Preparation and Magnetic Properties of [P(St-*co*-AA)]Ni Microspheres

YANMEI WANG, YOUXIANG WANG, LINXIAN FENG

Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, People's Republic of China

ABSTRACT: Seeded emulsifier-free emulsion polymerization was used to prepare poly(-styrene-*co*-acrylic acid)[P(St-*co*-AA)] microspheres. There are carboxyl groups on the surface of the P(St-*co*-AA) microspheres. Under appropriate conditions, the carboxyl react with NiCl$_2$, etc., to form magnetic [P(St-*co*-AA)]Ni microspheres which exhibit ferromagnetic properties. ESCA analysis shows that the valence of nickel on the surface of the magnetic [P(St-*co*-AA)]Ni microspheres is 2. IR analysis confirmed that there are carboxylate groups present in the magnetic [P(St-*co*-AA)]Ni microspheres. Magnetic properties of this kind of polymer microspheres were studied. Results showed that the magnetic susceptibility decreased with decreases in temperature. The result of magnetic hysteresis loop studies showed that the obtained magnetic microspheres are categorized as magnetically soft materials. The coercive force (Hc) is 32 Oe, and the saturation magnetization is 1.79 emu/g. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1843–1848, 1997

Key words: seeded emulsifier-free emulsion polymerization; magnetic polymer microspheres; magnetic properties; magnetic domain

INTRODUCTION

Magnetic polymer microspheres are composed of polymer and inorganic particles, so they exhibit many special properties. For example, their density, magnetic properties, mechanical properties, and fluidity are different from pure polymer and pure inorganic materials. The magnetic polymer microspheres are used extensively in the field of medical science, biology, magnetic materials, and many other areas.[1] The structure of magnetic polymer microspheres depends on its preparation method. Many methods are used to prepare the magnetic polymer microspheres with a polymer core and inorganic shell. Among these methods are suspension polymerization, emulsion polymerization, and chemical metal deposition.[2–4] The

particles produced by emulsion polymerization and suspension polymerization have a wide size distribution, so an important consideration of these methods lies in how to produce polymer microspheres of uniform size. The size distribution of polymer microspheres is considered to be determined by coalescence in the course of polymerization.[5] There have been few investigations on the preparation of the magnetic polymer microspheres by chemical metal deposition. No matter what synthesis methods are used, there are few studies on the magnetic properties of polymer microspheres.

Emulsifier-free emulsion polymerization is well known to produce submicrometer-size polymer particles. The advantages of using this method lies in the production of highly spherical polymer particles which are monodisperse in size.[6] Seeded emulsion polymerization can be used to prevent the formation of new nucleates in the polymerization process. Thus, in this article, seeded emulsifier-free emulsion polymerization techniques are used to prepare monodisperse polymer micro-

Table I   Conditions Used in the Preparation of P(St-*co*-AA) Microspheres

Ingredient		Seed	Second-stage Feed	Total
St	(g)	2.4	17.6	20.0
AA	(g)	0	4.0	4.0
APS	(g)	0.0144	0.0816	0.0960
H2O	(g)	158.5	17.5	176.0

Temperature, 70 ± 1°C; speed of stirrer, 300 rpm.

spheres with functional carboxyl groups; the carboxyl groups react with inorganic particles under certain conditions, thus forming magnetic polymer microspheres.

EXPERIMENTAL

Materials

Deionized water was used in all experiments. Styrene (St; chemical reagent, Central Chemical Plant of Shanghai Chemical Reagent Station) was distilled at 40°C/14.5 mmHg and stored at 4°C. Acrylic acid (AA; chemical reagent, Wulian Chemicals of Shanghai) was distilled at 40°C/12 mmHg before use. Ammonium persulfate (APS, Anjian Chemical Plant of Shanghai), tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$, Shanghai Fourth Chemical Plant), palladium chloride ($PdCl_2$, Dahao Chemical Plant of Guangdong), nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, Yixin Second Chemical Plant of Jiangsu), and sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$, Taicang Second Chemical Plant of Jiangsu) were analytical grade and used without further purification.

