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SHORT COMMUNICATION

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Preparation of styrene/methacrylic acid copolymer microspheres and their composites with metal particles

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Abstract Poly(styrene-*co*-methacrylic acid) [P(St-*co*-MAA)] microspheres were prepared by emulsifier-free emulsion copolymerization of St with MAA. Fourier transform IR spectroscopy and elemental analysis were used to study the change in the content of MAA in the microspheres. The results of X-ray photoelectron spectroscopy measurements indicated the presence of carboxylic functionality on the surface of the microspheres. The P(St-*co*-MAA) metal composite particles were prepared by chemical metal deposition. Transmission electron microscopy observation and X-ray diffraction measurement were used to study the distribution and structure of the metal particles deposited.

Key words Poly(styrene-*co*-methacrylic acid) microspheres · Composite particles · Chemical metal deposition

Introduction

Polymer microspheres (submicrometer) with surface functional groups have extensive applications in the fields of biology, medical analysis, protein synthesis, chromatography, coatings and so on [1–5]. Emulsion copolymerization and dispersion copolymerization are two methods for the preparation of these functional polymer microspheres. It is well known that emulsifier-free emulsion polymerization has been widely used to produce submicrometer polymer microspheres with various functional groups; therefore, many studies have been performed in order to understand the process of such polymerization and to monitor the type, quantity and distribution of the functional groups [6–9]. Such functional polymer microspheres were used as supports for the immobilization of fine metal particles, such as palladium or rhodium particles. These composite particles showed catalytic activity for some chemical reactions, such as hydrogenation [10–12]. When magnetic metal oxides were incorporated on the surface of polymer microspheres, the composite particles obtained exhibited magnetic properties, which could have extensive potential applications and they therefore intrigued strong interest [13, 14].

In this work, poly(styrene-*co*-methacrylic acid) [P(St-*co*-MAA)] microspheres on a submicrometer scale were prepared by emulsifier-free emulsion copolymerization of St with MAA. The distribution of carboxyl groups was studied by Fourier transform (FT) IR spectroscopy, elemental analysis and X-ray photoelectron spectroscopy (XPS) measurement. Then, by a method of chemical metal deposition (electroless plating) [15–19], metal particles, such as nickel or cobalt, were formed and deposited onto the surface of the microspheres, forming polymer metal composite particles which exhibited magnetic properties.

Experimental

Materials

St and MAA (both reagent grade) were purified by distillation under reduced pressure. Ammonium persulfate (APS) and other inorganic chemicals were all analytical grade and were used without further purification. Distilled water was used in the experiments.

Preparation of P(St-*co*-MAA) microspheres

St/MAA copolymer microspheres were prepared by emulsifier-free emulsion copolymerization of St with MAA using APS as the

initiator. The recipes of the copolymerization are listed in Table 1. The reaction was carried out under a nitrogen atmosphere at 70 °C while mechanical stirring at 350 rpm was used. The copolymer microspheres were purified by repeating dialysis for at least 1 week.

Preparation of polymer metal composite particles

P(St-*co*-MAA) microspheres in latex form after purification were used for the preparation of composite particles by chemical metal deposition. Firstly, a small amount of dilute acidic solution of $PdCl_2$ was added to the P(St-*co*-MAA) latex and the mixture was stirred for 0.5 h at 50 °C to allow the complexing of Pd^{2+} with copolymer microspheres. The weight ratio of copolymer particles to $PdCl_2$ was 500:1. Then, the reducing agent ($SnCl_2$) in acidic solution was added to reduce Pd^{2+} to Pd(0), forming "active" copolymer particles. This P(St-*co*-MAA)Pd dispersion was then dialyzed. The method of chemical metal deposition (electroless plating) was employed to prepare polymer metal composite particles [15, 19]. The deposition solution was composed of potassium sodium tartrate, metal salt (metal chloride), concentrated ammonia and reducing agent (sodium hypophosphate). The reaction was carried out at 70 °C for 1 h under mild stirring. The composite particles obtained were filtered and dried at room temperature. The amount of metal on the polymer microspheres was monitored by varying the content of metal salt in the deposition solution. Bimetal composite particles were obtained by bimetal deposition using the same procedure (e.g., Ni/Co, an indication of codeposition of Ni and Co). The variation of metal chloride in the initial deposition solution is given in Table 2.

