

P. H. Wang
C.-Y. Pan

Preparation of styrene/acrylic acid copolymer microspheres: polymerization mechanism and carboxyl group distribution

Received: 16 February 2001
Accepted: 8 August 2001

P. H. Wang
Department of Polymer Science
and Engineering, Hefei University
of Technology, Hefei
Anhui 230009, China

C.-Y. Pan (✉)
Department of Polymer Science
and Engineering, University of Science
and Technology of China, Hefei
Anhui 230026, China
e-mail: pcy@ustc.edu.cn

Abstract Poly(styrene-*co*-acrylic acid) (St/AA) copolymer microspheres were prepared by batch emulsifier-free emulsion copolymerization of St with AA. The monomer conversion, the morphology and the composition of the particles along the polymerization process were monitored by a gravimetric method, transmission electron microscopy observation and Fourier transform IR analysis, respectively. A shift of the polymerization locus from inside the particles to “outside” the particles in the postnucleation stage was

proposed. The results of the study of the distribution of carboxyl groups by a combination of elemental and X-ray photoelectron spectroscopy analyses implied a core/shell structure for the St/AA copolymer microspheres. By chemical metal deposition, nickel particles were formed and deposited on the surface of St/AA microspheres, forming polymer/metal composite particles.

Keywords Styrene/acrylic acid copolymer microspheres · Polymerization locus · Core/shell structure

Introduction

Polymer microspheres (submicrometer) with surface functional groups have extensive applications in the fields of biology, medical analysis, coatings, etc. [1–3]. Emulsifier-free emulsion polymerization, mainly with styrene (St), has been widely used to produce submicrometer monodisperse polymer microspheres with various functional groups. Many studies have been performed in order to understand the process of such polymerization and to monitor the type, the quantity and the distribution of surface functional groups [4–7]. Such functional polymer microspheres were used as supports for the immobilization of fine metal particles such as palladium and rhodium particles. These composite particles showed catalytic activity for some chemical reactions [8, 9]. When magnetic metal oxides were incorporated on the surface of polymer microspheres, the composite particles obtained showed magnetic properties, which could have extensive applications and therefore initiated strong interest [10, 11].

Of the functional polymer microspheres, carboxylated copolymer microspheres, which are generally prepared by emulsion copolymerization of hydrophobic monomer (usually St) with carboxylic acid monomers, belong to an interestingly important class of industrial emulsion polymer systems [12–14]. Carboxylic acid monomers are often completely soluble in water; however, they will still distribute to varying extents into the organic phase depending on their relative hydrophobicity. The most frequently studied acid monomers copolymerized with St are itaconic acid (IA), acrylic acid (AA) and methacrylic acid (MAA), listed in order of increasing hydrophobic nature.

Ceska [15] copolymerized IA, AA and MAA with St in separate reactions. The copolymerization rates were found to increase with the presence of carboxylic monomers in the order $IA < AA < MAA$. The rate increased as the hydrophobicity of the monomer increased.

Potentiometric and conductometric titration studies of copolymer latex systems containing acid monomers copolymerized with a more hydrophobic monomer such

as St have been performed by many researchers [15–18]. Most of the studies were aimed at determining the distribution of the acid groups between the aqueous phase, the particle surface and the particle interior, and the effects of the distributions on the rate of polymerization, particle stability, and particle generation. Kinetics studies by means of a gravimetric method together with or without gas chromatography were also reported with the aim of reaching a kinetics model [13, 19].

In this work, monodisperse St/AA copolymer microspheres were prepared by batch emulsifier-free emulsion copolymerization of St with AA. The progression of the copolymerization was monitored for monomer conversion, particle morphology and particle composition. A shift of the polymerization locus from inside the particle to “outside” the particle was proposed. X-ray photoelectron spectroscopy (XPS) and elemental analyses were combined to study the distribution of carboxyl groups. A core/shell structure was envisaged for the St/AA copolymer microspheres. Then, by chemical metal deposition [20–22], nickel particles were formed and deposited on the surface of St/AA microspheres, forming polymer-metal composite particles. These composite particles showed magnetic properties.

Experimental

Materials

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

Preparation of St/AA copolymer microspheres

St/AA copolymer microspheres were prepared by batch emulsifier-free emulsion copolymerization of St with AA using APS as the initiator. The preparation procedure was the same as in earlier reports [23–25]. The copolymerization recipes are listed in Table 1. The reaction was carried out under a nitrogen atmosphere at 70 °C with mechanical stirring at 350 rpm. The latex was purified by three centrifugation/dispersion cycles in water.

Preparation of polymer/metal composite particles

St/AA (AA2) microspheres in latex form after purification were used for the preparation of polymer/metal composite particles by chemical metal deposition. The procedure of preparation was similar to that reported earlier [21–23]. Nickel particles were deposited on the surface of AA2 copolymer microspheres, which is designated as AA2-Ni.