Preparation of Polymer Microspheres

A typical recipe for P(St-*co*-AA) microspheres is shown in Table I. The polymerization temperature was fixed at 70°C, and the speed of the stirrer was 350 rpm in a nitrogen atmosphere to eliminate oxygen effects. Total conversion was determined gravimetrically. First, batch polymerization was used to prepare PSt seed particles. All the ingredients except the APS solution were placed in a 250 mL five-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. After 3 h, the conversion was above 95%. PSt served as the seed and AA (feed rate: 0.02 g/min), St (feed rate: 0.1 g/min), and APS (dissolved in 17.5 mL of water, feed rate: 0.1 g/min) were added to this container. The reaction was continued for 3 h after the feed was finished. The conversion was above 90%. The resulting latex particles were cooled and filtered through a glass sinter filter; then, the resulting latex was centrifuged, taking over 10 min at 15,000 rpm and the precipitates were dispersed again in water using an ultrasonic bath. The centrifugation procedure was repeated three times. Then, the latex dialyzed for over 1 week and the water was changed each day.

Preparation of Magnetic Microspheres

Poly(St-*co*-AA) latex (5 g/50 mL) was dispersed in water (150 mL). To this dispersion, $SnCl_2 \cdot 2H_2O$

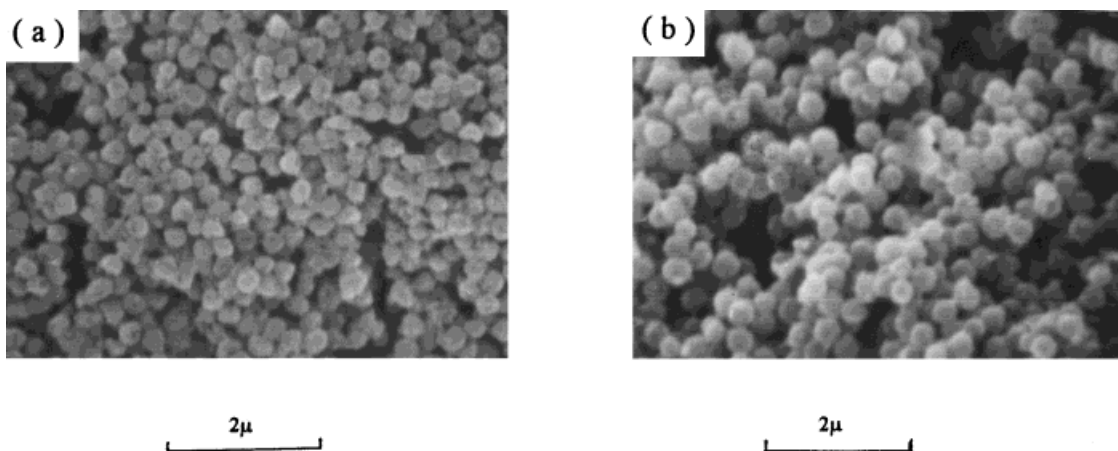**Figure 1**   SEM images of (a) P(St-*co*-AA) microspheres and (b) [P(St-*co*-AA)]Ni microspheres.
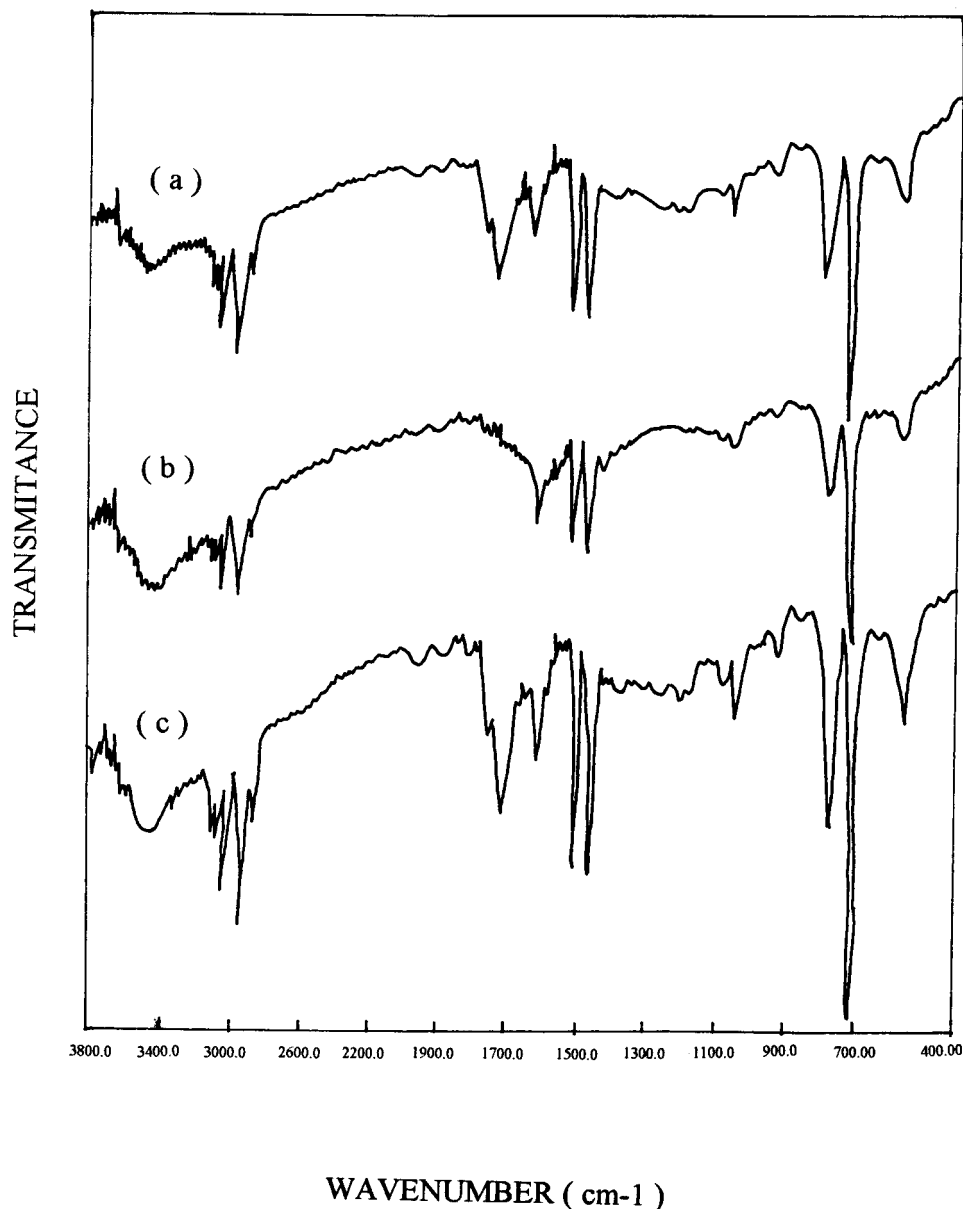
WAVENUMBER (cm-1)

