# Characterization and Magnetic Properties of P(St-*co*-4VP) Metal Microspheres

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Received 11 December 1997; accepted 4 June 1998

**ABSTRACT:** Monodispersed poly(styrene-*co*-4-vinylpyridine) [P(St-*co*-4VP)] microspheres were prepared by emulsifier-free emulsion polymerization. The chemical metal deposition was used to prepare magnetic P(St-*co*-4VP)Ni, and P(St-*co*-4VP)Co microspheres exhibited ferromagnetic properties. The morphology of P(St-*co*-4VP) and P(St-*co*-4VP)Ni or Co microspheres was studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Electron spectroscopy for chemical analysis (ESCA) and XRD were used to investigate the valence changement of metals in air. The magnetic properties of the magnetic microsphere were studied. The difference of soft magnetism between P(St-*co*-4VP)Ni and P(St-*co*-4VP)Co microspheres was discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2307–2312, 1998

**Key words:** emulsifier-free emulsion polymerization; chemical metal deposition; magnetic polymer microspheres; magnetic properties

# **INTRODUCTION**

Magnetic polymer microspheres have attracted considerable interest since they exhibit wide applications in the field of medicine, biochemistry, magnetic materials, and many other areas.<sup>1-4</sup> Magnetic polymer microspheres with a polymer core and inorganic shell were generally prepared by suspension polymerization, emulsion polymerization, and chemical metal deposition.<sup>5-10</sup> The particles produced by emulsion polymerization or suspension polymerization have a wide size distribution, and the metals are not all on the surface of the magnetic microsphere; thus, an important consideration is how to prepare uniform polymer microspheres. As we know, the emulsifier-free emulsion polymerization could produce submicrometer, spherical polymer particles with monodispersity, and without emulsifier on the surface. Therefore, it was used to prepare polymer microspheres, then the magnetic polymer microspheres were prepared by chemical metal deposition on the surfaces. To our knowledge, there have been few investigations on the properties of this kind of magnetic polymer microspheres. It might be interesting to proceed this investigations.

## **EXPERIMENTAL**

#### Materials

Deionized water was used in all experiments. Styrene (St, chemical reagent, Centeral Chemical Plant of Shanghai Chemical Reagent Station,

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Journal of Applied Polymer Science, Vol. 70, 2307-2312 (1998)

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Compound	Quantity (g)	
St	18.0	
4VP	3.0	
APS	0.0604	
H <sub>2</sub> O	199	

Table IConditions Used in the Preparationof P(St-co-4VP)Microspheres

Temperature, 70  $\pm$  0.1°C; speed of stirrer, 300 rpm.

Shanghai, China) was distilled at 40°C/14.5 mm Hg and stored at 4°C. 4-Vinylpyridine (4VP, MERCK-Schuchardt, München, Germany ) was distilled at 51°C/12 mm Hg before use. Ammonium persulfate (APS, Anjian Chemical Plant of Shanghai, Shanghai, China), tin chloride dihydrate (SnCl<sub>2</sub>  $\cdot$  2H<sub>2</sub>O, Shanghai Fourth Chemical Plant, Shanghai, China), palladium chloride (PdCl<sub>2</sub>, Dahao Chemical Plant of Guangdong, Guangzhou, China), nickel chloride hexahydrate (NiCl<sub>2</sub>  $\cdot$  6H<sub>2</sub>O, Yixin Second Chemical Plant of Jiangsu, Yixin, China), cobalt chloride hexahydrate (CoCl<sub>2</sub> · 6H<sub>2</sub>O, Shanghai Second Chemical Plant, Shanghai, China), and sodium hypophosphite monohydrate (NaH<sub>2</sub>PO<sub>2</sub>  $\cdot$  H<sub>2</sub>O, Taicang Second Chemical Plant of Jiangsu, Taicang, China) were analytical grade and were used without further purification.

## **Preparation of Polymer Microspheres**

A typical recipe of preparing P(St-co-4VP) microsphere is shown in Table I. All the ingredients except the APS solution were placed in a 250-mL 5-neck round-bottom flask equipped with stirrer, reflux condenser, thermometer, nitrogen inlet tube, and feeding funnel. The reaction system was purged with nitrogen for 1 h prior to the addition of the APS solution. The reaction lasted for 8 h at 70°C and 300 rpm speed of the stirrer. The latex obtained was cooled and filtered through a glass sinter filter, then centrifuged at 15000 rpm over 10 min, and the precipitates were dispersed again in water using an ultrasonic bath. The centrifugation procedure was repeated 3 times. Then, the formed latex dialyzed in deionized water until the specific conductivity of water kept constant, and the water was changed each day for removing the unreacted monomer and initiator.

