibited many properties such as magnetic, electrical, catalytic, and optical properties and, therefore, have extensive potential applications in the fields of medical science, biology, catalysts, and coatings and in many other fields.^{1–5}

For the preparation of composite particles with surface metal particles, chemical metal deposition (or electroless plating) appears to be very convenient and effective in modulating the content, morphology, and distribution of metal particles on the surface of polymer microspheres and,

thus, on the final properties of the composite particles.^{6,7} Up to the present, investigations on the preparation of polymer–metal composite particles by chemical metal deposition on submicrometer polymer microspheres are quite limited. Therefore, a systematic research was carried out in this laboratory regarding the preparation of polymer–metal composite particles and the morphologies, structures, as well as properties of the composite particles. In addition, ways to improve the stability of metal particles and to prevent their oxidation and mutual agglomeration were tried. To prepare polymer–metal composite particles by chemical metal deposition on the surface of polymer microspheres, some functional groups should be introduced onto the surface of microspheres.⁶ Emulsifier-free emulsion polymerization is well known to produce submicrometer-size polymer microspheres. Through emulsion copolymerization, it is possible to introduce suitable functional groups on the surface of polymer microspheres. In

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Table I Preparation of P(St-co-MAA) Microspheres

Sample	MAA1	MAA2	MAA3	MAA4
St (g)	20	20	20	20
MAA (g)	1	2	3	4
APS (g)	0.1	0.1	0.1	0.1
H ₂ O (mL)	200	200	200	200
Polymerization time (h)	7	7	7	7
Diameter (nm) ^a	—	300	175	—
Rb (nm) ^b	176	117	106	82

^a Measured on TEM photograph.

^b Hydrodynamic radius measured by dynamic light scattering (DLS, ALV/SP-125).

this work, an emulsifier-free emulsion copolymerization technique was used to prepare monodisperse polymer microspheres with surface carboxyl groups. Then, by the method of chemical metal deposition, nickel or palladium particles were formed and deposited on the surface of the polymer microspheres to form polymer-metal composite particles.

EXPERIMENTAL

Materials

Styrene (St, CR) and methacrylic acid (MAA, CR) were purified by distillation under reduced pressure. Ammonium persulfate (APS), tin chloride dihydrate (SnCl₂•2H₂O), palladium chloride (PdCl₂), nickel chloride hexahydrate (NiCl₂•6H₂O), and sodium hypophosphate (NaH₂PO₂•H₂O) were all analytical grade and used without further purification.

Preparation of Polymer Microspheres

P(St-co-MAA) microspheres were prepared by emulsifier-free emulsion copolymerization of St and MAA using APS as an initiator. The recipe and conditions are given in Table I. The reaction was carried out in a nitrogen atmosphere at 70°C with mechanical stirring at around 350 rpm. The resulting copolymer microspheres were purified by repeating dialysis of the latex. Conversion was determined by the gravimetric method.

Preparation of P(St-co-MAA)Ni Composite Particles

To the P(St-co-MAA) latex containing 2 g polymer microspheres, a certain amount of an acid solu-

tion of SnCl₂ was added and stirred for 1 h at 45°C. Then, the temperature was increased to 70°C, and a dilute acid solution of PdCl₂ (polymer/PdCl₂ = 500/L in weight ratio) was added and reacted for 1 h. The solution turned gray upon addition of PdCl₂, indicating a reduction of the Pd ion to the Pd metal, thus forming P(St-co-MAA)Pd "active" copolymer particles. This dispersion was dialyzed for 2 days until neutralization, then stored for the preparation of polymer-metal composite particles.

Into the aqueous dispersion of "active" copolymer particles [P(St-co-MAA)Pd, 1 g], an electroless plating solution containing NiCl₂•6H₂O (0.24 g), KNa-tartrate (1.4 g), and concentrated ammonia (2 mL) was added. The solution was heated at 50°C for 1 h. An aqueous solution of NaH₂PO₂•H₂O (0.21 g) was added. The reaction was kept at this temperature for 1 h. The solution turned dark, indicating reduction of the nickel ion. The composite particles were separated by filtration. A powder of deep gray was obtained. Its magnetic property could be qualitatively confirmed using a small magnet.

