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ORIGINAL CONTRIBUTION

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Morphological investigation of styrene and acrylamide polymer microspheres prepared by dispersion copolymerization

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Abstract The morphology of the styrene and acrylamide copolymer microspheres prepared by dispersion copolymerization in an ethanol/water medium was investigated. The effects of the styrene/acrylamide ratio, ethanol/water ratio and stabilizer concentration on the particle size and size distribution were studied. It was found that the initial solubility parameter of the system was the key factor in the process. The comonomer acrylamide also played an important role in the particle size and size distribution in the presence of cross-linking agent (divinylbenzene).

Key words Dispersion copolymerization · Micron-sized monodisperse polymer particles · Styrene · Acrylamide

Introduction

Micron-sized monodisperse polymer particles are used in a wide variety of scientific and technological applications, such as standard calibration, biomedical and clinical examinations, high-performance liquid chromatography fillers, catalyst carriers, coatings and ink additives, and information storage materials [1–4]. These particles are difficult to obtain because their size is between the size of the particles prepared by conventional emulsion polymerization (0.05–0.8 μm) and that of suspension polymerization (50–1000 μm). Several techniques for the preparation of such micron-sized monodisperse particles have been developed. Vanderhoff et al. [5] used the successive seed swelling method to produce such particles. Ugelstad et al. [6] synthesized particles with similar size by the two-step swelling method. However, these approaches are time-consuming and require several reaction steps.

In the past decade, considerable interest has been concentrated on the development of preparing micron-sized monodisperse particles by dispersion polymerization due to the inherent simplicity of its single-step process [7–9]. The preparation of such particles has been extensively and intensively studied, especially the polystyrene (PSt) and poly(methyl methacrylate) systems; however, up to now, few studies on single-step dispersion copolymerization have been reported [10–13]. The key factor is that dispersion polymerization is highly sensitive to little changes in the reaction parameters and thus it requires strict control. Tseng et al. [9] studied sketchily dispersion copolymerization, synthesizing PSt microspheres containing a small number of functional groups, such as hydroxyl, amine, and carboxyl. Ober and Lok [11] and Horak et al. [12] have intensively studied the dispersion polymerization of styrene (St) and *n*-butyl methacrylate in ethanol/water media. Recently, the morphology and kinetics of the dispersion copolymerization of St and butyl acrylate were investigated in detail by Saenze and Asua [13, 14]. In our previous work, we studied the synthesis of micron-sized monodisperse St and glycidyl methacrylate copolymer microspheres by single-step copolymerization [15].

In this article the morphology of the microspheres prepared by dispersion copolymerization of St and acrylamide (Am) was investigated. Because St is oil-soluble while Am is water-soluble and the polarities of their corresponding monopolymers are remarkably different, this system is very sensitive to the reaction parameters and conditions; therefore, the influences of various polymerization parameters, such as the St/Am ratio, the water/ethanol ratio, the concentration of

Table 1 Effect of acrylamide (*Am*) weight fraction in the monomer feed on the particle size and size distribution. Ethanol/H_2O = 80 g/5g; 2,2′-azobis(isobutyronitrile) (*AIBN*) 0.3 g, 0.3 wt% based on total weight; poly(vinylpyrrolidone) (*PVP*) 0.6 g, 0.6 wt% based on total weight

Sample code	Styrene/Am (g/g)	$\bar{D}_n$ (μm)[a]	S (μm)	ε (%)	δ_{init} (cal/cm^3)$^{1/2}$	Remark
A1	15/0	1.4	0.1	9	13.13	Spherical
A2	14.5/0.5	1.2	0.2	13	13.14	Spherical
A3	14/1	1.3	0.2	17	13.15	Spherical
A4	13/2	2.2	0.6	26	13.18	Spherical
A5	11/4	0.5–15	–	–	13.23	Particle formed during cooling
A6	9/6	–	–	–	13.29	No particle formed

[a] Diameter calculated from the scanning electron microscope photograph

stabilizer, and the existence of cross-linking agent, on the particle size and size distribution were studied.

