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SHORT COMMUNICATION

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# Preparation of styrene/acrylonitrile copolymer microspheres and their composites with metal particles

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**Abstract** Monodispersed poly(styrene-*co*-acrylonitrile) [P(St-*co*-AN)] microspheres were prepared by emulsifier-free emulsion copolymerization of St with AN. Fourier transform IR spectroscopy and elemental analysis were used to measure the content of AN in the poly(St-*co*-AN) microspheres. X-ray photoelectron spectroscopy (XPS) measurements indicated the presence of an AN unit on the surface of the microspheres. The combined results of the elemental analysis and the XPS measurements showed that the copolymer on the surface of the P(St-*co*-AN) particles was rich in AN compared with that in the interior of the particles. P(St-*co*-AN)–metal composite particles were prepared by chemical metal deposition. The addition of nickel could improve the distribution of cobalt on surface of the polymer microspheres. The preparation of polymer–bimetal composite particles was tried. Transmission electron microscopy and XRD were used to study the distribution and structure of the deposited metal particles.

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

## Introduction

Polymer microspheres (submicron) with surface functional groups have extensive applications in the fields of biology, medical analysis, protein synthesis, chromatography, coating, 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 is widely used to produce sub-micron-sized polymer microspheres with various functional groups; therefore, many studies have been conducted in order to understand the process of such polymerization and to monitor the types, quantity and distribution of functional groups [6–9]. Such functional polymer microspheres are used as supports for the immobilization of fine metal particles, such as palladium or rhodium particles. These composite particles show catalytic activity for some chemical reactions, such as hydrogenation [10–12]. When magnetic metal oxides are incorporated on the surface of polymer microspheres, the composite particles obtained exhibit magnetic properties and could have extensive potential applications and have, therefore created much interest [13, 14].

In this work, styrene/acrylonitrile copolymer [P(St-*co*-AN)] microspheres of submicron sites were prepared by copolymerization of St with AN by the emulsifier-free emulsion polymerization technique. Then, using the method of chemical metal deposition (electroless plating) [15, 16], metal particles, such as nickel or cobalt, were formed and deposited onto the surface of these polymer microspheres, forming polymer–metal composite particles. These composite particles exhibited magnetic properties. Aspects of the preparation and characterization of both P(St-*co*-AN) microspheres and polymer–metal composite particles are reported.

## Experimental

### Materials

St and AN 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*-AN) microspheres

P(St-*co*-AN) microspheres were prepared by copolymerization of St with AN by emulsifier-free emulsion polymerization using APS as an initiator. The recipes for the copolymerization are given in Table 1. The reaction was carried out under nitrogen at 70 °C with mechanical stirring at 350 rpm. The copolymer microspheres were purified by repeated dialysis for 1 week.

### Preparation of polymer–metal composite particles

P(St-*co*-AN) microspheres in latex form after purification were used for the preparation of composite particles by chemical metal deposition. Firstly, a small amount of dilute acid solution of palladium chloride ($PdCl_2$) was added to the P(St-*co*-AN) latex and was stirred mechanically for 1 hour at room temperature to allow the complexation reaction of palladium ions with copolymer microspheres to occur. The weight ratio of copolymer particles to $PdCl_2$ was 500:1. Then, this dispersion was heated to 70 °C and a reducing agent (tin chloride) in acid solution was added to reduce the $Pd^{2+}$ to Pd(0), forming "active" copolymer particles. This P(St-*co*-AN)Pd dispersion was then dialyzed. The method of chemical metal deposition (electroless plating) was employed to prepare polymer–metal composite particles [15]. The deposition solution was composed of potassium sodium tartrate, metal salt (metal chloride), concentrated ammonia (about 29% w/v) and a reducing agent (sodium hypophosphate). The reaction was conducted at 70 °C for 30 min under mild stirring. The composite particles obtained were filtered and dried at room temperature. The amount of metal on the polymer particles was monitored by varying the content of the metal salt in the deposition solution. Bimetal composite particles were obtained by bimetal deposition using the same procedure (e.g. nickel/cobalt, an indication of codeposition of nickel and cobalt). The variation of the metal chloride content in the initial deposition solution is shown in Table 2.