Characterization

The conversion of monomers was calculated by a gravimetric method. At different time intervals, a small amount of emulsion was withdrawn and immediately mixed with a small amount of hydroquinone to terminate the polymerization. After weighing, the emulsion was dried to determine the solid content, from which the monomer conversion was obtained. Meanwhile, some of the emulsion withdrawn at different intervals (1–6 h) during the polymerization process in AA2 was dried at 50–55 °C for the study of the composition of the microspheres by Fourier transform (FT) IR spectroscopy. IR spectra were recorded using a VECTOR-22 IR spectrometer with KBr pellets. The size and morphologies of the St/AA copolymer microspheres and the polymer/metal composite particles were investigated by transmission electron microscopy (TEM) using a Hitachi-800 microscope. XPS measurements were conducted using an ESCALAB Mark II system with a residual pressure of 3×10^{-9} mbar. A Mg K α radiation source (1253.6 eV) with an overall energy resolution of 1.0 eV was used. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. For both XPS and elemental analyses, the latex after centrifugation were dried overnight at 68 °C, and was then dried in vacuo at the same temperature for 24 h. The samples in powder were then stored in a desiccator for subsequent analysis. X-ray diffraction (XRD) analysis was carried out with an X-ray diffractometer (Y-4Q, China).

Results and discussion

Progression of copolymerization of St with AA

Rate of copolymerization

Emulsifier-free emulsion copolymerization has been extensively used to prepare polymer microspheres on the submicrometer scale. Generally, the hydrophilic monomer tends to locate on the surface of polymer microspheres and therefore provides stability to the microspheres.

The influence of AA on the copolymerization rate of St with AA is illustrated in Fig. 1. As the polymerization proceeds, the conversion, as generally observed, increases rapidly in the initial period and then increases slowly at higher conversion. For AA2, the threshold time for this change in conversion is at about 4 h. In addition, it can be seen that the copolymerization rate in AA2 was somewhat higher than that in AA1. Generally, the function of carboxylic acid monomer is twofold [15]: it induces the formation of polymer particles, thereby increasing the polymerization rate, and it stabilizes the growing particles. Qualitatively, the ability of acid monomer inducing particle formation can be explained

Table 1 Conditions for the preparation of styrene (St)/acrylic acid (AA) copolymer microspheres

| Sample | St (g) | AA (g) | Ammonium persulfate (g) | H ₂ O (ml) | T (°C) | t (h) | D (nm) | $I_{1,704}/I_{1,601}$ ^a |
|--------|--------|--------|-------------------------|-----------------------|--------|-------|--------|------------------------------------|
| AA1 | 20 | 2 | 0.1 | 200 | 70 | 7 | 347 | 0.62 |
| AA2 | 20 | 3 | 0.1 | 200 | 70 | 7 | 330 | 0.93 |

^aIntensity ratio of the peak at 1,704 cm⁻¹ to the peak at 1,601 cm⁻¹ in the IR spectra in Fig. 7

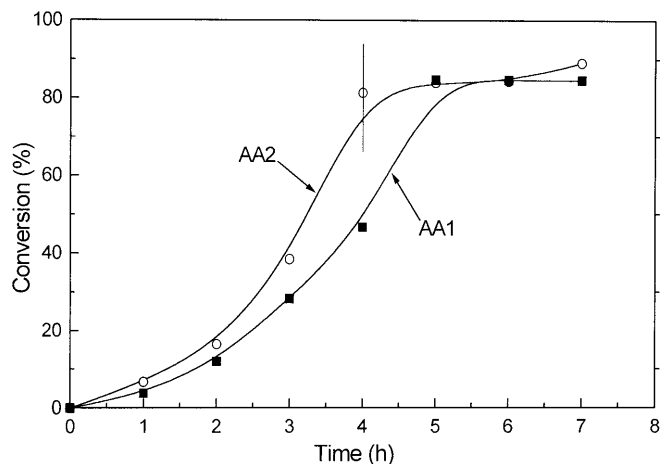


Fig. 1 Rate of copolymerization versus polymerization time

by the homogeneous nucleation theory [26, 27]. Persulfate radicals induce polymerization of St and acid comonomer in the aqueous phase, resulting in oligomer radicals. As the oligomer radicals reached a “critical length”, they precipitated and agglomerated to form primary particles. Particles growth continues inside the particles. The particle maintains its stability from the hydrophilic shell provided by the carboxyl groups which concentrate at the particle/water interface.

On the basis of this theory, the higher rate of copolymerization in AA2 as observed in Fig. 1 can be explained as follows. In the case of higher AA content in the copolymerization feed, the rate of formation of oligomers or oligomer radicals is increased to some extent owing to the fact that the polymerization begins in the aqueous phase. As a result, more primary particles will be formed. Consequently, the polymerization rate will be increased owing to the presence of more particles in the system. It can be inferred that the final particle size will decrease provided that the monomer feed is the same. The TEM photographs of the resulting polymer microspheres of AA1 and AA2 are shown in Fig. 2. The particle sizes measured from the photographs are listed in Table 1. As can be seen, the results reflect the inference made earlier, i.e. the particle size in AA2 is smaller than that in AA1. Since the amount of St is the same, smaller particle size in AA2 suggests more particles are formed in AA2; this helps to enhance the copolymerization rate as observed in Fig. 1.

