

Preparation and Characterization of P(St-co-4VP) Particles Produced by Using Emulsifier-Free Emulsion Polymerization

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ABSTRACT: Emulsifier-free emulsion polymerization of styrene (St) and copolymerization of St and 4-vinyl pyridine (4VP) in the presence of ammonium persulfate were studied. A comparison between the two polymerization systems was made. It was found that there were big differences comparing polymerization rate, the number and size of the particles and distribution, and molecular weight. For the St-4VP system, it was found that the additional amount of 4VP influenced the copolymerization of St and 4VP, molecular weight, and particle size. The formation mechanism of the particles was discussed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1502–1507, 1999

Key words: emulsifier-free emulsion polymerization; homogeneous coagulative nucleation; monodispersed particles; 4-vinyl pyridine; styrene

INTRODUCTION

Emulsifier-free emulsion polymerization was used extensively to prepare the particles having functional groups on their surface, and their application as catalysts, biomedical materials, magnetic materials,^{1,2} and adhesives were studied. In such polymerization systems, polymer particles were stabilized by the polymer capped with hydrophilic groups produced by using ionizable initiators, such as potassium persulfate,^{3,4} or by ionic polymers obtained by adding comonomers with ionic groups, such as carboxylic monomers,^{5,6} sodium sulfoethyl methacrylate (NaSEM),⁷ sodium styrene sulfonate (NaSS),⁷ and sodium undecylenic isethionate (NaUI),⁸ etc., and some nonionic monomers, such as glycidyl methacrylate⁹ and 2-hydroxyethyl methacrylate,¹⁰ were also used as comonomer for stabilizing the parti-

cles. Several mechanisms on particle nucleation and growth in emulsion polymerization without emulsifier were proposed to account for the water solubility of the monomers. For example, in the presence of the water-soluble initiator, potassium persulfate (KPS), the slightly water-soluble monomers, such as styrene (St), were initiated and polymerized in aqueous phase to produce oligomeric radicals with terminal sulfate group; then micelles were formed.³ However, for more water-soluble monomers, such as methacrylates,^{11,12} the particles were formed by the precipitation of growing chains at different critical chain length on monomers; for example, the critical chain length of methyl methacrylate (MMA) is 60–80. In both cases, subsequent polymerization occurred in monomer-swollen particles. In recent years, a coagulative nucleation of precursor particles theory was proposed,¹³ describing that the stable latex was formed from the coagulation and growth of unstable precursor particles formed through homogenous nucleation. The rate of particle formation was determined by (1) the

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Table I Recipe and Results of Emulsifier-Free Emulsion Polymerization^a

No.	St (g)	4VP (g)	APS (g)	H ₂ O (g)	N ^b in the Copolymer (wt %)	4VP Conversion ^c (%)	Total Conversion ^d (%)	<i>d</i> (nm)	<i>M_w</i> (10 ⁴)
V-0	18.0	0	0.2010	202	—	—	33.2	580 ± 80, 850 ± 140	2.1
V-1	18.0	1.0	0.1474	201	0.30	42.9	46.7	763	2.4
V-2	18.0	2.0	0.0800	200	1.22	91.7	76.8	421	5.2
V-3	18.0	3.0	0.0604	199	1.80	94.7	77.6	274	5.5
V-4	18.0	4.0	0.0541	198	2.30	95.9	93.5	270	6.2

^a Polymerization condition: temperature, 70°C; polymerization time, 8 h.

^b Elementary analysis data.

^c Calculated on the elementary analysis data.

^d Calculated on gravimetric analysis data.

rate of homogenous nucleation to form primary precursors, (2) the rate of coagulation of precursor particles, and (3) the rate of propagational growth.

Although extensive studies were reported for the emulsifier-free emulsion polymerization of St, only a very few of them were concerned with the copolymerization of St and 4-vinyl pyridine (4VP).¹⁴ The copolymerization of St and 4VP in acidic or basic emulsifier-free aqueous medium was investigated.¹⁴ In this article, the copolymerization of St with 4VP without acid or base was carried out and the mechanism of particle nucleation was discussed on the basis of polymerization rate and the diameter of latex particles. The relationship between the polymerization mechanism and molecular weight distribution was studied.