Characterization

The size and morphology of the P(St-*co*-MAA) microspheres and the polymer metal composite particles were investigated by transmission electron microscopy (TEM) using a Hitachi-800 microscope. IR spectra were recorded on a VECTOR-22 spectrometer. The XPS analysis was performed on a VG ESCALAB MKΠ system using Mg Kα radiation. Bulk elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. X-ray diffraction (XRD) analysis was carried out on an X-ray diffractometer (Y-4Q, China).

Results and discussion

Preparation of P(St-*co*-MAA) microspheres

P(St-*co*-MAA) microspheres were prepared by emulsifier-free emulsion copolymerization of St with MAA. A typical TEM micrograph (MAA1) is given in Fig. 1. The microspheres obtained were spherical in shape and monodisperse in size.

The IR spectra of the P(St-*co*-MAA) microspheres are shown in Fig. 2. The spectra of both MAA1 and MAA2 reveal well-defined characteristic bands of the St unit. A characteristic peak at 1698 cm^{-1} is attributed to carbonyl stretching of carboxyl groups, indicating the copolymerization of MAA and St. With the increase in the MAA content in the copolymerization system (MAA1 $\rightarrow$ MAA2), the intensity ratio of the peak at 1698 cm^{-1} to that at 1453 cm^{-1} or 1493 cm^{-1} clearly increases, suggesting that more MAA was copolymerized with St, thereby leading to a higher content of MAA in the copolymer microspheres.

The surface functionality of the P(St-*co*-MAA) microspheres was investigated by XPS. The results of XPS on MAA2 are shown in Fig. 3. The full-scan spectrum (Fig. 3a) indicates that the main elements on the particle surface were carbon and oxygen (hydrogen cannot be detected by XPS). The C1*s* spectrum in Fig. 3b clearly shows the presence of carboxyl groups (binding energy at 289.3 eV), on the surface of the microspheres.

The distribution of carboxyl groups both on the surface and in the bulk of the microspheres was studied by XPS C1*s* shape analysis and bulk elemental analysis. The results are given in Table 1. The ratio $C_{COOH}/$

Table 1 Recipes and results of preparing poly(styrene-*co*-methacrylic acid) [*P*(*St-co-MAA*)] microspheres at 70 °C for 7 h

Sample	St (g)	MAA (g)	Ammonium persulfate (g)	H_2O (ml)	Conv. (%)	Elemental analysis				X-ray photoelectron spectroscopy	MAA
						C	O	O/C	C_C/C_T[a]	C_C/C_T	C_C/C_T[b]
MAA1	20	2	0.064	200	91.7	88.42	3.06	0.026	1.30	2.05	25
MAA2	20	3	0.064	200	95.2	86.71	4.93	0.043	2.15	2.63	25

[a] Atomic ratio of carbon in the COOH groups to carbon in the copolymer, calculated based on elemental analysis
[b] Calculated based on the amount of carbon in the COOH groups and the total amount of carbon in MAA

Table 2 The conditions for preparation of copolymer metal composite particles. The number in *parentheses* indicates the weight of the copolymer microspheres used

Sample no.	Copolymer particle (g)	Amount of $NiCl_2 \cdot 6H_2O$ (g)	Amount of $CoCl_2 \cdot 6H_2O$ (g)	*T* (°C)	*t* (h)	Size of metal particles (nm)
MAA1-a	MAA1 (1)	0.48	0	70	1	20–40
MAA1-b	MAA1 (1)	0.048	0.432	70	1	20–40
MAA2-A	MAA2 (1)	0.48	0	70	1	15–25
MAA2-B	MAA2 (1)	0.048	0.432	70	1	
MAA2-C	MAA2 (1)	0.096	0.384	70	1	