Particle morphology and composition

The morphology of the microspheres during the copolymerization course in AA2 was observed by TEM and the photographs are shown in Fig. 3. The corresponding particle size is given in Fig. 4. The polymer microspheres are spherical, stable and uniform along the process. As

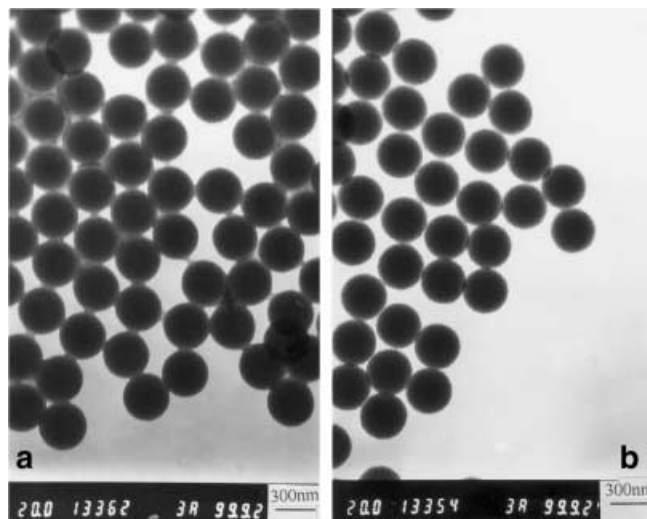
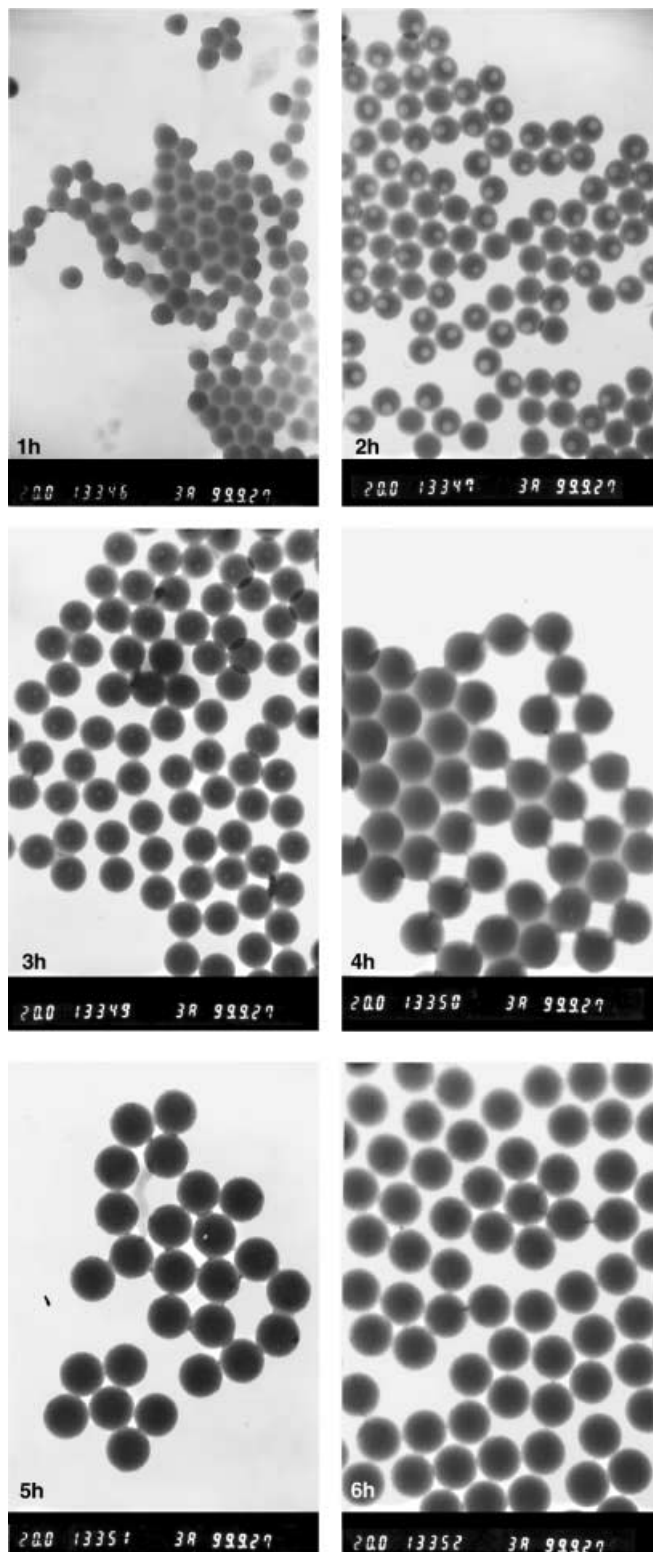