Experimental

Materials

St was purified by washing with a 10% sodium hydroxide solution and was then distilled under reduced pressure. Am, 2,2′-azobis(isobutyronitrile) (AIBN) and benzoyl peroxide were purified by recrystallization from ethanol. Poly(vinylpyrrolidone) (PVP, M_W = 360,000) and ethanol were both reagent grade and were used as received. Divinylbenzene (DVB) with a purity of 45% was also used as received. Deionized water was used throughout this work.

Preparation of copolymer microspheres by dispersion copolymerization

In a typical example, 2 g Am 0.6 g PVP were dissolved in a mixture of 78 g ethanol and 7 g deionized water in a 250-ml four-necked round-bottomed flask equipped with a reflux condenser, a stainless steel stirrer, a thermometer, and a nitrogen gas inlet and outlet. Then a solution of 0.3 g AIBN in 12 g St was added. After stirring at room temperature for 30 min under the nitrogen purge, the flask was immersed into a 70 °C oil bath. Under a nitrogen atmosphere, the polymerizations were carried out at 70 °C for 24 h.

Table 2 Solubility parameter and density of component

	H_2O	Ethanol	Styrene	Am
δ (cal/cm^3)$^{1/2}$	23.4	12.7	9.3	12.43
d (kg/m^3)	1.000	0.798	0.906	1.122

Measurement

The particle size and size distribution were measured by scanning electron microscopy (SEM, Hitach S-520 SEM) and were calculated without any washing (which may increase the monodispersity of the dispersions). Specimens were prepared by diluting the particles with distilled water and placing drops on a cover glass. The drops were dried at room temperature and then coated under vacuum with a thin layer of gold. About 300 individual particle diameters were measured from SEM photographs and the average size and the size distribution index were obtained as follows:

$$\bar{D} = \frac{\sum_{i=1}^{n} D_i}{n} \ ,$$

$$S = \sqrt{\frac{\sum_{i=1}^{n} (D_i - \bar{D})^2}{n-1}} \ ,$$

$$\varepsilon = S/\bar{D} \ ,$$

where $\bar{D}$ is the number-average diameter, D is the diameter of particle i, n is the total number counted, S is the particle size standard deviation, and ε is the size distribution index. Fourier transform (FT) IR spectra were recorded on a Magna 550 spectrophotometer, using KBr pellets. Glass-transition temperatures (T_g) were determined on a Setaram DSC-92 differential scanning calorimeter under nitrogen at a heating rate of 10 °C/min.

Results and discussion

Dispersion polymerizations usually start as a homogeneous solution of the monomer, a radical initiator, and a polymeric steric stabilizer in organic solvents, such as hydrocarbons or ethanol. First of all, polymerization in the solution formed oligomeric radicals. Because the

Table 3 Effect of the medium polarity on the particle size and size distribution. Styrene/Am = 13/2; AIBN 0.3 g, 0.3 wt% based on total weight; PVP 0.6 g, 0.6 wt% based on total weight

Sample code	Ethanol/H_2O (g/g)	$\bar{D}_n$ (μm)[a]	S (μm)	ε (%)	δ_{init} (cal/cm^3)$^{1/2}$	Remark
B1	83/2	2.4	0.9	36	12.64	Spherical, no aggregation
B2	80/5	2.2	0.6	26	13.18	Spherical, no aggregation
B3	78/7	1.8	0.3	15	13.53	Spherical, aggregation <10%
B4	75/10	1.2	0.1	9	14.02	Spherical, aggregation <30%
B5	65/20	0.5	0.01	3	15.52	Spherical, no aggregation