Preparation of P(St-co-MAA)Pd Composite Particles

For preparation of P(St-co-MAA)Pd composite particles, P(St-co-MAA) latex (MAA2, containing 1 g polymer microspheres) was heated and maintained at 70°C under a N₂ atmosphere. The acid solution (PdCl₂, 40 mg) was added through a funnel and kept at this temperature for 40 min. The temperature of the solution was decreased to 40°C and NaH₂PO₂•H₂O (0.2 g) in an aqueous solution was added. The reaction was carried out at 40°C for 0.5 h. The color of the solution turned purple-gray. After the reaction, the dispersion was dialyzed for 1 day and then dried.

Characterization

The size and morphology of the copolymer microspheres and the composite particles were investigated by a Hitachi-800 transmission electron microscope (TEM). FTIR spectra measurements were performed on a VECTOR-22 IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB Mark II system with MgKα radiation. XRD patterns were measured by an X-ray diffractometer (Y-4Q, China).

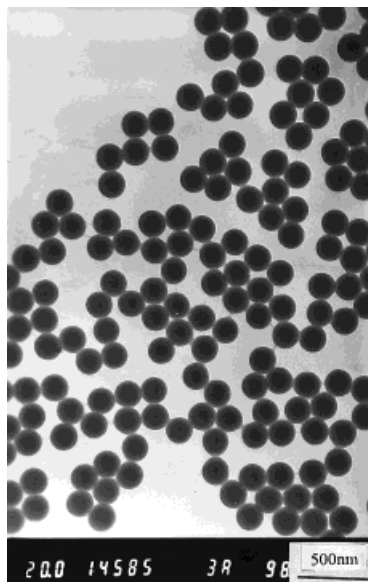


Figure 1 TEM photograph of P(St-co-MAA) microspheres (MAA3).

RESULTS AND DISCUSSION

Preparation of P(St-co-MAA) Copolymer Microspheres

Emulsifier-free emulsion polymerization has been widely used to prepare monodisperse microspheres. By copolymerization of St with MAA, it is feasible to introduce carboxyl groups on the surface of polymer microspheres. (The recipe and conditions are listed in Table I).

Figure 1 shows a typical TEM photograph of the P(St-co-MAA) microspheres (MAA3, MAA/St = 15%). It can be seen that the microspheres with a diameter of 175 nm are spherical in shape and monodisperse in size.

Figure 2 illustrates the effect of the concentration of MAA in the polymerization system on the polymerization rate of St. As the concentration of MAA increased from 15 to 20%, the polymerization rate increased. As we know, the classical Smith-Ewart theory interpreted that in emulsion polymerization the polymerization proceeds inside the monomer-swollen particles which originated from micelles formed from surfactant molecules. The rate of polymerization is proportional to the number of the particles, which is affected by the concentration of the emulsifier. The function of MAA can be explained by the theory of Fitch and Tsao.⁸ Persulfate radicals initiated the polymerization of St and MAA in the aqueous

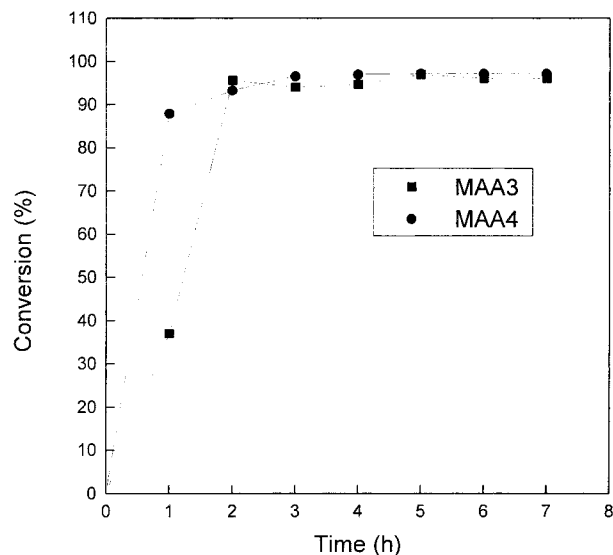


Figure 2 Conversion of copolymerization of St and MAA versus time.

phase to form an oligomer rich in MAA. They combined and nucleated to form particles and also stabilized the monomer drops. Polymerization continued inside the monomer-swollen particles. Therefore, a higher concentration of MAA was used, more stable particles were formed, and the diameter of the particles decreased (see Table I).