Total conversion was determined gravimetrically. Into about 1 g of latex sampled at set intervals, 0.01 g of hytroquinone, then about 0.2 mL of anhydrous alcohol were added successively. The mixture was dried in vacuum at 80°C until the weight of the sample was kept constant. The total conversion was calculated by:

$$C(\%) = \frac{W_1/W_2}{m_1/m_1 + m_2} \times 100\%$$
(1)

Here, C is the total conversion of the polymer particles,  $W_1$  is the weight of dried sample,  $W_2$  is the weight of the sample withdrawn from the reactor,  $m_1$  is the weight of total monomer, and  $m_2$  is the weight of all medium.

#### **Preparation of Magnetic Microsphere**

P(St-co-4VP)Ni and P(St-co-4VP)Co magnetic microsphere were prepared by chemical metal deposition. The preparation was the same as that in our previous work.<sup>11</sup>

#### Characterization

The size and morphology of polymer microspheres and magnetic microspheres were investigated by JCM-100CX transmission electron microscopy (TEM) and X-ray diffraction (XRD,  $D/\max-\gamma A$ ) analysis. The latex particle size was calculated based on the sizes of about 100 particles on different regions of TEM photos. Weight-average diameter (D) was calculated based on equation (2), as follows:

$$D = \sum n_i d_i^3 / \sum n_i d_i^2 \tag{2}$$

where  $n_i$  is the number of particles with diameter  $d_i$ .

The nitrogen content was quantified using CarloErba 1106 Elementary Analysis Apparatus. The metal content was determined by Hitachi 180-50 Atomic Absorption Spectrum using acetylene-air mixture at  $\nu = 230$  nm.

Electron spectroscopy chemical analysis (ESCA) spectra were obtained using an ESCALAB Mark II with an Alk $\alpha$  X-ray source radiation generated at 15 keV and 20 mA.

Magnetic measurements at room temperature were performed on vibrating sample magnetometer (VSM, EG&G, Inc., Princeton, New Jersey USA). The variation of magnetic susceptibility with temperature was tested on Model 5210



monodispersed and spherical. The weight-average diameter d was about 292 nm.

Figures 1(b) and 1(c) are TEM photos of P(St-co-4VP)Ni and P(St-co-4VP)Co microspheres, respectively. Compared with particles shown in Figure 1(a), the surface of the particles containing metals was not so smooth. It is very difficult to disperse these magnetic polymer microspheres because of static magnetism between the particles.

Figure 2 shows the XRD profiles of P(St-co-4VP), P(St-co-4VP)Ni, and P(St-co-4VP)Co microspheres, respectively. In addition to the diffraction peaks of the P(St-co-4VP) microspheres, some additional peaks occurred in the patterns of P(St-co-4VP)Ni and P(St-co-4VP)Co microspheres. Comparison with data listed in the Powder Diffraction File,<sup>12</sup> these new phases were identified as Ni and Co components. It is clear that P(St-co-4VP)Ni and P(St-co-4VP)Co microspheres are composed of P(St-co-4VP) and nickel or cobalt, respectively. Tamai et al. reported that the emulsifier-free emulsion copolymerization of styrene and hydrophilic monomers resulted in the water soluble polymer, such as acrylamide and 2-hydroxyethyl methacrylate, located on the surface of the particles.<sup>13,14</sup> Therefore, we can imagine that P4VP (4VP is soluble in hot water) existed on the surface layer of the particles, and Ni



**Figure 1** TEM of (a) the P(St-*co*-4VP) microsphere, (b) the P(St-*co*-4VP) Ni microsphere, and (c) the P(St*co*-4VP) Co microsphere.

Lock-In Amplifier (EG&G Princeton Applied Research, Princeton, New Jersey).

# **RESULTS AND DISCUSSION**

TEM photos of the P(St-co-4VP) particles shown in Figure 1(a) demonstrated that the particle was



**Figure 2** XRD of (a) the P(St-*co*-4VP) microsphere, (b) the P(St-*co*-4VP) Ni microsphere, and (c) the P(St-*co*-4VP) Co microsphere.





**Figure 3** ESCA spectra of (a) the P(St-*co*-4VP) Ni microsphere and (b) the P(St-*co*-4VP) Co microsphere.

or Co was formed on the surface of P(St-co-4VP) microspheres. TEM observation confirmed this result.

The P(St-*co*-4VP)Ni and P(St-*co*-4VP)Co microspheres were investigated by ESCA analysis (see Fig. 3).