EXPERIMENTAL

Materials

Deionized water was used in all experiments. St (Chemical reagent, Central Chemical Plant of Shanghai Chemical Reagent Station, Shanghai, China) was distilled at 40°C/14.5 mmHg and stored at 4°C. 4VP (Merck-Schuchardt, München, Germany) was distilled at 55°C/18 mmHg before use. Ammonium persulfate (APS; Anjian Chemical Plant of Shanghai, Shanghai, China) was analytical grade and used without further purification.

Polymerization Procedure

A typical recipe for preparation of St-co-4VP copolymer latex is shown in Table I. The polymer-

ization was carried out at 70°C and 350 rpm of stirrer speed in nitrogen atmosphere. Total conversion was determined gravimetrically. All the ingredients except APS solution were placed in a 250-ml five-neck round-bottom flask equipped with a mechanical 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 APS solution. The resulting latex particles were cooled and filtered through a glass sinter filter, then centrifuged for over 10 min at 15,000 rpm. The precipitates were dispersed again in water by using an ultrasonic bath. The centrifugation–dispersion procedure was repeated three times. The obtained latex dialyzed over 1 week and the water was changed each day. The composition of copolymer was calculated on the basis of its elemental analysis.

Characterization

The size and morphology of the P(St-co-4VP) microspheres were investigated with a JCM-100CX transmission electron micrograph (TEM); weight-average diameter (*D*) was calculated on the basis of $\sum n_i d_i^3 / \sum n_i d_i^2$, where n_i was the number of particles with diameter d_i . The latex particle size distribution was calculated on the basis of the sizes of about 100 particles in different regions of TEM photos. The number of latex particles in unit volume of aqueous medium was calculated from *D*, the conversion, and the average density of copolymer. Number-, weight-average molecular weights, and molecular weight distribution of the polymers obtained were measured on a Waters 208 gel permeation chromatograph with Ultrastaygel Columns (Waters Co.) at 1.5 mL/min with THF as solvent and polystyrene as standard.

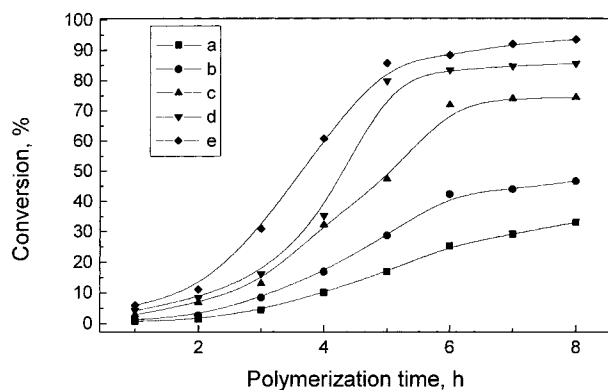


Figure 1 Time-conversion curves for the emulsion copolymerization of St with 4VP. (a) V-0; (b) V-1; (c) V-2; (d) V-3; (e) V-4, the recipe of V-0 to V-4 are the same as that in Table I.

RESULTS AND DISCUSSION

Conversion

The recipe of emulsifier-free polymerization is listed in Table I. It was found that the conversion could not exceed 10% in the first 1 hour; otherwise, coacervation phenomenon in the polymerization occurred, and the latices could not be obtained. When the fraction of 4VP fraction increased, the amount of initiator had to be reduced (see Table I). These interesting phenomena are under further study.

The time-conversion curves for the emulsifier-free emulsion polymerization are shown in Figure 1. The V-0 curve of Figure 1 shows the polymerization progress of slightly water-soluble St. Before 3 h polymerization, very low conversion indicates that time was needed to produce enough oligomer with sulfate group. The micelle nucleation was proposed as the mechanism of particle formation.³ The initiating rate was much faster than the chain propagation rate; a quantity of oligomeric free radicals, with sulfate group existing in aqueous solution, formed stable micelles at first, then the monomer or propagation chain was diffused into the micelle and polymerized. With the volume increase of the particles, there was insufficient oligomer capped with sulfate group to stabilize the particles, thus aggregation of particles occurred. The process would be repeated until stable colloidal particles were formed. Because the particles were stabilized only by oligomer stabilizer produced from APS, and the amount of this stabilizer was restricted, the polymerization rate was slow [see Fig. 1(a)].