[a] Diameter calculated from the scanning electron microscope photograph

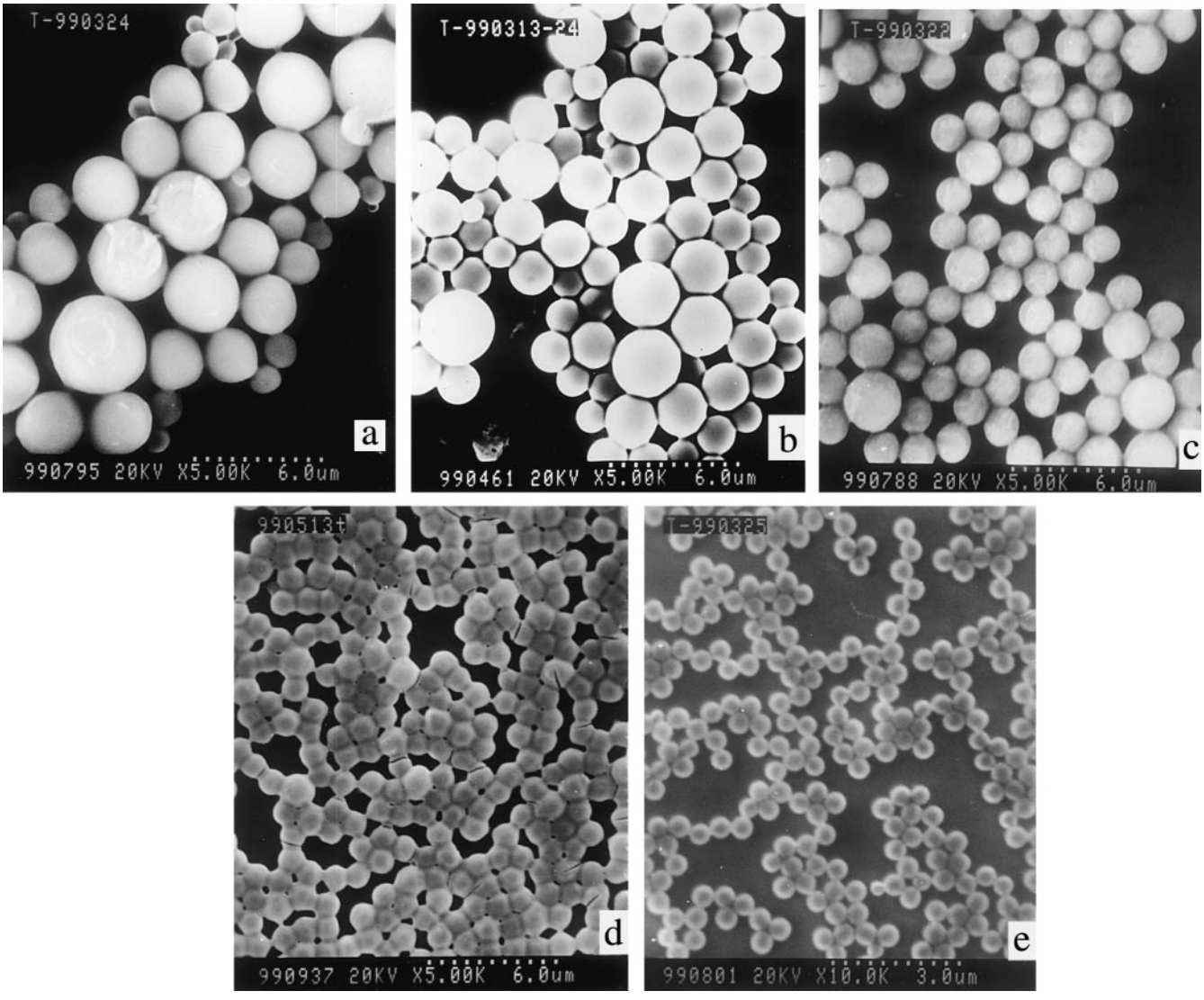


Fig. 1 Effect of the medium polarity on the particle size and size distribution: **a** B1; **b** B2; **c** B3; **d** B4; **e** B5

reaction medium of the dispersion polymerization does not dissolve the resultant polymer, the polymers formed precipitate and perhaps aggregate to form colloidally unstable precursor particles (nuclei). These nuclei may further coalesce and adsorb enough stabilizers from the medium onto their surface to become sterically stable. At this point, the total number of particles is fixed, and particle nucleation ceases. Subsequently, the oligomers and precursors produced are captured by the existing particles before they can adsorb enough stabilizers to create a second generation of stable particles. This process of particle nucleation could be applied for all stabilizers, including the graft copolymers formed in situ. Although the nucleation period in dispersion polymerization is very short (usually about 10 min) [16], it exerts a critical influence on the resultant particle size and size distribution.