Fig. 2 Transmission electron microscopy (TEM) photographs of styrene (St)/acrylic acid (AA) copolymer microspheres: a AA1, b AA2

observed in Fig. 4, the particle size keeps increasing dramatically up to a polymerization time of about 4 h. After this point, the particle size increases slowly and nearly levels off. This phenomenon is similar to that observed in Fig. 1, i.e. the increase in the rate of conversion changes at about the same point. The progression of the composition of the copolymer microspheres during the copolymerization course in AA2 was studied by FTIR spectroscopy; the spectra are shown in Fig. 5. The spectra reveal well-defined bands of the St unit. The characteristic peak at $1,704\text{ cm}^{-1}$ was attributed to carbonyl stretching in the carboxyl group, indicating copolymerization of St with AA. Since the peaks at $1,704$ and $1,601\text{ cm}^{-1}$ are due to stretching of the carbonyl bond in the COOH group and to stretching of benzene ring, respectively, the intensity ratio of these two peaks ($I_{1,704}/I_{1,601}$) can be a qualitative indication of the relative quantity of AA and St in the copolymer microspheres. The intensity ratios of these two peaks along the polymerization course were therefore calculated on the basis of the IR spectra in Fig. 5 and are plotted in Fig. 6. Examination of Figs. 5 and 6 indicates that prior to a polymerization time of 4 h, the peak intensity at $1,704\text{ cm}^{-1}$ is relatively weak and the peak intensity ratio ($I_{1,704}/I_{1,601}$) is relatively low, suggesting a low AA content in the copolymer microspheres. From 4 to 6 h, the intensity of this peak increases significantly, indicating a significant increase in AA content in the microspheres. This implies that a polymerization time of 4 h was also a “critical point” in the variation of AA content in the microspheres. Combination of the results of the total monomer conversion, the particle size and the particle composition appears to infer that the polymerization behavior before and after the “critical point”, i.e. 4 h, was different. Prior to 4 h, the polymer-



(For all photos in Fig.3)

Fig. 3 TEM photographs of St/AA microspheres during the polymerization process (AA2)

ization of St was dominant, and the polymerization occurred mainly within the St swollen particles till most of St was consumed, while after 4 h, polymerization of AA became relatively important. Owing to the hydrophilic nature of AA, the polymerization of AA could be assumed to occur mainly “outside” the particles. This suggests that a shift of the polymerization locus from inside the particles to “outside” the particles occurred in the particle growth stage or the postnucleation stage. If this happens, the composition of the final St/AA copolymer microspheres would vary from inside to the surface shell. The polymerization of St occurred inside the particles, resulting in a polystyrene-rich core, while the polymerization of AA was “outside” the particles and therefore could possibly yield a surface shell rich in

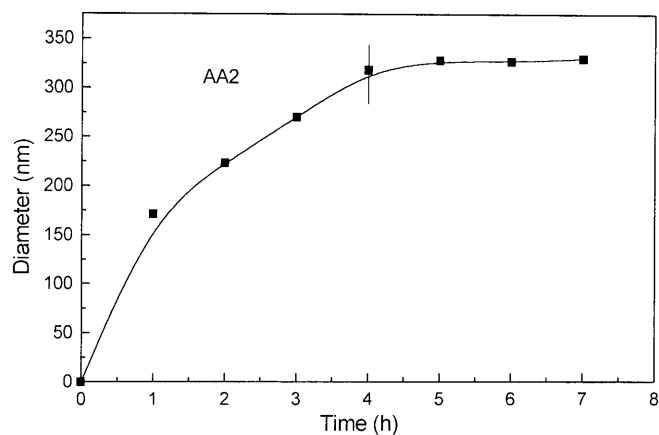


Fig. 4 Variation of the diameter of St/AA microspheres versus time (AA2)

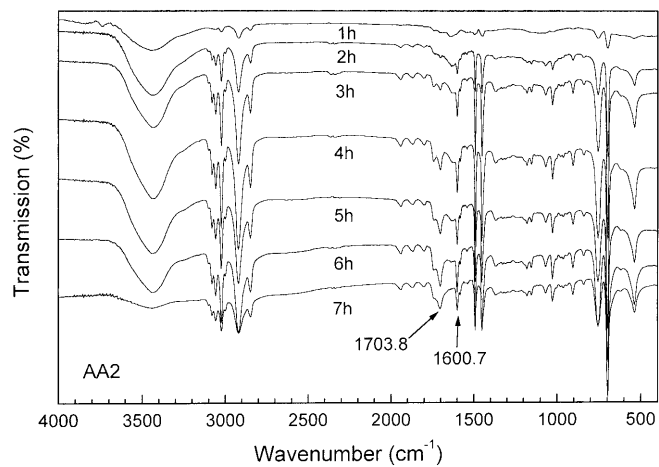


Fig. 5 IR spectra of the St/AA microspheres during the polymerization process (AA2)