FTIR spectra of the P(St-co-MAA) copolymer microspheres are shown in Figure 3. A characteristic peak at 1698 cm^{-1} is attributed to carbonyl stretching of the carboxyl groups, indicating the copolymerization of MAA and St. With increase of the MAA content in the copolymerization system, the intensity ratio of the peak at 1698 cm^{-1} to that at 1453 or 1493 cm^{-1} clearly increases, sug-

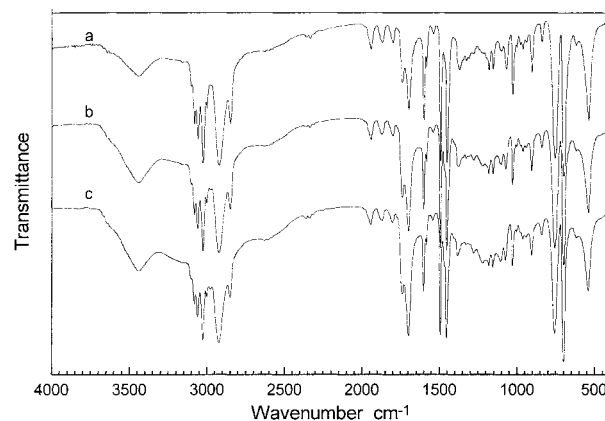


Figure 3 IR spectra of poly(St-co-MAA) microspheres: (a) MAA1; (b) MAA2; (c) MAA3.

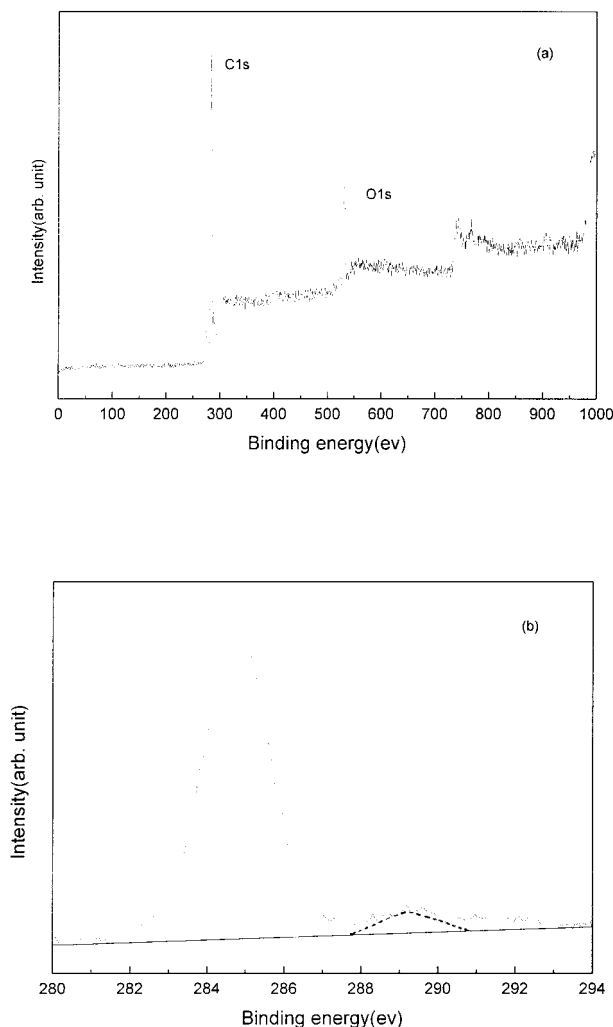


Figure 4 XPS spectra of P(St-co-MAA) microspheres: (a) full-scan; (b) C1s spectrum.

gesting more MAA was copolymerized with St, thereby leading to higher content of MAA in the copolymer microspheres.

As we mentioned, the oligomers rich in MAA acted as emulsifiers; thus, they should be prone to locate on the surface of the particles. To confirm this deduction, P(St-co-MAA) microspheres purified by dialysis were studied by XPS. The results are shown in Figure 4. The full-scan spectrum [Fig. 4(a)] indicates that the surface elements are carbon and oxygen (hydrogen cannot be detected by XPS). The C1s spectrum in Figure 4(b) clearly shows the presence of carboxyl groups (binding energy at 289.2 eV) on the surface of the microspheres. This observation proves that when MAA is copolymerized with St it stayed at the particle-water interface due to its hydrophilicity and thus stabilized the copolymer particles.

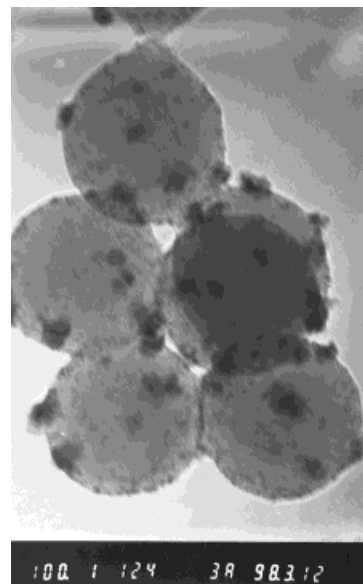


Figure 5 TEM photograph of P(St-co-MAA)Ni composite particles (MAA3).