Effect of the St/Am ratio

As shown in Table 1, with the increase in weight fraction of Am in the monomer feed, the particle size first decreased and then increased. Minsk et al. [17] have studied in detail the effect of solvents on the copolymerization of Am and St. They concluded that when Am monomer is highly hydrogen bridged or strongly affected by the dipolar interaction, St has little tendency to copolymerize with Am and the resultant copolymer is rich in St. This means that a copolymer with an Am-rich segment and a St-rich segment was usually obtained when copolymerization was carried out in a strong polar solvent. They also measured the monomer reaction ratios of Am and St in ethanol at 70 °C, for which

Table 4 Effect of PVP concentration on the particle size and size distribution. Styrene/Am = 13/2; AIBN 0.3 g, 0.3 wt% based on total weight

Sample code	Ethanol/H_2O (g/g)	PVP (g)	$\bar{D}_n$ (μm)[a]	S (μm)	ε (%)	Remark
C1		0.3	3.2	0.3[b]	9	Spherical (>50%) with a lot of very small coagulum (0.05–0.55 μm)
C2	78/7	0.6	1.8	0.3	15	Spherical with slight aggregation
C3		0.9	0.9	0.05	6	Spherical, no aggregation
D1		0.3	1.1	0.1	6	Spherical, coagulum ~30%, severe aggregation
D2		0.6	1.2	0.1	9	Spherical, coagulum <30%, aggregation
D3	75/10	0.75	1.0	0.03	3	Spherical, coagulum <15%, no aggregation
D4		0.9	1.0	0.04	4	Spherical, coagulum <5%, no aggregation
D5		1.2	0.8	0.03	4	Spherical, coagulum <3%, no aggregation

[a] Diameter calculated from the scanning electron microscope photograph
[b] Bimodal size distribution. The standard deviation of the particle size was calculated by ignoring small coagula

r_1(Am) = 0.3 and r_2(St) = 1.44. Ohtsuka et al. [18] investigated the emulsifier-free emulsion polymerization of Am/St. They found that the whole polymerization process was divided into three steps.

1. Am was initiated and the polyacrylamide (PAm) fragment proliferated.
2. The PSt fragment mainly proliferated until almost all the St monomer had been consumed.
3. The PAm fragment proliferated again.

This result conformed with the conclusion of Minsk et al. Ohtsuka et al. also found that the particle size increased with a decrease in the amount of Am, and they supposed that the PAm fragment just served as a stabilizer and was not incorporated into the particles. In our work, since the polymerization was carried out in a strong polarity medium, it was assumed that similar polymerization steps occurred. Therefore, when a small amount of Am was incorporated into the system, most of the PAm produced acted as a costabilizer, which led to a decrease in the particle size; however, the more Am was incorporated in the reaction, the more PAm fragments participated in the structure of the particles. Because PAm could dissolve in the ethanol/water medium at the reaction temperature (70 °C), the copolymer richer in PAm was more soluble, resulting in the appearance of larger particles.

In addition, the particle size distribution became wider with an increase in the Am fraction in the monomer feed because the copolymer richer in PAm was more soluble, leading to the critical molecular weight of the copolymers increasing and to a prolongation of the nucleation period. In run A5, when the fraction of Am was 4/15, the polymerization system was half muddy and lot of particles were obtained while the temperature decreased from 70 °C to room temperature; however, in run A6, the fraction of Am increased to 0.4, and during the whole reaction the system was transparent and acted as a solution polymerization. Even when the system was cooled, no particles but gel-like copolymers were obtained.