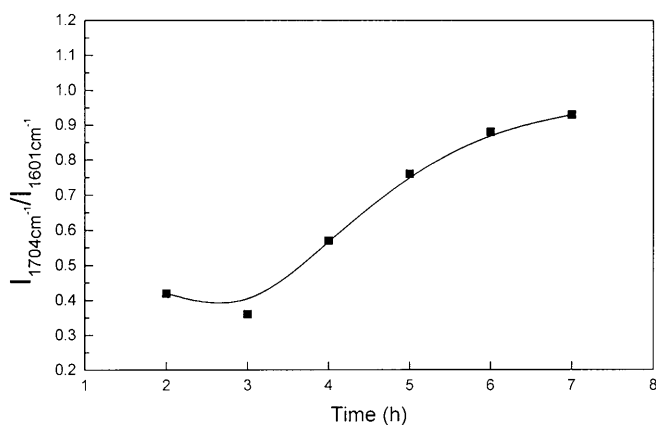


Fig. 6 Peak intensity ratio in IR spectra during the polymerization process

AA. To confirm this inference, a combination of IR, elemental analysis and XPS was applied to study the composition of the resulting St/AA microspheres.

Composition of the St/AA copolymer microspheres

The IR spectra of the AA1 and AA2 microspheres are shown in Fig. 7. Except for the typical peaks of polystyrene, a relatively strong adsorption peak appears at $1,704\text{ cm}^{-1}$. As discussed earlier, the peaks at $1,601$ and $1,704\text{ cm}^{-1}$ are due to stretching of the benzene ring and the carbonyl bond, respectively, and the intensity ratio of these two peaks (see Table 1) can qualitatively indicate the relative quantity of AA and St units in the microspheres. A comparison between AA1 and AA2 in Fig. 7 and Table 1 indicates more AA in the AA2 microspheres. This suggests that more AA in the initial copolymerization feed yields copolymer microspheres with a higher content of AA.

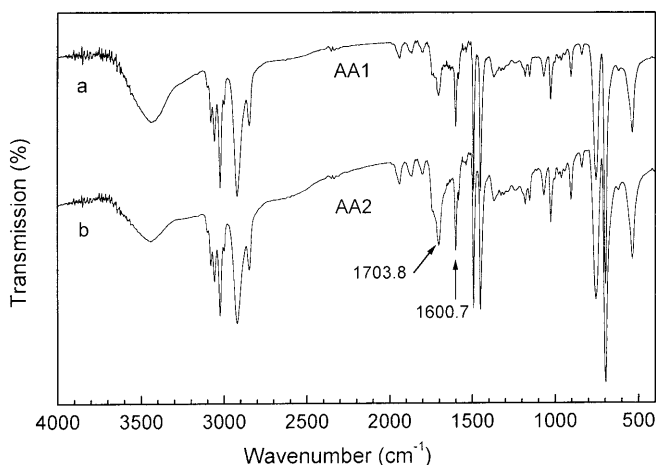


Fig. 7 IR spectra of St/AA copolymer microspheres

Quantitative determination of the composition of the St/AA microspheres was achieved by combination of elemental analysis and XPS measurements. The full-scan spectra are shown in Fig. 8a. The main elements on the microsphere surface as measured by XPS are carbon and oxygen (hydrogen cannot be detected by XPS). The C1s spectra in Fig. 8b clearly show the presence of two types of carbons, at binding energies of 284.8 and 289.2 eV, respectively. The former is attributed to the carbon in C–C and C–H linkages, while the latter is attributed to the carbons in carboxyl groups. These data prove the presence of carboxyl groups on the surface of the St/AA copolymer microspheres.

The results of the bulk elemental analysis and surface XPS measurements are listed in Table 2. The ratio of $C_{\text{COOH}}/C_{\text{total}}$ was calculated from the percentage of carbons at 289.2 eV against the combination of carbon atoms at 284.8 and 289.2 eV in Fig. 8b. The elemental analysis data for AA1 and AA2 show that with increasing AA in the copolymerization feed (AA1→AA2), the carbon content in the microspheres decreases, while the oxygen and O/C ratio increases,