### Characterization

The size and the morphology of the P(St-*co*-AN) 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. X-ray photoelectron spectroscopy (XPS) analysis was performed on a VG ESCALAB MKΠ system using Mg Kα radiation. 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).

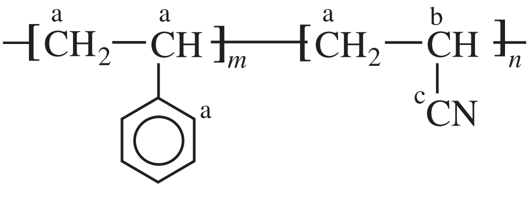
## Results and discussion

### Preparation of P(St-*co*-AN) microspheres

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

IR spectra of P(St-*co*-AN) microspheres (AN1 and AN2) are shown in Fig. 2. Both spectra reveal well-defined bands characteristic of the St unit. A characteristic peak appears at 2237 $cm^{-1}$ corresponding to CN groups. These data confirmed that P(St-*co*-AN) microspheres resulted from the copolymerization of St and AN. On comparing the IR spectra of AN1 and AN2, the latter shows stronger peak intensity at 2237 $cm^{-1}$, suggesting that it had a higher content of the AN unit in the microspheres.

The surface functionality of the P(St-*co*-AN) microsphere was investigated by XPS. The results for AN1 are shown in Fig. 3. The full-scan spectrum (Fig. 3a) indicates that the main elements on the particle surface were carbon and nitrogen (hydrogen cannot be detected). The small peak at a binding energy of 532.2 eV in Fig. 3a demonstrates the existence of a small amount of oxygen on the surface of the particles, probably resulting from initiator fragments ($-SO_4-$) and/or minor surface contamination or oxidation [10]. Shape analysis of the C1*s* spectrum (Fig. 3b) reveals three peaks with binding energies at 284.8, 286.1 and 286.9 eV. These three peaks correspond to three different carbons in the copolymer backbone structure as shown here [17, 18].



The N1*s* spectrum of the P(St-*co*-AN) microspheres (AN1) is shown in Fig. 4. The peak at 399.7 eV is

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

| Sample | St (g) | AN (g) | Ammonium persulfate (g) | $H_2O$ (ml) | Diameter (nm) | Conversion (%) | Elemental analysis (%) | | | N/C[a] | X-ray photoelectron spectroscopy (N/C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | C | H | N | | |
| AN1 | 16 | 8 | 0.084 | 200 | 408 | 83.5 | 85.90 | 7.11 | 5.56 | 0.06 | 0.15 |
| AN2 | 12 | 12 | 0.084 | 200 | 446 | 85.0 | 81.67 | 6.84 | 10.74 | 0.11 | 0.26 |

[a] Atomic ratio, calculated based on elemental analysis

**Table 2** Variation of the content of metal salt in the initial deposition solution

| Sample[a] | A[b] | B[b] | C[b] | a[c] | b[c] | c[c] |
|---|---|---|---|---|---|---|
| $NiCl_2 \cdot 6H_2O$ | 0.48 | 0.6 | 0.72 | 0.048 | 0.096 | 0 |
| $CoCl_2 \cdot 6H_2O$ | | | | 0.432 | 0.384 | 0.48 |

[a] Copolymer microspheres (1 g) were used for each sample
[b] Deposited on AN2 microspheres
[c] Deposited on AN1 microspheres

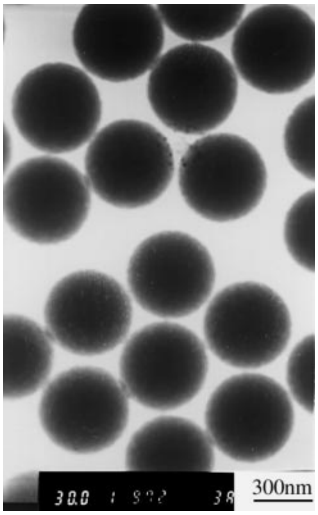


**Fig. 1** Transmission electron microscopy (*TEM*) micrograph of polystyrene-*co*-acrylonitrile [P(St-*co*-AN)] microspheres (AN2)