Preparation of P(St-co-MAA)Ni Composite Particles

P(St-co-MAA) microspheres having carboxyl groups on the surface were used to prepare polymer-metal composite particles by the chemical metal deposition method (electroless plating). Figure 5 shows a typical TEM photograph of P(St-co-MAA)Ni composite particles. It can be seen that small nickel particles (20–40 nm in size) were formed on the surface of the P(St-co-MAA) microspheres.

XRD measurement of the P(St-co-MAA)Ni composite particles was conducted and is shown in Figure 6. The peaks at $2\theta = 44.1^\circ$ and 51.6° observed in

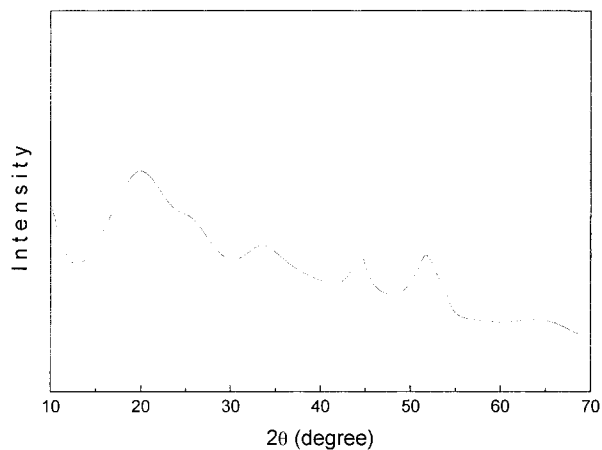


Figure 6 XRD pattern of poly(St-co-MAA)Ni composite particles.

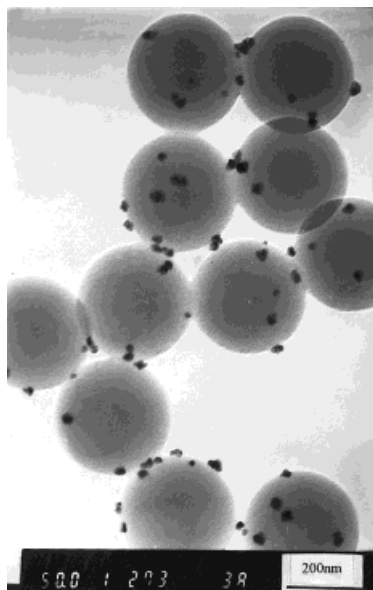


Figure 7 TEM photograph of P(St-co-MAA)Pd composite particles (MAA2).

Figure 6 are attributed to the (111) and (200) planes of zerovalent nickel, respectively. This indicates that the zerovalent nickel in the particles was formed on the microsphere surface. Such P(St-co-MAA)Ni composite particles showed a magnetic property, which was proved by using a small magnet. It should be noted that alkaline (usually at higher PH) chemical metal deposition gave crystalline nickel which contained no or a very small amount of phosphorus.⁹ However, when the PH of the deposition solution decreased, the amount of phosphorus was changed (usually increased) and phosphorus was dispersed in the nickel phase, re-

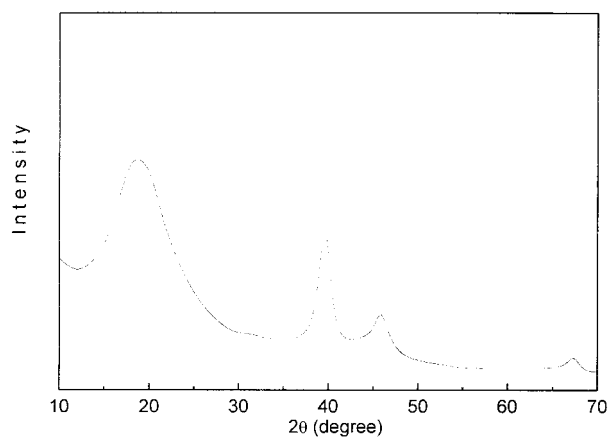


Figure 8 XRD pattern of Poly(St-co-MAA)Pd composite particles.

sulting a different structure, even an amorphous Ni—P structure, thereby leading to a significant change in the magnetic properties. Since an amorphous Ni metal (or alloy) magnet has important potential applications, for example, as a soft magnet, the chemical metal deposition method provides a easy and feasible route to prepare such kinds of materials. Thus, further studies on preparing magnetic, amorphous metal composite particles are under progress in our lab.