Effect of the initial medium polarity

The reaction medium of the dispersion polymerization should be able to dissolve the steric stabilizer but not be able to dissolve the resultant polymers. In dispersion polymerization, the key factor behind the particle size and size distribution is the medium polarity or solvency because it controls the critical molecular weight above which the polymer will precipitate. One method of estimating the polarity of a mixture of miscible liquids is averaging the solubility parameter of each component [19]. The solubility parameter, δ, is an empirical quantity that permits the calculation of a value representing the polarity of a solvent medium. The calculation of δ for a solvent mixture is carried out by taking the average based on the volume fraction of solvent in the mixture [20]:

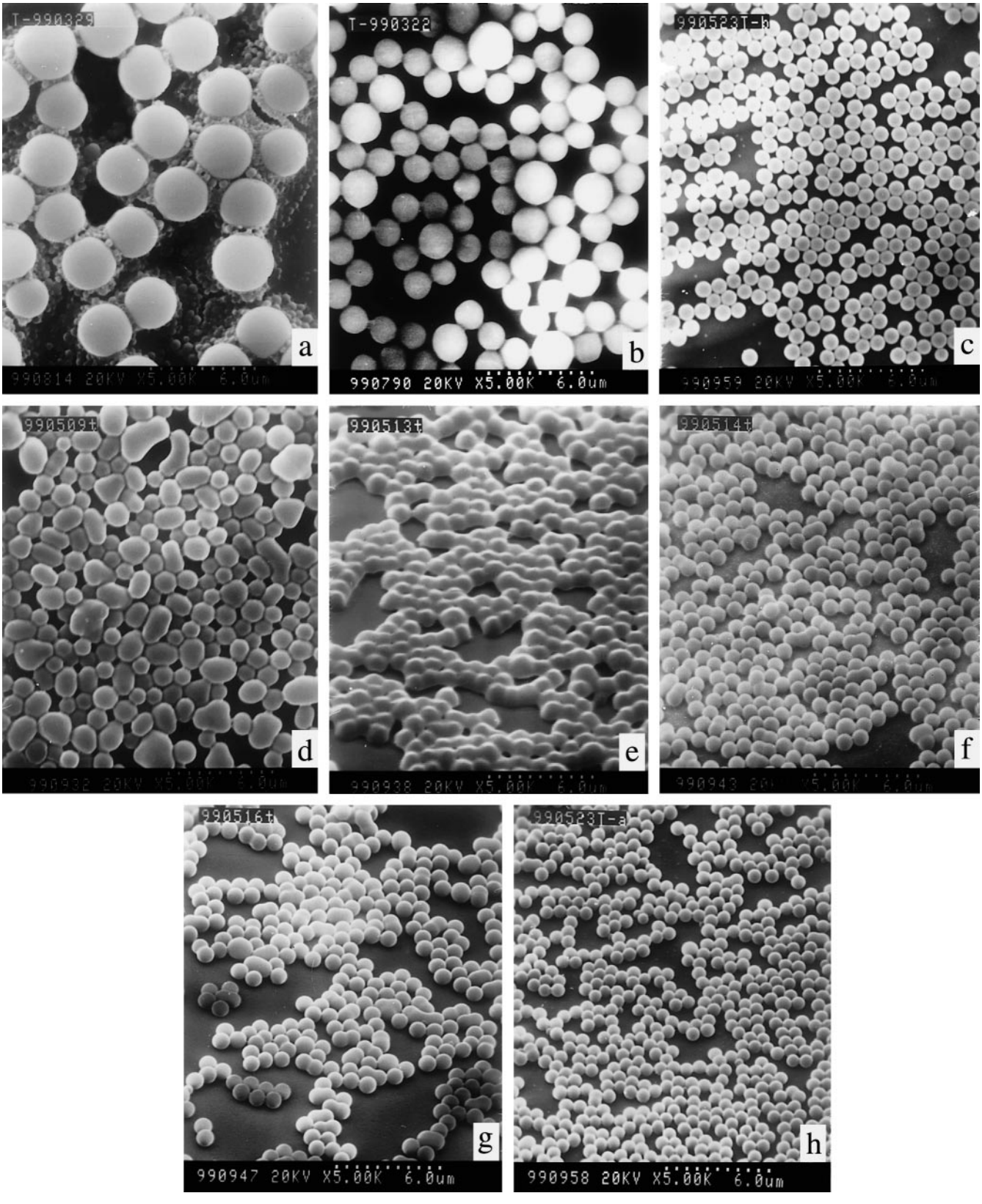
$$\delta = \left(\sum \Phi_i \delta_i^2\right)^{1/2} ,$$