Figure 2   IR spectra of (a) P(St-*co*-AA) particles, (b) [P(St-*co*-AA)]Ni particles, and (c) [P(St-*co*-AA)Ni particles treated with HCl.

was added and stirred at 350 rpm for 1 h at 45°C, and the mixture was separated by centrifugation and redispersed in water. The centrifugation was repeated three times. The solids of the removed particles were dispersed in water (150 mL), and an aqueous solution of $PdCl_2$ (10 mg) was then added with stirring for 1 h at 70°C. These particles were again removed. The product was dispersed in water (150 mL) and $NiCl_2 \cdot 6H_2O$ (1.19 g) was added. The dispersion was stirred at 70°C for 1 h; then, $NaH_2PO_2 \cdot H_2O$ (1.06 g) was added. The mixture was stirred for 1 h and the dispersion was separated using a filter and redispersed in the water. The

above procedure was repeated until the filtrate was colorless and transparent; then, the particles were dried at room temperature in a vacuum. A black powder resulted. The magnetic properties of these particles were qualitatively confirmed using a simple magnetic stirring bar.

Washed Magnetic Microspheres

A prescribed amount of hydrochloric acid (HCl) was added to a beaker with a specific quantity of [P(St-*co*-AA)]Ni microspheres, stirred, and washed with water, and the process was repeated until there was
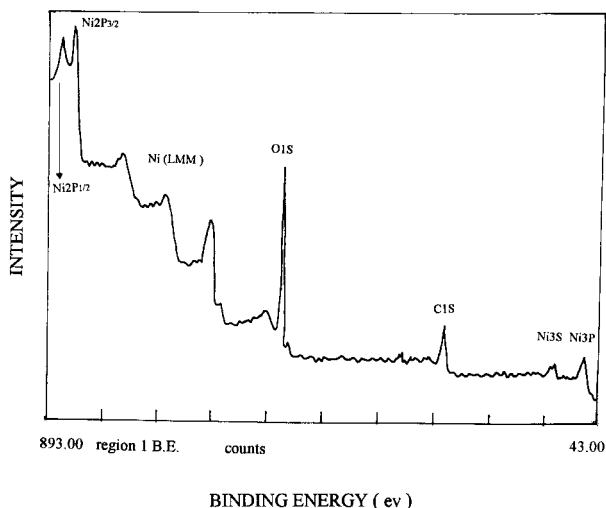
Figure 3 ESCA curve for [P(St-*co*-AA)]Ni; the binding energy for Ni2P3/2 is 854.1 eV.

no nickel present in the [P(St-*co*-AA)]Ni; the black powder become the same color as that of the original P(St-*co*-AA) particles. All of the filtrate was saved for atomic absorption analysis.

Characterization

The size and morphology of the P(St-*co*-AA) microspheres were investigated by scanning electron microscopy (SEM) and a Malvern Autosizer 2C. An SEM (JSM-T20 scanning microscope) was used to study the size and morphology of the [P(St-*co*-AA)]Ni particles.

The surface carboxyl groups was quantified using an acid–base titration.[7] A prescribed amount of dry P(St-*co*-AA) particles ($\sim$ 0.1 g) was dissolved in the mixed solution of methanol (CH_3OH) and tetrahydrofuran (THF), the volume ratio of which is $V_{CH_3OH}/V_{THF} = \frac{1}{4}$. The indicator is phenolphthalein. The solution was titrated using a standard sodium hydroxide solution; then, the content of the carboxyl groups was measured.

The composition and structure of the particles were confirmed by IR analysis (Nicolet 5DX FTIR). Electron spectroscopy chemical analysis (ESCA) spectra were obtained using an ESCALAB Mark II with an AlKα X-ray source radiation generated at 15 keV and 20 mA. The nickel content in the [P(St-*co*-AA)]Ni particles was measured by an atomic absorption spectrum, using an acetylene–air mixture, at a wavelength of 230 nm.

Magnetic measurements at room temperature were obtained for the [P(St-*co*-AA)]Ni microspheres using a vibrating sample magnetometer (VSM; EG&G, Inc., USA). The variation of mag-

netic susceptibility with temperature was tested by a mutual inductance method (EG&G Princeton Applied Research, Model 5210, Lock-In Amplifier).

RESULTS AND DISCUSSION

Particle Characterization

A scanning electron micrograph of the P(St-*co*-AA) particles is shown in Figure 1(a). The micrograph the P(St-*co*-AA) is monodisperse and somewhat deformed. The diameter of the particle is about 200 nm. This result is in agreement with the result obtained using the Malvern Auto Sizer 2C: 197.0 nm.

Figure 1(b) is a scanning electron micrograph of the magnetic polymer particle [P(St-*co*-AA)]Ni; these particles are highly spherical. In Tamai et al.'s previous work[8,9] on the characteristics of fine copolymer particles prepared by emulsifier-free emulsion polymerization, they reported that the copolymerization of hydrophilic monomers such as acrylamide and 2-hydroxyethyl methacrylate resulted in the formation of a water-soluble polymer layer on the surface of the particles. From this result, we can imagine the presence of flexible polymer chains (carboxyl group) protruding from the surface of these copolymer particles, but when the carboxyl groups react with nickel chloride hexahydrate ($NiCl_2 \cdot H_2O$), the flexibility of the polymer chains decreased, so the rigid [P(St-*co*-AA)]Ni microspheres increased, the shape of them becoming highly spherical compared to the P(St-*co*-AA) microspheres.