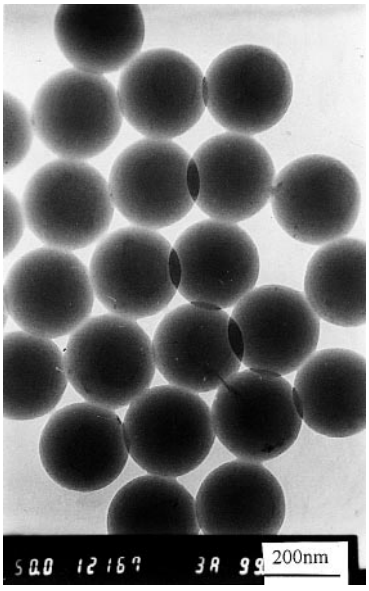

Fig. 1 Transmission electron microscopy (*TEM*) photograph of poly(styrene-*co*-methacrylic acid) [*P*(*St-co-MAA*)] microspheres (MAA1)

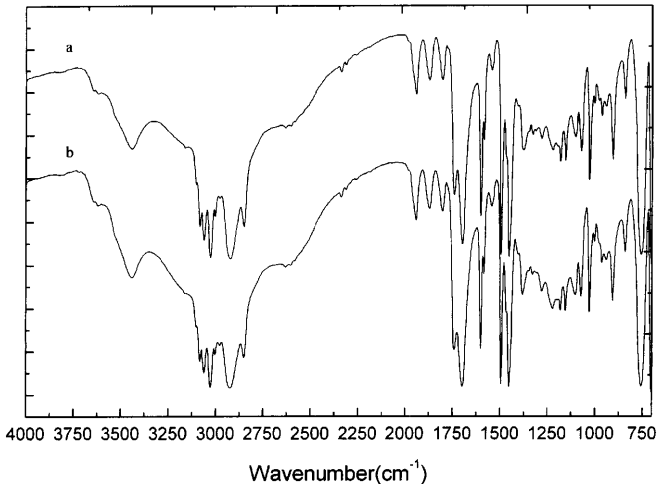

Fig. 2 IR spectra of P(St-*co*-MAA) microspheres: MAA1(*a*) and MAA2(*b*)

C_{TOTAL} was calculated from the amount of carbon at 289.3 eV and the total number of carbon atoms. The results of elemental analysis on MAA1 and MAA2 show that with an increase in the amount of MAA in the copolymerization feed (MAA1 → MAA2), the carbon content of the microspheres decreased, suggesting more MAA content in the microspheres, which is consistent with the results observed in the IR spectra (Fig. 2). The ratio of C_{COOH}/C_{TOTAL} on the surface as measured by XPS is higher than that in the bulk as measured by elemental analysis (Table 1). This observation indicates that more carboxyl groups were distributed on the

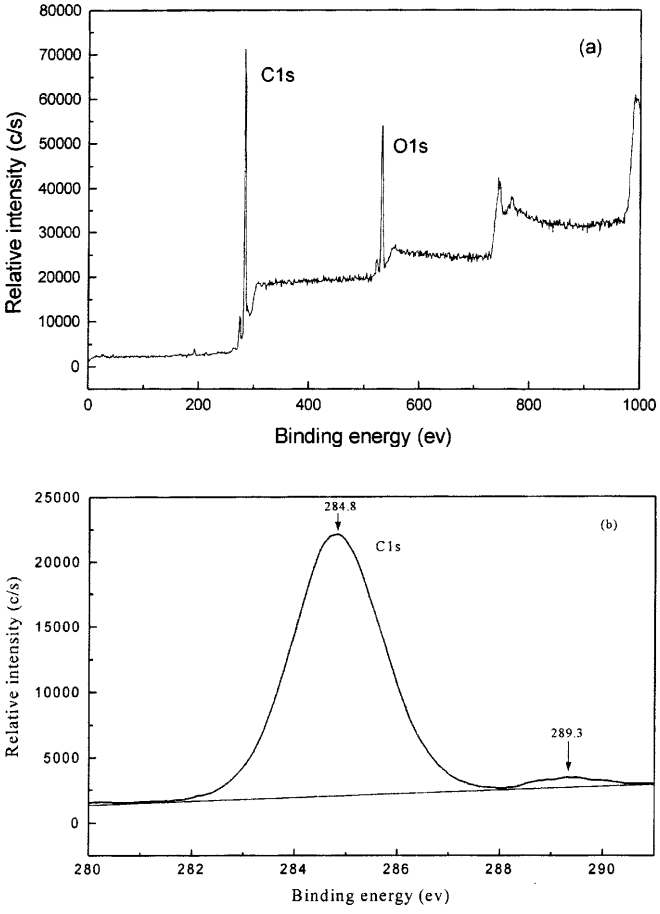

Fig. 3a, b X-ray photoelectron spectroscopy spectra of P(St-*co*-MAA) microspheres (MAA2). **a** Full-scan spectrum, **b** C1*s* spectrum