where Φ_i is the volume fraction of component i. Usually, neither the polymeric stabilizer nor the initiator is used in the estimation since they are present in small quantities. The polymer produced from the monomers is not included in the calculation since it is located in a separate phase. The solubility parameters of the individual components used in this study are summarized in Table 2 [21].

The effect of the water content in the solvent mixture on the solubility parameter of the system is indicated in Table 3. The solubility parameter increased with

►

Fig. 2 Effect of poly(vinylpyrrolidone) concentration on the particle size and size distribution: **a** C1; **b** C2; **c** C3; **d** D1; **e** D2; **f** D3; **g** D4; **h** D5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T-990322
b
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990509+
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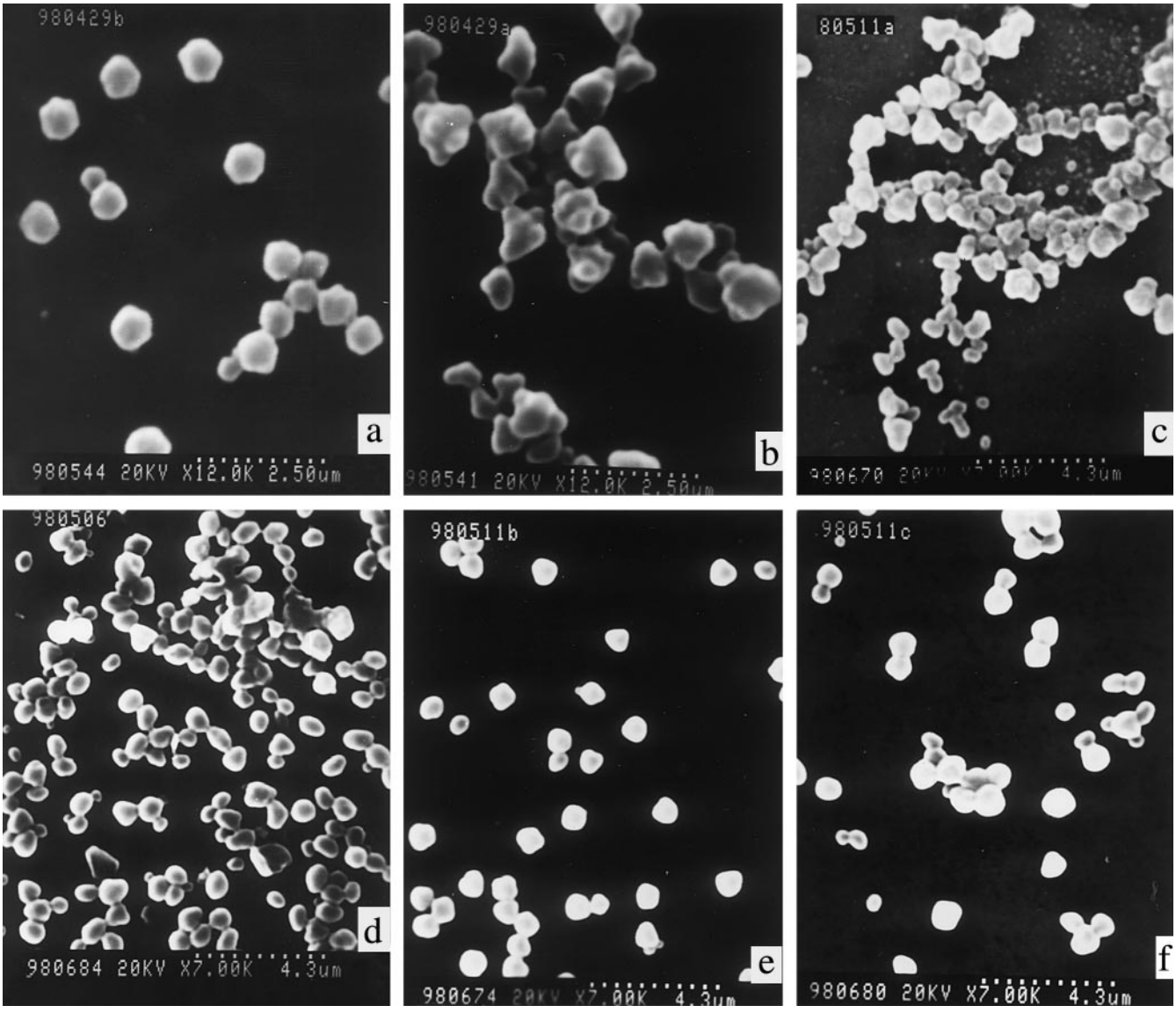