In the V-1 to V-4 system, 4VP was used as a comonomer. The curves b to e in Figure 1 are, respectively, the results of polymerization of V-1 to V-4 in Table I. Three stages of polymerization were observed from the curves; for example, in the case of e curve, the polymerization rate increased as polymerization proceeded during the first 2 h of polymerization (Stage I), then it stayed constant from 2 to 4 h (Stage II) of polymerization; at last it decreased (Stage III). This is the same as that in conventional emulsion polymerization. The main difference in rate from conventional emulsion polymerization was the low polymerization rate in Stage I, because time was needed to produce enough oligomers of St capped with sulfate group for the formation of micelles and stabilization of the particles formed. Therefore, the mechanism of nucleation is also different from conventional emulsion polymerization. It was thought that the mechanism of particle formation was attributed to the homogeneous nucleation process.^{15,16} At the beginning of the polymerization, APS was thermally decomposed into primary radicals to initiate the copolymerization of St and 4VP in the aqueous phase. The formed copolymer or radicals could either be soluble in the aqueous phase or coagulate to form primary particles, depending on their molecular weight (M_w) and the content of 4VP. In Chen and Lee's work, describing the copolymerization system of St and acrylamide (AAM), they found that during the nucleation formation, the AAM content in the polymer was higher than that calculated from the copolymer composition equation. Most of the AAM-rich chains would preferably locate on the surface of particles and stabilize the particles.¹⁷ Therefore, for the copolymerization of 4VP and St, two factors influencing the stability of particles should be considered. One was the amount of ionic groups produced from the decomposition of APS; another was the content of water-soluble 4VP. When the content of 4VP increased, the rate of copolymerization of St and 4VP was accelerated in the aqueous solution during nucleation, thus the rate of nucleation increased and the primary particle was more stable. These led to an increase in the number of particles. This was confirmed by the result shown in Figure 2. As we know, the polymerization rate is proportional to the number of the particles. The constant rate of polymerization during Stage II (see e curve of Fig. 1) indicates that the number of particles did not change after Stage I of polymerization. The reduction of

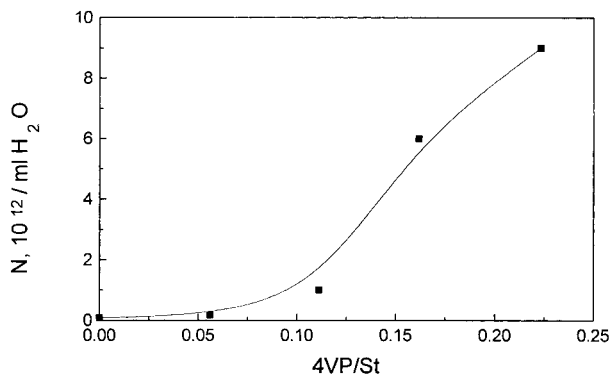


Figure 2 Dependence of particles' number on the content of 4VP in the polymerization system.

polymerization rate in Stage III should be due to the disappearance of monomer droplets.

Particle Size and Its Distribution

Figure 3 is the TEM photography of V-0. A bimodal distribution of particle size was observed as in Figure 4. This indicates that part of the formed particles was aggregated to produce new growing particles, or new primary particles were formed after the nucleation period. From the slope values of the V-0 curve in Figure 1, it was found that the polymerization rate during 3–6 h of polymerization time was higher than that after 6 h. This probably was the result of a decrease in the number of particles. As we know, the particles of V-0 were only stabilized by oligomer stabilizer produced from the decomposition of APS. As polymerization proceeded, the increase of the particles size caused them to become unstable. There-

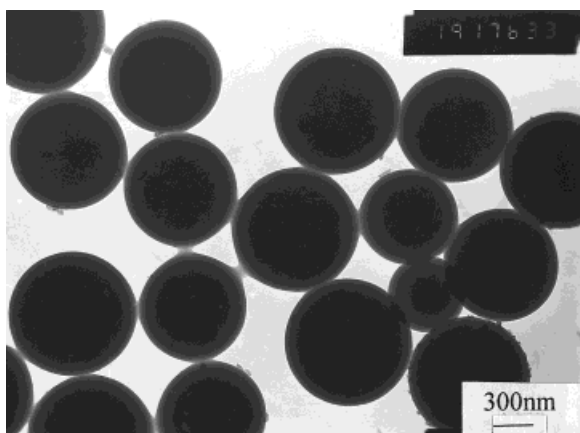


Figure 3 Transmission electron micrograph photo of V-0. Polymerization conditions, see Table I.