surface of the microspheres. In addition, the surface ratio of C_{COOH}/C_{TOTAL} in MAA2 was higher than that in MAA1, suggesting more surface carboxyl groups in MAA2; however, compared with C_{COOH}/C_{TOTAL} = 25% of MAA monomer, the surface C_{COOH}/C_{TOTAL} in both cases are quite small (Table 1). This result indicates that in batch emulsion copolymerization of MAA with St, a part of MAA was copolymerized on the surface, while more MAA was probably copolymerized inside the particles. Similar results were observed by Ceska [20] and Santos et al. [21] and were attributed to the less-hydrophilic properties of MAA.

Since the chemical metal deposition on the P(St-*co*-MAA) microspheres was conducted at 70 °C under alkaline conditions, it was assumed that the surface carboxyl groups were converted to carboxylate groups. Such polymer metal composite particles were then treated with hydrochloric acid in order to transform the carboxylate group to carboxylic acid. The results are shown in Figs. 4 and 5 for MAA1 and MAA2, respectively. In curve b of both figures, the peak at 1698 cm^{-1} significantly decreased in intensity but did

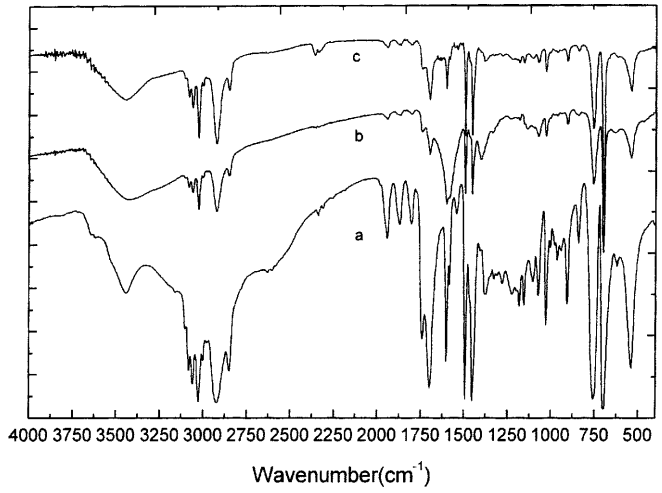

Fig. 4 IR spectra of P(St-*co*-MAA) microspheres (MAA1) (*a*), P(St-*co*-MAA)Ni composite particles (*b*) and P(St-*co*-MAA)Ni composite particles after treatment with hydrochloric acid (*c*)

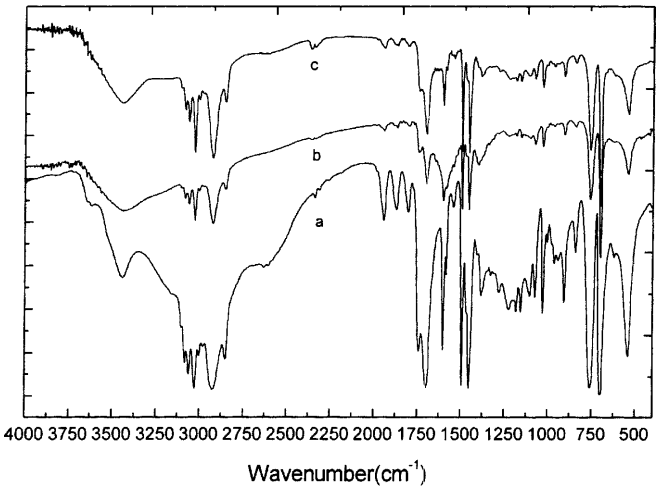

Fig. 5 IR spectra of P(St-*co*-MAA) microspheres (MAA2) (*a*), P(St-*co*-MAA)Ni composite particles (*b*) and P(St-*co*-MAA)Ni composite particles after treatment with hydrochloric acid (*c*)