Fig. 3 Effect of acrylamide fraction in the monomer mixture on the cross-linked particles: **a** E1 at 4 h of reaction; **b** E1 at 8 h of reaction; **c** E2; **d** E3; **e** E4; **f** E5

increasing water content. As seen in Table 3 and Fig. 1, the particle size decreased and the size distribution narrowed with the increases in water content and solubility parameter. When the polarity of the system is enhanced, the critical molecular weight of the copolymers or the critical chain length decreases and the rate of adsorption of the stabilizer-grafted copolymer onto the nuclei increases, resulting in smaller particles. Meanwhile, the precipitation rate of the polymer chains increases and the particle formation stage becomes shorter, which is advantageous for obtaining a narrower distribution. However, if the medium polarity is too high, there may not be enough time for the stabilizer to be grafted onto the polymer chains and adsorbed onto the nuclei. Thus, the nuclei may become unstable and coagulation occurs; therefore, in runs B3 and B4, a lot of coagulum was produced. In run B5, however, the particles were very stable and no coagulum occurred. The particle size was about 500 nm, similar in size to the particles prepared by emulsifier-free emulsion copolymerization. Compared with the dispersion polymerization of pure St in such polarity media, this system had lots of coagulum; so we suppose that PAm, as a costabilizer, played a key role in the very high polarity medium.

Effect of the stabilizer concentration

The stabilizer plays an important role in the preparation of micron-sized particles by dispersion polymerization

Table 5 Effect of the comonomer Am on the morphology and the glass-transition temperature (T_g) of the particles in the presence of cross-linking agent. In all the reactions benzoyl peroxide (0.6 g) and PVP (0.6 g) were used

Sample	Ethanol/H_2O (g/g)	Styrene/Am (g/g)	Divinylbenzene (g)	$\bar{D}_v$ (μm)[a]	T_g (°C)	Remark
E1	70/15	13.35/1.5	0.15	0.90	–	Well-dispersed, cone-shaped
E2	74/11	7.9/2.0	0.1	1.22	106.7	Odd shape
E3	74/11	8.9/1.0	0.1	0.88	106.4	Odd shape
E4	74/11	9.4/0.5	0.1	0.79	104.2	Almost spherical
E5	74/11	9.7/0.2	0.1	0.86	103.6	Spherical with slight coagulation

[a] Diameter calculated using a Coulter LS230

[10, 12, 22, 23]. In this study, the effects of the stabilizer concentration on the particle size and size distribution were studied in a relatively low polarity medium and a high polarity medium. From Table 4 and Fig. 2, it can be seen that the effects were different. In the low polarity medium series, an increase in the concentration of stabilizer, PVP, increases the viscosity of the medium and the rate of physical adsorption of PVP. In run C1, due to the low concentration of PVP, the particles were large and the total particle number was small, thus reducing the surface area of all the particles. Therefore, the ability of stable particles to capture the copolymer chains in the continuous phase was also reduced, resulting in postnucleation and a bimodal size distribution. In the higher PVP concentration system, such as run C3, the stage of the formation of stable particles became shorter, reducing the nucleation time, and particles with a small and narrow size distribution were obtained. The series results conformed to those of others systems [12, 15, 22]; however, in the high polarity medium, the effect was different. With an increase in PVP concentration, the particle size changed slightly. Increasing the PVP concentration was beneficial to resisting coagulation and reducing the number of triplets and doublets. The reason for the formation of coagulum is still not very clear.