Figure 2 shows the infrared (IR) data for the P(St-*co*-AA) microspheres [curve (a)] and the magnetic [P(St-*co*-AA)]Ni [curve (b)]. Figure 2 [curve (c)] represents the IR data for the washed [P(St-*co*-AA)]Ni particles. The IR spectrum of the polymer colloid [curve (a)] reveals well-defined bands at 700, 760, 1030, 1080, and 3010 cm^{-1}, characteristic of the phenyl group, a peak at 2920 cm^{-1} due to the CH_2 group, and a peak at 1700 cm^{-1} due to C=O group. All these data confirm that the composition of the P(St-*co*-AA) microspheres is styrene and acrylic acid. In curve (b), the peaks at 1700 and 1250 cm^{-1} have disappeared, but a new peak appeared at 1410 cm^{-1}.
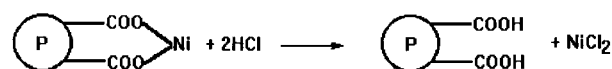
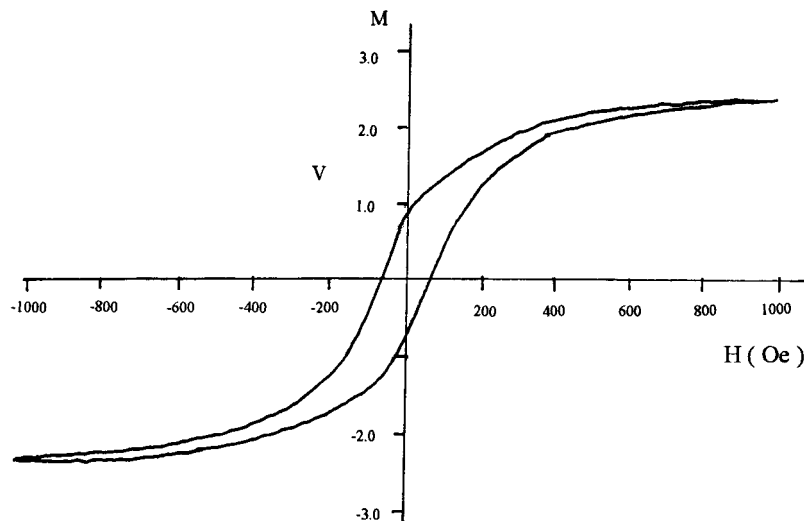**Scheme 1** The process for washed [P(St-*co*-AA)]Ni particles with HCl.

Figure 4   Magnetic hysteresis loop of magnetic [P(St-*co*-AA)]Ni microspheres.

This implies that the carboxylate group is formed. Generally,[10] when carboxyl acid is converted into its inorganic salt, the five characteristic peaks at $3000-2500$, 1710, 1420, $1300-1200$, and 920 cm^{-1} are replaced by two peaks ($1610-1550$ cm^{-1} and 1400 cm^{-1}). The peaks at $1610-1550$ and 1400 cm^{-1} are C—O asymmetric and symmetric

stretching bands, respectively, of —C$\begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$)$^{-}$. There

are absorption bands at $2500-3000$, 1600, 1450, and 910 cm^{-1} not only in P(St-*co*-AA), but also in PSt. So, in Figure 2 [curve (b)], the peaks at

$2500-3000$, 1450, and 910 cm^{-1} should not disappear. In Figure 3 [curve (c)], the peaks at 1700 and 1250 cm^{-1} appeared again while the peak at 1400 cm^{-1} disappeared. Curve (c) is the same as curve (a). Thus, the structure obtained after the removal process of P[St-*co*-AA)Ni can be depicted as shown in Scheme 1.

Additional support for this result is shown in the ESCA spectrum, given in Figure 2, which demonstrates that the valence of the nickel on the surface of [P(St-*co*-AA)]Ni is 2, as was expected.