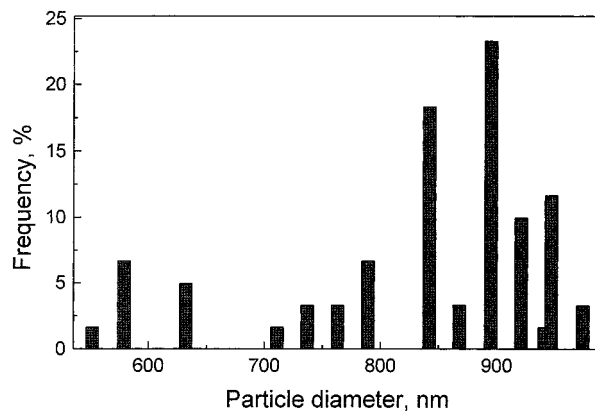


Figure 4 Size distribution of V-0.

fore, coagulation of the particles occurred, and new bigger particles were formed.

For the 4VP/St/APS/H₂O system, the diameters of the obtained particles decreased with an increase of 4VP, and the monodispersity of the particle size was observed (see Fig. 5). The particle size distribution data are listed in Table I.

Higher conversion of 4VP than that of St (see Table I) demonstrated that the polymer produced in the nucleation period was rich in 4VP. Different from the V-0 system, this polymer, located on the surface of the particles, acted as an emulsifier. As the content of 4VP in the polymerization system increased, more oligomer molecules rich in 4VP were formed; then more primary particles were produced (see Fig. 2). Compared with the V-0 system in the V-1 to V-4 system, the rate of nucleation increased in aqueous solution with the content increase of 4VP. The possibility of polymerization in each particle was almost the same. Therefore, the particles with monodispersity were obtained. The same results were observed by Chen and Lee in the P(St-co-AAm) system.¹⁷

Molecular Weight and Distribution

After emulsion polymerization was finished, the particles were collected and dried. The polymer solution obtained by dissolving some particles in THF were used to measure M_w and distributed by GPC method. The results are shown in Figure 6. A bimodal distribution of molecular weight of polymer V-0 was observed in Figure 6; however, this phenomenon did not appear in V-1 to V-4 system. In the emulsifier-free emulsion polymerization of St, Goodall et al.³ found that the distribution of molecular weights altered significantly as the polymerization proceeded. In the early