not disappear, while a new peak appeared at 1401 cm^{-1}, and the peak at 1600 cm^{-1} was broadened. This implies that carboxylate groups were formed during the chemical metal deposition. However, since the peak at 1698 cm^{-1} did not completely disappear, it suggests that some carboxyl groups were buried inside the microspheres and were not converted to carboxylate groups, as discussed earlier. Generally, when carboxylic acid is converted to its inorganic salt, two bands at 1610–1550 and 1400 cm^{-1}, belonging the C-O asymmetric stretching bands of the COO^- group, appear in the IR spectra [22]. In Fig. 4, curve c and Fig. 5, curve c, the peak at 1401 cm^{-1} disappeared. This result indicates that after treatment with hydrochloric acid, the surface carboxylate groups were converted to their acidic form. All these results demonstrate that in batch emulsion copolymerization of MAA with St, in addition to the surface carboxyl groups, some carboxyl groups were buried inside the microspheres. Efforts to increase the quantity of surface carboxyl groups by methods such as seeded copolymerization or partially neutralizing MAA monomer are in progress.

Preparation of polymer metal composite particles

P(St-*co*-MAA) metal composite particles were prepared by chemical metal deposition (electroless plating). Typical TEM photographs of the P(St-*co*-MAA)Ni and Ni/Co bimetal composite particles prepared from MAA1 microspheres are shown in Fig. 6. It can clearly be seen that small metal particles (20–40 nm) were closely attached on the surface of the copolymer microspheres. Both the composite particles showed relatively strong magnetic attraction when a small magnet was used. The

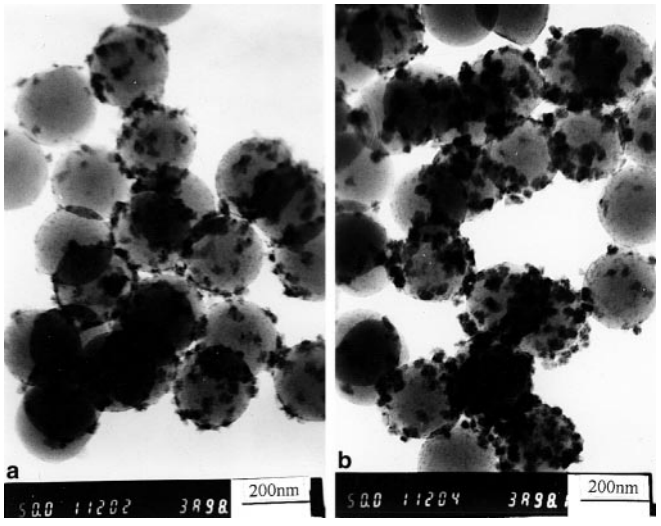

Fig. 6 TEM photographs of **a** MAA1/Ni and **b** Ni/Co composite particles

results of XRD measurements of the composite particles are given in Fig. 7. In the case of pure nickel particles (MAA1/Ni, Fig. 7, curve a), peaks at $2\theta = 44.4°$ and 51.5° are observed, which are attributable to the (1 1 1) and (2 0 0) planes of zerovalent nickel, respectively. The results confirm the formation of zerovalent nickel particles on the surface of the microspheres during chemical metal deposition. In the case of bimetal composite particles (MAA1/Ni/Co, Fig. 7, curve b), three main peaks appear at $2\theta = 42.0°$, 44.6° and 47.7°, which can be attributed to the (1 0 0), (0 2 2) and (1 0 1) planes of zerovalent cobalt. In addition, a weak peak at 51.5° is observed. For the nickel particles, the peak at 44.4°, which is overlapped with the peak at 44.6°

belonging to cobalt particles, is much stronger than the peak at 51.5°; therefore, the appearance of a weak peak at 51.5° in Fig. 7, curve b indicates the existence of nickel. These results confirmed the formation of nickel and cobalt particles on the surface of the copolymer microspheres due to bimetal deposition. On comparing the TEM photographs of the composite particles of MAA1/Ni (Fig. 6a) and MAA1/Ni/Co (Fig. 6b) it seems there is no significant difference in the size and uniformity of the metal particles between these two composite particles. However, it was observed in our previous work [19] that in the case of deposition of pure cobalt particles, the cobalt particles were significantly more prone to agglomerate than nickel particles and therefore resulted in less uniformity of the metal particle distribution. The reason might be due to the fact that the mutual magnetic attraction of cobalt particles is stronger than that of nickel particles. Therefore, the quite comparable result in the size and uniformity of metal particles in Fig. 6a and b suggests the formation of bimetal composite particles.