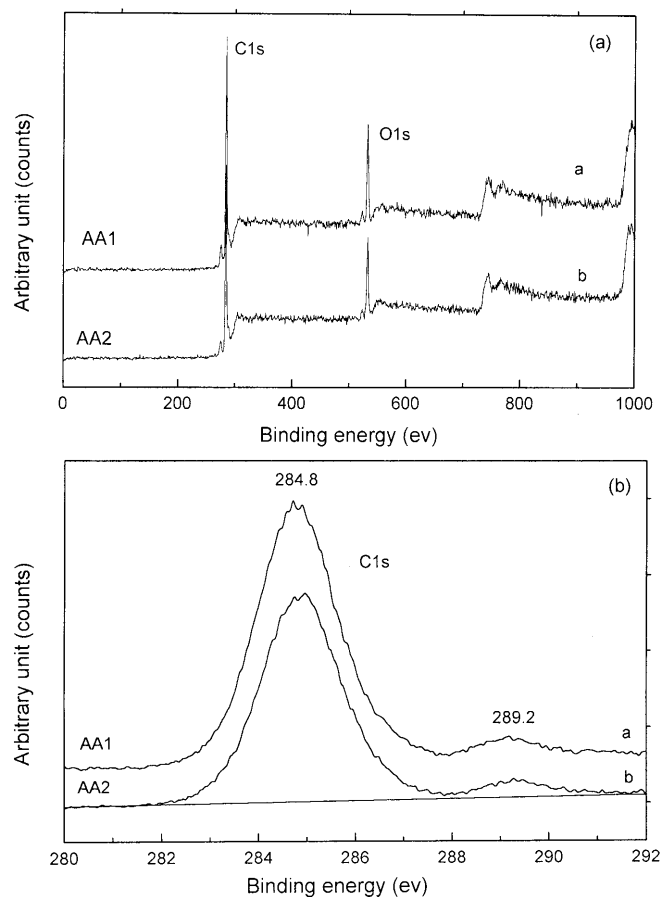


Fig. 8 XPS spectra of the St/AA copolymer microspheres: **a** full-scan spectra, **b** C 1s spectra

Table 2 Results of elemental and X-ray photoelectron spectroscopy (XPS) analyses of AA1 and AA2 microspheres

| Sample | Elemental analysis | | | | XPS $C_{\text{COOH}}/C_{\text{total}}^{\text{b}}$ |
|--------|--------------------|------|--------|---|--|
| | C | O | O/C | $C_{\text{COOH}}/C_{\text{total}}^{\text{a}}$ | |
| AA1 | 90.29 | 1.58 | 0.0131 | 0.66 | 6.64 |
| AA2 | 90.02 | 1.72 | 0.0143 | 0.72 | 6.62 |

^aBased on atomic ratio of O/C assuming all oxygens come from COOH groups

^b $C_{\text{total}} = C_{284.8} + C_{289.2}$

suggesting higher AA content in the AA2 microspheres, consistent with the IR spectra (Fig. 7). The ratio of $C_{\text{COOH}}/C_{\text{total}}$ on the surface as measured by XPS is nearly 10 times higher than that in the bulk as measured by elemental analysis. This indicates that the carboxyl groups (or AA) were predominantly distributed on the surface layer or shell of the St/AA microspheres. These observations suggest a nonhomogeneous structure in the cross-section for the St/AA microspheres, i.e. a core/shell structure with the core composed mainly of polystyrene, while the shell is rich in AA. The core/shell structure was reported by Chen and Lee [27] for St/MAA microspheres. Comparison of surface $C_{\text{COOH}}/C_{\text{total}}$ between AA1 and AA2 shows no obvious difference, implying no significant influence of AA content in the copolymerization feed on the surface AA content, in contrast to the St/MAA system [22]. This suggests a saturated level of AA on the surface region but this obviously needs further evidence.

To further examine the distribution of carboxyl groups, the composite particles of AA1-Ni prepared by chemical metal deposition in alkaline solution (pH \approx 10) were treated with hydrochloric acid by immersing the composite particles in dilute hydrochloric acid solution. As predicted, the surface carboxyl groups of the St/AA microspheres were transferred to carboxylate groups when undergoing chemical metal deposition. After hydrochloric acid treatment, these carboxylate groups were transferred back. The point to be underlined is that the transfer was only confined to the groups in the surface layer, while the groups buried inside the particles could not be influenced. The results for AA2 are shown in Fig. 9. After chemical metal deposition (curve b), the peaks at 1,704 and 1,248 cm^{-1} disappeared completely, while a weak peak at 1,418 cm^{-1} appeared. These changes imply that carboxyl groups were converted to carboxylate groups. The nearly complete disappearance of the peak at 1,704 cm^{-1} suggests that the carboxyl groups were predominantly distributed in the surface layer. When undergoing hydrochloric acid treatment (Fig. 9, curve c), the peaks at 1,704 and 1,248 cm^{-1} reappear, while the peak at 1,418 cm^{-1} disappears. The results indicate that the surface carboxylate groups were transferred to their original acid forms. The IR results here help to support a core/shell structure for St/AA copolymer microspheres as discussed previously, i.e. a core rich in polystyrene and a shell rich in AA.