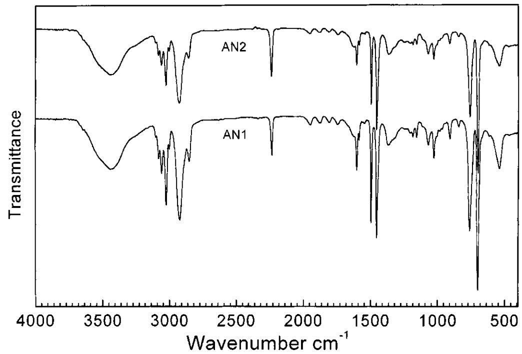


**Fig. 2** IR spectra of P(St-*co*-AN) microspheres

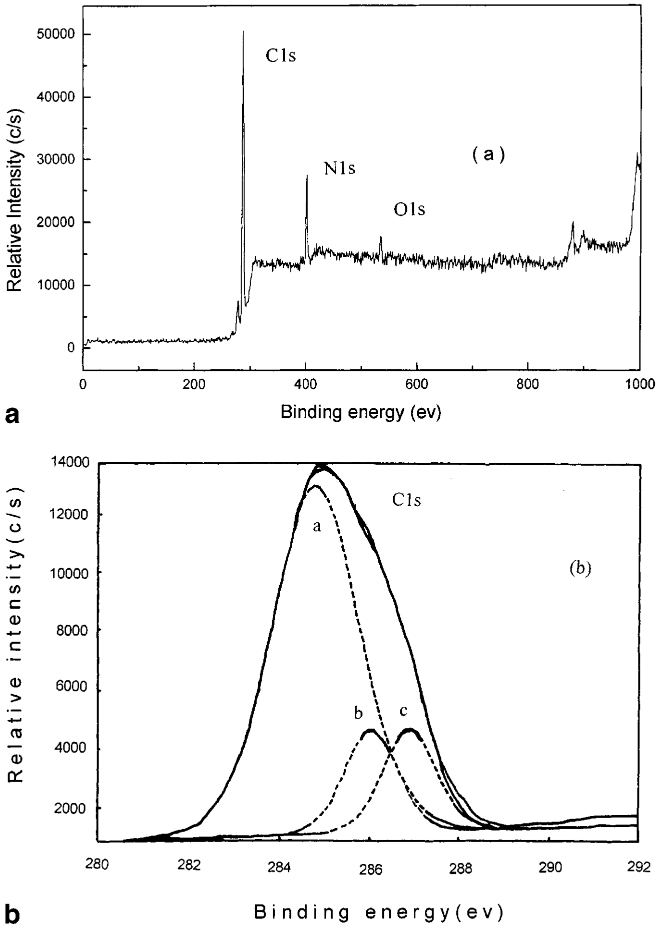


**Fig. 3a, b** X-ray photoelectron spectroscopy (*XPS*) spectra of P(St-*co*-AN) microspheres. **a** Full-scan spectrum, **b** C1*s* spectrum