The same process was applied to MAA2 microspheres to prepare MAA2/Ni and Ni/Co bimetal composite particles. A typical TEM micrograph of MAA2/Ni composite particles is shown in Fig. 8. Small nickel particles (15–25 nm) were distributed on the surface of the copolymer microspheres. XRD patterns of both MAA2/Ni and Ni/Co bimetal composite particles are shown in Fig. 9. The diffraction profiles clearly show the existence of the copolymer and the deposited metal. In the case of pure nickel particles (Fig. 9, curve A), peaks at 44.5° and 51.9° are observed, indicating the formation and deposition of zerovalent nickel particles on the surface of the copolymer microspheres. In the case of bimetal composite particles (Fig. 9, curves B, C), three main peaks appear at 41.9°,

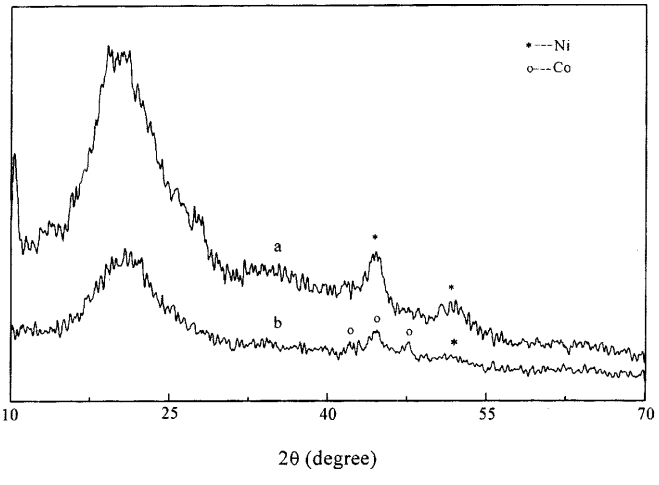

Fig. 7 X-ray diffraction (*XRD*) profiles of MAA1/Ni (*a*) and MAA1/Ni/Co (*b*) composite particles. The samples are the same as those listed in Table 2

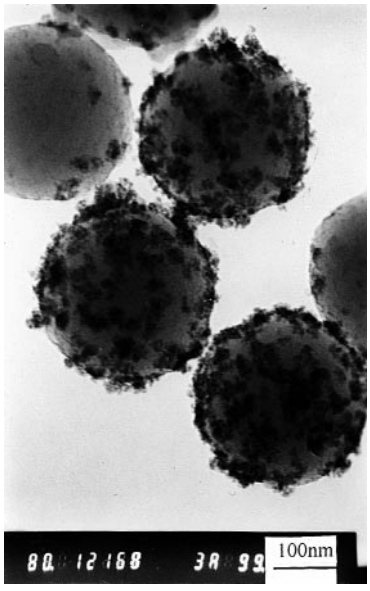

Fig. 8 TEM photograph of MAA2/Ni composite particles

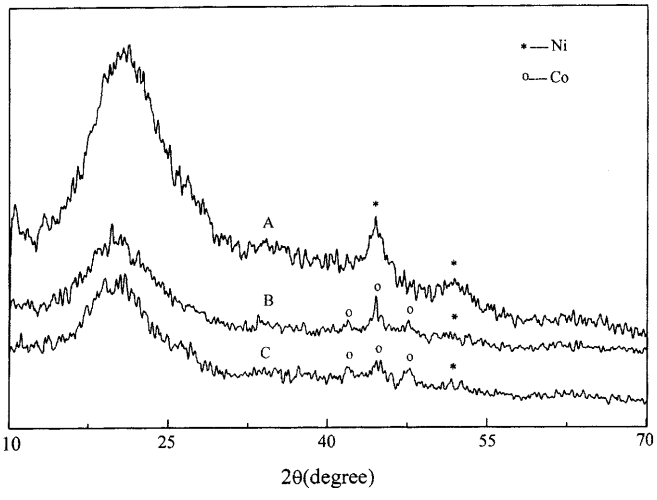

Fig. 9 XRD profiles of MAA2/Ni (*A*) and Ni/Co (*B*, *C*) composite particles. The samples are the same as those listed in Table 2