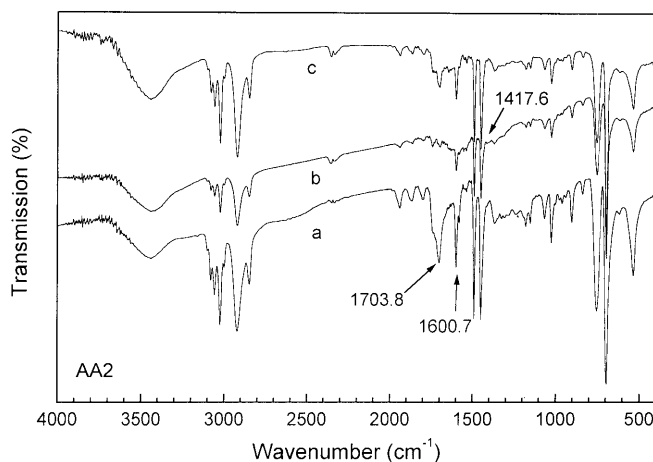


Fig. 9 IR spectra of AA2 copolymer microspheres (a), AA2-Ni composite particles (b) and AA2-Ni composite particles after treatment with hydrochloric acid (c)

Polymerization mechanism in the particle growth stage

Combination of all the results and the inferences made tempts us to presume, on a qualitative basis, a copolymerization mechanism of St with AA. Two stages were envisaged in the particle growth stage.

The first stage begins from the end of nucleation and continues up to the “critical time” (4 h in AA2). The nucleation was occurred via homogeneous nucleation. In stage 1, the polymerization locus was predominantly inside the particles which were swollen by St. In other words, the polymerization of St was dominant. The amount of AA through diffusion into the particles to copolymerize was relatively small; therefore, the AA content in the microspheres was relatively low, as indicated in the IR spectra (0–4 h in Fig. 5). As the polymerization of St proceeded, the particle size increased. The depletion of most of the St symbolized the end of the first stage.

When reaching the “critical time”, most of the St in the system has been consumed. Beginning from this moment, the polymerization of AA in the system became relatively significant. Owing to the hydrophilic nature of AA, the polymerization locus was shifted from inside the particles to “outside” the particles. “Outside” here includes the surface layer (shell) and the

aqueous phase. The “propeller” for this shift lies in two factors.

1. Since most of the St in the system was depleted, the oligomer radicals formed in the aqueous phase contained more AA and became quite hydrophilic; therefore, the diffusion of these oligomer radicals into the particles was difficult.
2. The copolymerized AA in the first stage (the copolymerization of AA was achieved either through forming oligomer radicals with St or through diffusion into the particles participating in the copolymerization) tended to build up on the surface of the microspheres forming a poly(acrylic acid) layer. The presence of this layer is confirmed as discussed earlier. This hydrophilic poly(acrylic acid) coating would act to barrier or even trap hydrophilic oligomer radicals, thus preventing their penetration into the polymer particles.

Both factors would force the oligomer radicals to either remain in the aqueous phase or stay within the surface layer. Owing to the presence of the hydrophilic poly(acrylic acid) layer on the surface of the microspheres, AA could swell this layer. Once the oligomer radicals entered this layer, they would initiate the polymerization of AA. This reaction would undoubtedly help to significantly increase the AA content in the surface layer, and thus enhance the hydrophilicity and the thickness of the surface layer. As a result, a shell structure rich in AA was constructed. On the other hand, the oligomer radicals could also initiate the polymerization of AA in aqueous phase, yielding water-soluble poly(acrylic acid). The data here are not enough to determine the relative ratio of the reactions of AA in the two sites; however, the presence of an AA-rich shell structure as confirmed in the resulting St/AA microspheres seems to imply the preferential occurrence of polymerization of AA in the surface layer.

In conclusion, a shift of the polymerization locus from inside the polymer particles to “outside” the polymer particles occurred during the particle growth stage of the copolymerization of St with AA.

Preparation of polymer/metal composite particles

AA2-Ni composite particles were prepared by chemical metal deposition. A TEM photograph of the composite particles is shown in Fig. 10. It can be seen that nickel particles are closely attached to the surface of the copolymer microspheres. Some of the metal particles agglomerate with adjacent particles and form a thin metal shell. The composite particles show relatively strong magnetic attraction when using a small magnet. The XRD pattern of the AA2-Ni composite particles is given in Fig. 11. Despite the scattering ($2\theta = 20.3^\circ$) for