Effect of the comonomer Am under the existence of cross-linking agent (DVB)

The cross-linked micron-sized polymer particles prepared by single-step dispersion polymerization were studied [24, 25]. Because of the nonswellability of the highly cross-linked primary particles, the dispersion polymerization mechanism of DVB was proposed such that the particle growth occurred through the precipitation of the nucleated oligomers or the adsorption of the particles onto the surface of the primary particles. It was also reported that due to the nonswellability of the cross-linked particles, stable particles were usually not obtained when the cross-linking agent (DVB) content was over 3% of total monomer weight. In this work, we induced DVB into the particles to investigate the effect of comonomer Am on the particle morphology. In order to obtain stable particles, a suitable amount of DVB was induced. As shown in Fig. 3a, at the reaction time of 4 h, the particles formed were basically spherical with very little protrusions; however, while the reaction continued, the protrusions grew and finally conelike particles were obtained (Fig. 3b). The result proved that due to the remarkable difference in the monomer reaction ratios of Am and St, in the first step of the process, cross-linked PSt fragments mainly proliferated in the particle and later PAm fragments proliferated. Because the primary particles were rigid and unable to adjust the internal chains and the PSt fragment is oil-soluble while the PAm fragment is water-soluble, phase separation of the PAm-rich fragment and the PSt-rich fragment occurred on the surface of the particles; thus, the protrusions were formed and the particles became odd. When the feed amount of Am decreased (E2–E5), the surface of the particles became smooth and spherical particles were obtained. This also supported the previous assumption. As seen in Table 5, with a decrease in the amount of Am, the particle size decreased first and then increased. The result was similar to the previous experiment (A1–A4).

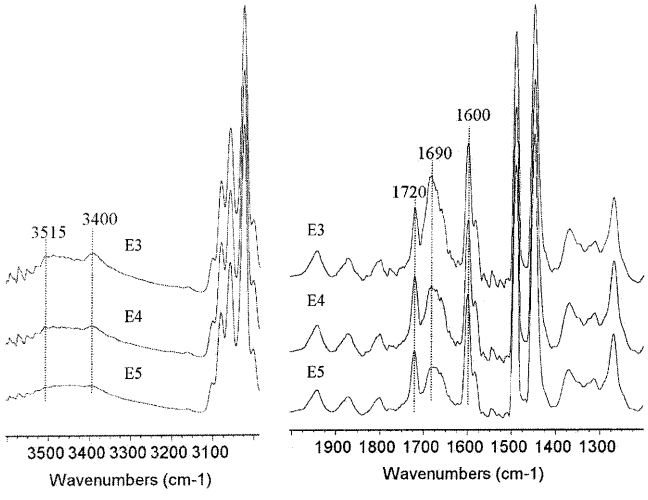

Fig. 4 Fourier transform IR spectra of the cross-linked particles

The FTIR spectra of the E3–E5 cross-linked copolymer particles are shown in Fig. 4. The absorption peaks of the copolymers at 3515 and 3400 cm^{-1} can be assigned to the vibrations of the hydrogen atoms of the primary amide. Compared with the peak at 1600 cm^{-1}, the height of the absorption at 1690 cm^{-1}, which is the peak of the carbonyl group of the amide, decreased with decreasing amount of Am in the monomers (from E3 to E5). This indicated that the amount of the amide group in the copolymer particles is proportional to the amount of Am in the monomers. Differential scanning calorimetry measurements showed that the decrease in the amount of Am in the monomers caused the T_g to decrease (Table 5), and this also proved the earlier result.

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