44.5° and 47.6°, which are attributed to the (1 0 0), (0 2 2) and (1 0 1) planes of zerovalent cobalt. This observation confirmed the formation and deposition of cobalt particles on the MAA2 microspheres. In addition, the quite weak peak at about 51.9° is accounted for by zerovalent nickel in the cases of samples B and C. So weak peaks at 51.9° in Fig. 9 curves B and C could be understandable because of the small amount of nickel chloride in the initial deposition solution (Table 2) and the relatively low power of our X-ray diffractometer. On comparing MAA1/Ni (Fig. 6a) with MAA2/Ni (Fig. 8), it appears that the metal particles in Fig. 8 are somewhat smaller and more uniform than those in Fig. 6a. This is

probably due to there being more carboxyl groups on the surface of the MAA2 microspheres as confirmed by XPS analysis (Table 1). The attraction of carboxyl groups and metal particles somewhat prevents the mutual agglomeration of the metal particles, resulting in stable, small and uniform metal particles.

Conclusions

Monodispersed St/MAA copolymer microspheres were prepared by emulsifier-free emulsion copolymerization of St and MAA. Both FTIR and elemental analysis showed that the MAA content in the microspheres increased as the amount of MAA monomer in the copolymerization system increased. XPS measurements proved there was a higher content of carboxyl groups on the surface than in the interior of the microspheres; however, it was found that some carboxyl groups were buried inside the copolymer microspheres.

By the method of chemical metal deposition, nickel or/and cobalt particles were formed and deposited on the surface of the P(St-*co*-MAA) microspheres, forming polymer metal or bimetal composite particles. TEM observation and XRD measurements indicated that zerovalent metal particles were formed and were deposited on the surface of the copolymer microspheres. The composite particles obtained exhibited magnetic properties.

References

1. Kitano H, Nakamura K, Ise N (1982) J Appl Biochem 4:34
2. Clonis Y (1987) J Chromatogr 179:407
3. Kamei S, Okubo M, Matsuda T, Matsumoto T (1987) Colloid Polym Sci 264:743
4. Okubo M, Yamamoto Y, Uno M, Kamei S, Matsumoto T (1987) Colloid Polym Sci 265:1062
5. Chattha MS, Theodore AN (1985) J Coat Technol 57:721
6. Ohtsuka Y, Kawaguchi H, Sugi Y (1981) J Appl Polym Sci 26:1637
7. Tamai H, Murakami T, Suzawa T (1985) J Appl Polym Sci 30:3857
8. Chang HS et al (1988) J Polym Sci Part A Polym Chem Ed 26:1207
9. Kim JH, Chainey M, El-Aasser MS et al (1989) J Polym Sci Part A Polym Chem Ed 27:3187
10. Tamai H, Sakurai S, Hirota Y, Nishiyama F, Yasuda H (1995) J Appl Polym Sci 56:441
11. Tamai H, Hamamoto S, Nishiyama F, Yasuda H (1995) J Colloid Interface Sci 171:250
12. Tamai H, Sumi T, Nishiyama F, Yasuda H (1996) J Appl Polym Sci 60:1727
13. Noguchi H, Yanase N, Uchida Y, Suzuta T (1993) J Appl Polym Sci 48:1539
14. Lee J, Senna M (1995) Colloid Polym Sci 273:76
15. Warshawsky A, Upson DA (1989) J Polym Sci PartA Polym Chem Ed 27:2963
16. Warshawsky A, Upson DA (1989) J Polym Sci PartA: Polym Chem Ed 27:1539
17. Wang YM, Feng LX, Pan CY (1998) J Appl Polym Sci 70:2307
18. Wang PH, Pan CY (2000) Eur Polym J (accepted)
19. Wang PH, Pan CY (2000) Colloid Polym Sci 278:245
20. Ceska GW (1974) J Appl Polym Sci 18:427
21. Santos AMD, McKenna TF, Guillot J (1997) J Appl Polym Sci 65:2343
22. Koji N, Solomon PH (1977) Infrared absorption spectroscopy, 2nd edn Holden-Day