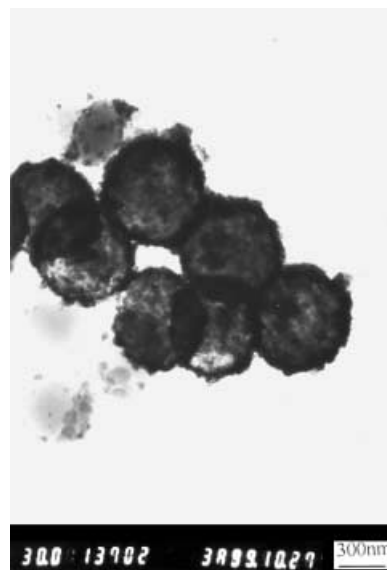


Fig. 10 TEM photographs of AA2-Ni composite particles

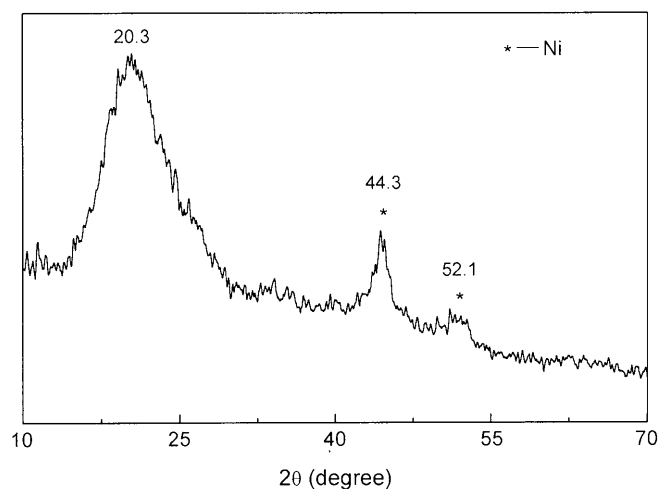


Fig. 11 X-ray diffraction pattern of AA2-Ni composite particles

the copolymer microspheres, peaks at $2\theta = 44.3^\circ$ and 52.1° are observed, which are attributed to the (111) and (200) planes of zero-valent nickel, respectively. The results confirm the formation and deposition of zero-valent nickel particles on the surface of AA2 microspheres by chemical metal deposition.

Conclusions

The primary polymerization locus might shift from inside the polymer particles to “outside” the polymer particles in the particle growth stage in the copolymerization of St with AA.

The composition of St/AA copolymer microspheres was studied by elemental analysis and XPS measurements. A core/shell structure was assumed, with the core rich in polystyrene and the shell rich in AA.

By chemical metal deposition, nickel particles were formed and deposited on the surface of St/AA copolymer microspheres, forming polymer/metal composite particles.

References

1. Kitano H, Nakamura K, Ise N (1982) *J Appl Biochem* 4:34
2. Kamei S, Okubo M, Matsuda T, Matsumoto T (1987) *Colloid Polym Sci* 264:743
3. Chattha MS, Theodore AN (1987) *J Coat Technol* 57:721
4. Ohtsuka Y, Kawaguchi H, Sugi Y (1982) *J Appl Polym Sci* 26:1637
5. Tamai H, Murakami T, Suzawa T (1985) *J Appl Polym Sci* 30:3857
6. Chen SA, Chang HS (1990) *J Polym Sci Part A Polym Chem* 28:2547
7. Yan C, Zhang X, Sun Z (1990) *J Appl Polym Sci* 40:89
8. Tamai H, Sakurai S, Hirota F, Nishiyama F, Yasuda H (1995) *J Appl Polym Sci* 56:441
9. Tamai H, Hamamoto S, Nishiyama F, Yasuda H (1995) *J Colloid Interface Sci* 171:250
10. Noguchi H, Yanase N, Uchida Y, Suzuta T (1993) *J Appl Polym Sci* 48:1539
11. Lee J, Senna M (1995) *Colloid Polym Sci* 273:76
12. Zosel A, Heckann W, Ley G, Malhtrie W (1987) *Colloid Polym Sci* 265:113
13. Shoaf GL, Poehlein GW (1991) *J Appl Polym Sci* 42:1239
14. Santos AM, Vindevoghel P, Graillat C, Guyot A, Guillot J (1996) *J Polym Sci Part A Polym Chem* 34:1271
15. Ceska GW (1974) *J Appl Polym Sci* 18:427
16. Sakota K, Okaya T (1977) *J Appl Polym Sci* 21:1035
17. Egusa S, Makuuchi K (1982) *J Polym Sci* 20:863
18. Martins A, Santos D, Mckenna TF, Guillot J (1997) *J Appl Polym Sci* 65:2343
19. Yan CE, Cheng SY, Feng LX (1999) *J Polym Sci Part A Polym Chem* 37:2649
20. Warshawsky A, Upson DA (1989) *J Polym Sci Part A Polym Chem* 27:1539
21. Wang PH, Pan CY (2000) *Colloid Polym Sci* 278:245
22. Wang PH, Pan CY (2000) *Colloid Polym Sci* 278:581
23. Wang PH, Pan CY (2000) *J Appl Polym Sci* 75:1693
24. Wang PH, Pan CY (2000) *Eur Polym J* 36:2297
25. Wang PH, Pan CY (2001) *Colloid Polym Sci* 279:171
26. Fitch RM, Tsai CH (1970) *Polym Lett* 8:703
27. Chen SA, Lee ST (1991) *Macromolecules* 24:3340