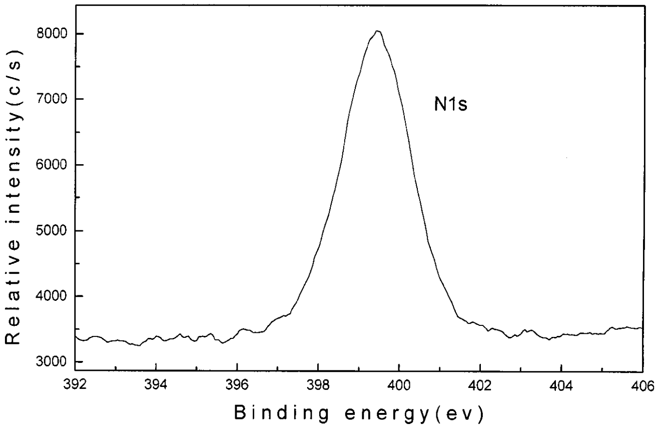


**Fig. 4** XPS N1*s* spectrum of P(St-*co*-AN) microspheres

attributed to the nitrogen atom in the cyano group [18]. XPS studies on the AN2 microspheres gave similar results. All these data verified the presence of a CN group on the surface of the P(St-*co*-AN) microspheres. The atomic ratios of nitrogen/carbon calculated from the elemental analysis and the XPS results are listed in Table 1. The former is the mole ratio of AN/St of all the P(St-*co*-AN) particles, while the latter is that of poly(St-*co*-AN) on the surface of the particles. The higher value of the latter compared to the former proved the presence of more CN groups on the surface of the P(St-*co*-AN) microspheres than in the interior. The CN functional groups on the surface could then be employed to complex palladium ions and became sites for the reduction and deposition of metal particles. In comparison with AN1, the AN2 particles contained more AN units on the surface and in all the microspheres. The results are similar to the copolymer microspheres prepared by the emulsifier-free copolymerization of St with water-soluble functional monomers such as acrylic acid, acrylamide, vinylpyridine and hydroxyethyl methacrylate [7, 19–21].

## Preparation of polymer–metal composite particles

Poly(St-*co*-AN)–metal composite particles were prepared by chemical metal deposition (electroless plating). A typical TEM photograph of P(St-*co*-AN)Ni composite particles from AN2 microspheres is shown in Fig. 5. It can be clearly seen that small nickel particles were closely attached to the surface of the copolymer microspheres. No palladium particles were detected because a very small amount of $PdCl_2$ (2 mg for 1 g copolymer microspheres) was used and acted as a catalyst for the reduction of $Ni^{2+}$. The composite particles showed relatively strong magnetic attraction when a small magnet was used. The results of XRD measurements of the composite particles are given in Fig. 6; the sample corresponds to that in Table 2. Compared with the XRD profile of AN2 microspheres, peaks at $2\theta = 44.4°$ and $51.6°$ are observed for all the P(St-*co*-AN)Ni composite particles; these peaks 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 P(St-*co*-AN) microspheres during chemical metal deposition. In addition, with an increase in the amount of nickel chloride in the initial deposition solution (AN2-A $\rightarrow$ AN2-B $\rightarrow$ AN2-C), the diffraction intensities at $2\theta = 44.4°$ and $51.6°$ due to the nickel particles increased, suggesting more nickel particles were formed during chemical metal deposition.

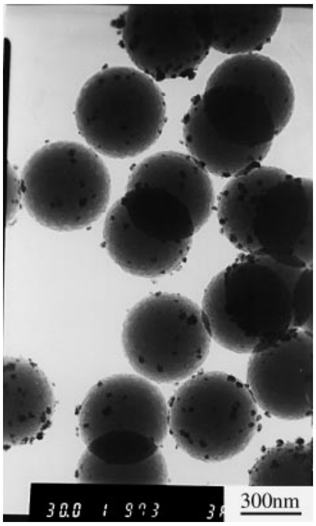


**Fig. 5** TEM micrograph of P(St-*co*-AN)Ni composite particles (AN2)

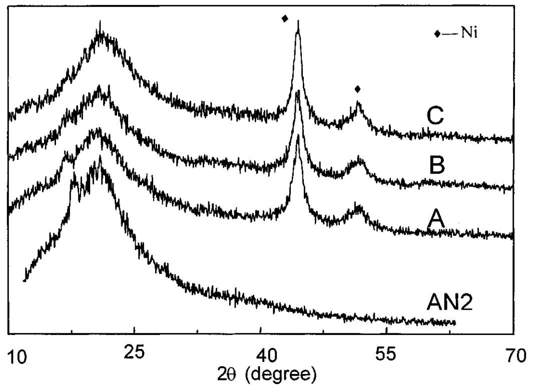
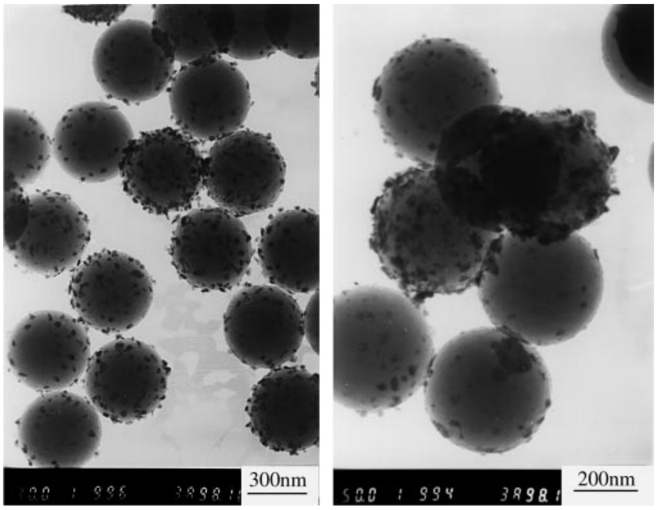