Preparation of P(St-co-MAA)Pd Composite Particles

P(St-co-MAA)Pd particles prepared by chemical metal deposition were examined by TEM observation. A typical photograph is shown in Figure 7.

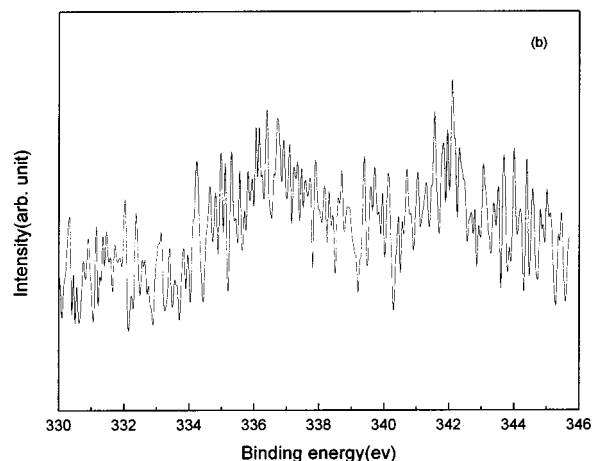
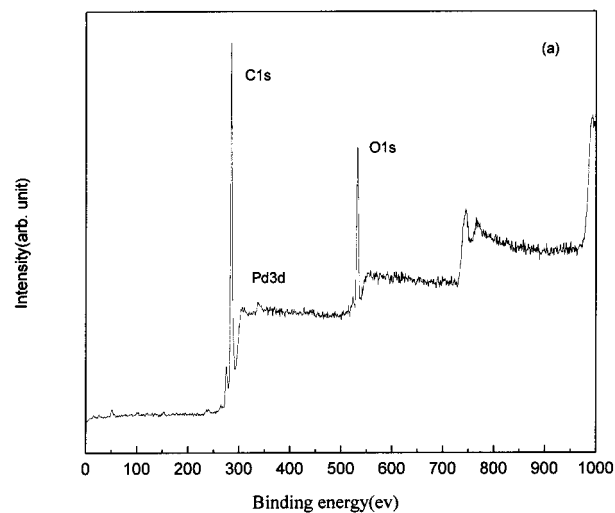


Figure 9 XPS spectra of P(St-co-MAA)Pd particles: (a) full-scan; (b) Pd3d spectrum.

It can be seen that very small palladium particles (20–30 nm in size) were distributed over the surface of the P(St-co-MAA) microspheres. The resulting P(St-co-MAA)Pd latex was quite stable and could not be separated by filtration; thus, it was first dialyzed for 1 day until neutral and then dried at 60°C. XRD measurement of the dried particles was conducted, and the diffraction profile is shown in Figure 8. The peaks at 39.5°, 45.7°, and 67.3° that appear in Figure 8 could probably be attributed to the (111) (40.1°), (200) (46.6°), and (220) (68.1°) planes of palladium metal. This suggests that metal particles were formed on the surface of P(St-co-MAA) microspheres by the reduction of palladium ions.

Results of the XPS measurement of composite particles are given in Figure 9. From the full-scan spectrum [Fig. 9(a)], it can be seen that palladium was present on the surface of the composite particles. The binding energy of the Pd3d peak is close to that of PdO,¹⁰ indicating that the palladium on the surface was in an oxidation state.

CONCLUSIONS

Emulsifier-free emulsion copolymerization of St and MAA was used to prepare P(St-co-MAA) microspheres with a monodisperse size distribution. With increase of MAA content in the emulsion polymerization system, the rate of polymerization and the content of MAA in the copolymers were increased. XPS measurement proved the presence of carboxyl groups on the surface of P(St-co-MAA) microspheres.

P(St-co-MAA)Ni composite particles could be prepared by the chemical metal deposition method. TEM observation and XRD measurement indicated that zerovalent nickel particles were present on the surface of the copolymer microspheres. P(St-co-MAA)Pd composite particles were prepared by the reduction of palladium ions in the presence of P(St-co-MAA) microspheres. XRD measurement and TEM observation confirmed that palladium metal particles with diameters of 20–30 nm were distributed over the surface of the P(St-co-MAA) microspheres.

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