Magnetic Properties

Ferromagnetic substances are classified according to the value of the coercive force (Hc). One class is the soft magnetic materials, whose coercive force is small (10^{-2} Oe). The remanent magnetic induction is very small and the magnetic hysteresis loop is long and narrow. Another class of ferromagnetic substances are the hard magnetic materials, whose coercive force is large (10^2-10^4 Oe). The remanent magnetic induction is large and the magnetic hysteresis loop is wide. It can be inferred from Figure 4 that the [P(St-*co*-AA)]Ni microspheres can be classified as soft magnetic materials. The coercive force is 32 Oe, the saturation magnetization is 1.79 emu/g, and the shape of the magnetic hysteresis loop is long and narrow. We take the relative magnetic susceptibility, $\chi_a = a \cdot \chi$ (χ_a: relative magnetic materials, a: proportional its coefficient, χ: magnetic susceptibility) as a function of temperature (Fig. 5). Figure 5 shows that as the temperature decreased, the magnetic susceptibility also de-
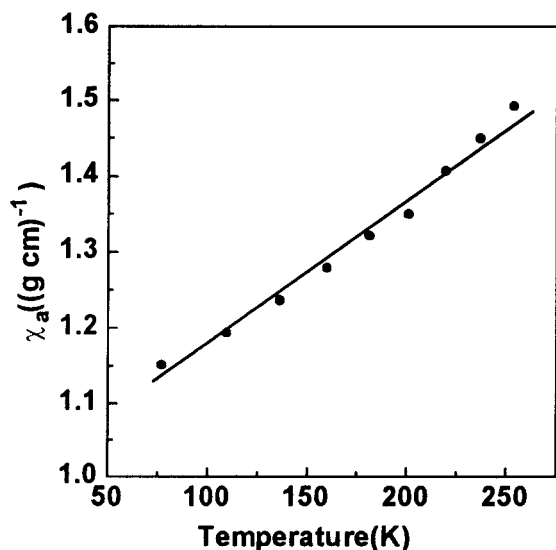

Figure 5   Relative magnetic susceptibility vs. temperature.

creased, this result is opposite to that of general ferromagnetic materials.

Magnetic susceptibility, χ, is defined in terms of the magnetic moment, M, produced by a magnetic intensity, H, as

$$\chi = M/H \qquad (1)$$

Generally,[11] below the Curie temperature (T_c), the magnetic material is subdivided into domains, each of which is spontaneously magnetized in accord with eq. (2), but in which the direction of magnetization changes between one domain and the next:

$$M = M_0(1 - aT^n) \qquad (2)$$

where M_0 is the magnetization at $0\ K$ and $n = \frac{3}{2}$.

So, at very low temperatures ($T \ll T_c$), variations of the magnetic susceptibility are in accord with eq. (2). Of course, all these theories are appropriate for magnetic inorganic materials.

Magnetic [P(St-co-AA)]Ni particles are composed of polymer and magnetic materials, nickel, so the variation in regularity of magnetic susceptibility with temperature may be different from that of pure inorganic magnetic materials. It is well known that the external factor of the polymer resulting in internal rotation is the environmental temperature.[12] The higher the temperature, the larger the energy of thermal motion, so that internal rotation of the molecular is freer and the polymer chains become more flexible. Conversely, when the temperature decreased, the internal rotation of the molecular is limited: The flexible polymer becomes rigid. The surface of [P(St-co-AA)]Ni microspheres have carboxyl groups, so at normal atmospheric temperatures, the microspheres are very flexible and the magnetic domains of nickel move freely. The process of magnetization of a ferromagnet entails a change in the arrangement of the domains so that their magnetization becomes more nearly parallel. When the temperature is decreased, the flexibility of the polymer decreased. The polymer chains may be frozen, which limited the movement of magnetic domains, so the susceptibility decreased with the decrease of temperature.

CONCLUSIONS

Monodisperse P(St-co-AA) microspheres, 200 nm, were prepared by seeded emulsifier-free emulsion polymerization. Magnetic [P(St-co-AA)]Ni microspheres were prepared by chemical metal deposition which exhibits ferromagnetic properties. The variation regularity of magnetic [P(St-co-AA)]Ni microspheres with temperature is opposite to that of the inorganic magnetic materials, and the magnetic susceptibility decreased with decrease in temperature.

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