As shown in Figure 3, the electron binding energy of  $Ni_{2P3/2}$  was 853.25 eV, close to that of NiO ( $Ni_{2P3/2} = 853.10$  eV),<sup>15</sup> rather than that of Ni ( $Ni_{2P3/2} = 852.20$  eV). There was a shoulder

peak in low kinetic energy region (858.93 eV). Usually, the shoulder peak is called the shake-up peak. The binding energy of shoulder peak is higher by several electron volt than the binding energy of main peak. Generally, the emergence of shake-up peak is the characteristic of transition metal's oxide.<sup>16</sup> This indicates the existence of NiO in P(St-co-4VP)Ni microsphere. However, the XRD result showed that no NiO-only Ni-existed in P(St-co-4VP)Ni particles. The same results was obtained for P(St-co-4VP)Co particles. Therefore, it is reasonable from these results that Ni(0) or Co(0) located on the surface, and the metal nanoparticles were spontaneously oxidized in air to form NiO or CoO. Tamai et al.<sup>17</sup> discovered the same phenomenon and gave the same conclusion when they studied the catalyst P(Stco-Vlz-co-DVB)Pd and P(St-co-Vlz-co-DVB)Pt using ESCA and XRD analyses.

## **Magnetic Properties**

The alternating magnetic susceptibility of P(Stco-4VP)Ni and Co,  $\chi$  as a function of temperature is shown in Figure 4. It indicated that as the temperature decreased, the magnetic susceptibility also decreased. Thus, P(St-co-4VP)Ni and P(St-co-4VP)Co magnetic microspheres are not paramagnetic substances. Generally, the paramagnetic substance accords with the following Curie–Weiss law:



**Figure 4** Magnetic susceptibility versus temperature: (a) P(St-*co*-4VP) Ni microsphere; (b) P(St-*co*-4VP) Co microsphere.

$$\chi = \frac{C}{T - T_c} \tag{3}$$

where C is Curie constant, and  $T_c$  is the Curie temperature.

The value of magnetic susceptibility of magnetic microsphere is not only positive but also large. Therefore, P(St-co-4VP)Ni and P(St-co-4VP)Co magnetic microspheres are ferromagnetic materials. Comparing to the P(St-co-4VP)Co magnetic microsphere, the P(St-co-4VP)Ni magnetic microsphere was easily magnetized because of its higher magnetic susceptibility.

According to the value of the coercive force  $(H_c)$ , the ferromagnetic substance is classified



**Figure 5** Magnetic hysteresis loop of (a) the P(St-*co*-4VP) Ni microsphere and (b) the P(St-*co*-4VP) microsphere.

Table IIMagnetic Properties of MagneticPolymer Microspheres

Magnetic Particle	$H_c$ (Oe)	$\sigma_{\!s} \ ({ m emu/g})^{ m a}$	$\sigma_r$ $(emu/g)^b$
P(St-co-4VP)Ni P(St-co-4VP)Co	$52\\740$	2.9 19.9	1.17.9

<sup>a</sup>  $\sigma_s$  is the saturated magnetization intensity.

<sup>b</sup>  $\sigma_r$  is the remanent magnetization intensity.

into 2 types. One is soft magnetic material, whose coercive force is small, and the magnetic hysteresis loop is long and narrow; another is hard magnetic material, whose coercive force is large  $(10^2-10^4)$ . The remnant magnetic induction is large, and the magnetic hysteresis loop is wide. It can be inferred from Figure 5 that the magnetic polymer microspheres can be classified as soft magnetic materials. The soft magnetism of P(Stco-4VP)Ni microspheres is superior to P(St-co-4VP)Co microspheres (Table II).

## CONCLUSIONS

Spherical particles of P(St-co-4VP) with narrow distribution and poly(4-vinylpyridine) located on the surface were prepared by emulsifier-free emulsion polymerization. Under appropriate conditions, the Ni or Co ion coordinated with the pyridine group on the surface of the particles could be easily reduced to Ni(0) and Co(0), and magnetic P(St-co-4VP)Ni and P(St-co-4VP)Co microspheres with ferromagnetic property were formed. The results of magnetic properties showed that the magnetic susceptibility decreased with decrease of temperature; they are classified as soft magnetic material. The coercive force  $(H_c)$  of P(St-co-4VP)Ni microsphere is 52 Oe, its saturation magnetization intensity is 2.9 emu/g, and the remnant magnetic intensity is 1.1 emu/g; the coercive force of P(St-co-4VP)Co microsphere is 740 Oe, its saturation magnetization intensity is 19.9 emu/g, and the remnant magnetic intensity is 7.9 emu/g.

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