**Fig. 6** X-ray diffraction (*XRD*) profiles of P(St-*co*-AN)Ni composite particles (*AN*2, *A*, *B*, and *C* are the same samples as listed in Table 2)

The P(St-*co*-AN) bimetal (nickel and cobalt) and cobalt composite particles were prepared by chemical metal deposition on AN1 microspheres. Typical TEM micrographs showing the distribution of these metal particles on the surface of AN1 microspheres are given in Fig. 7. In the case of P(St-*co*-AN)Ni/Co composite particles (Fig. 7a), small metal particles of nanometer size (10–50 nm) were distributed on the surface of the copolymer microspheres. In the case of P(St-*Co*-AN) composite particles (Fig. 7b), the distribution of cobalt particles was relatively less uniform compared with



(a) (b)

**Fig. 7** TEM micrographs of **a** P(St-*co*-AN)Ni/Co and **b** Co composite particles

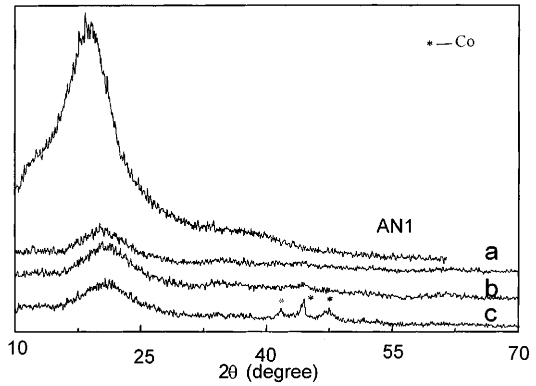


**Fig. 8** XRD profiles of P(ST-*co*-AN)Co and Ni/Co composite particles (*AN*1, *a*, *b*, and *c* are the same samples as listed in Table 2)

that of bimetal composite particles. It is interesting to note that cobalt had a stronger mutual magnetic interaction than nickel. Codeposition of a small amount of nickel seemed to improve the uniformity of the distribution of cobalt particles on the surface of the microspheres as observed in Fig. 7a. XRD patterns of these bimetal composite particles are given in Fig. 8. In the case of pure cobalt particles, compared with the profile of AN1 microspheres, three additional peaks appear at $2\theta$ = 41.7°, 44.4° and 47.5°, 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 AN1 microspheres. Moreover, both the cobalt and the bimetal composite particles demonstrated evident magnetic properties; however, in the case of the bimetal composite particles, no obvious peaks due to metal particles were observed. The reason might be that the diffraction intensity of metal particles of either nickel or cobalt was quite weak and was not detected. Further studies are needed to elucidate the mechanism of bi- or multi-metal deposition and their influence on the crystalline structure and the magnetic properties of the composite particles.

## Conclusions

Monodispersed P(St-*co*-AN) microspheres were prepared by emulsifier-free emulsion copolymerization of St and AN. Both Fourier transform IR measurements and elemental analysis showed an increase in the AN content in the microspheres with an increase in the AN monomer content in the copolymerization feed. Comparison of elemental analysis with XPS results proved that there are more AN units on the surface than in the interior of the P(St-*co*-AN) microspheres.

Using the method of chemical metal deposition, nickel and/or cobalt particles were formed and were deposited on the P(St-*co*-AN) microspheres, forming polymer metal or bimetal composite particles. The codeposition of nickel with cobalt could improve the distribution of the cobalt particles on the surface of the polymer microspheres; these particles showed magnetic properties.

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