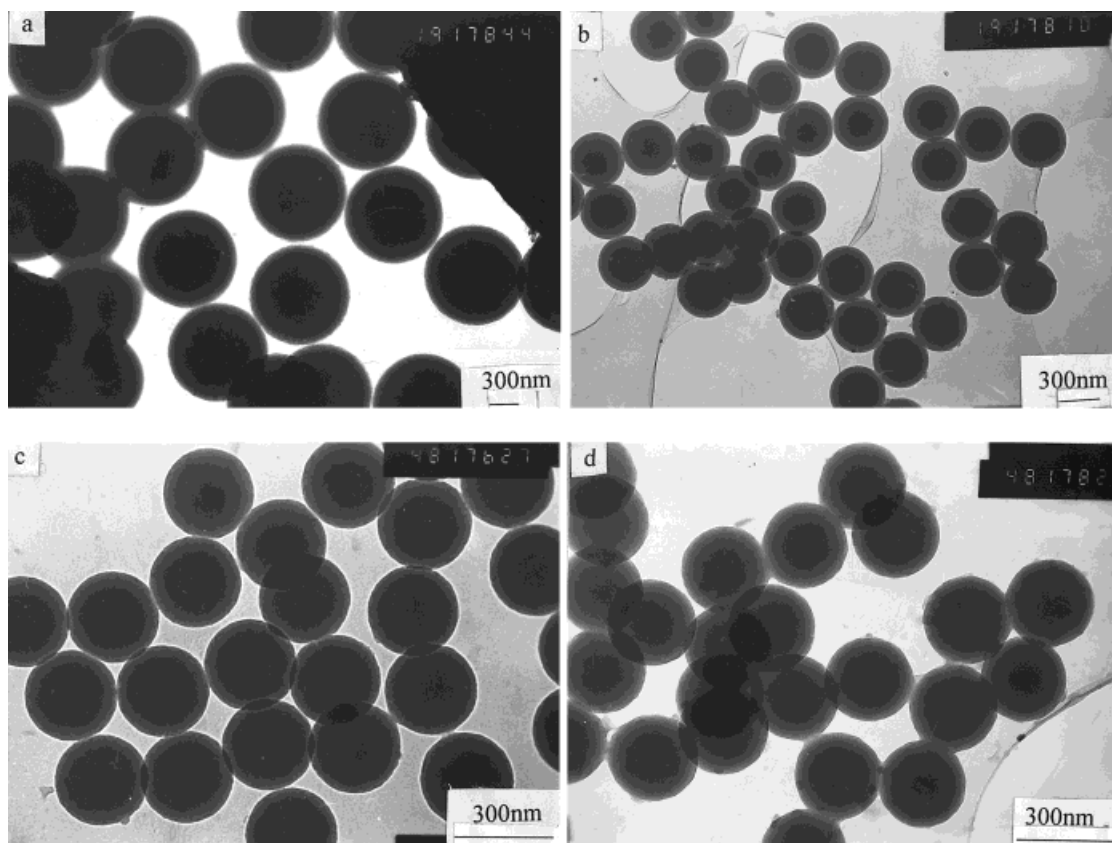


Figure 5 Transmission electron micrograph photos of particles. (a) V-1; (b) V-2; (c) V-3; (d) V-4.

stages of the polymerization, a significant amount of the polymers with low molecular weights (ca. 1000) was presented in the system. Two peaks were noted in the GPC curve of the obtained polymer. As the polymerization proceeded, the

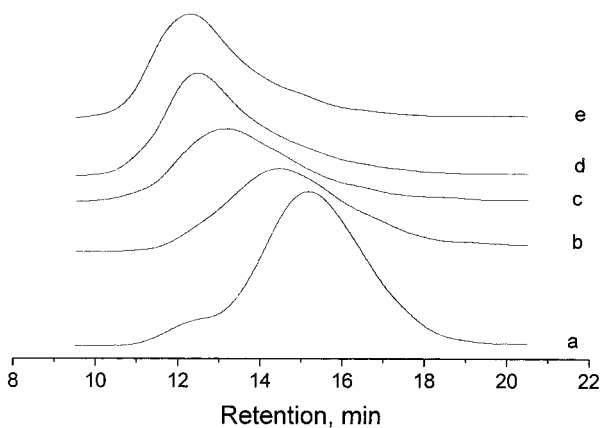


Figure 6 GPC curves of the polymers. (a) V-0; (b) V-1; (c) V-2; (d) V-3; (e) V-4.

amount of low molecular weight polystyrene decreased in comparison with the total polymer. The double peak disappeared at last, but there was tail on the GPC curve. However, in our research, for the St system, two peaks still existed on the GPC curve even for the polymer obtained at the end of emulsion polymerization [see Fig. 6(a)]. The reason for this result is, for V-0 system, when the oligomers capped with sulfate group were not enough, the initially formed particles became unstable, and as polymerization proceeded, thus the aggregation of the particles occurred, resulting in the decrease of particle number. As we know, the polymerization degree (DP) of the polymers obtained in emulsion polymerization system is generally proportional to the number of the particles. Thus, a small amount of higher M_w PSt and relatively large amount of lower M_w PSt was produced [see Fig. 6(a)].

The V-1 to V-4 curves in Figure 6 and the data listed in Table I showed that the polymers obtained from V-1 to V-4 system have broad distri-

bution of M_w , and the M_w increased as the content of 4VP increased. The latter results in the increase of particle number with the increase of 4VP as shown in Figure 2. In the St-co-AAm system, Chen and Lee¹⁷ found a bimodal molecular weight distribution in the initial period of polymerization, and, as the polymerization proceeds, the major peak shifted gradually to the higher M_w region; finally, a broad curve was formed. In the St-4VP system, higher conversions were obtained in 8 h (see Table I). The double peak disappeared early. Tail phenomenon occurred on the GPC curves of the polymers V-1 to V-4 (see Fig. 6) and demonstrated that the polymer produced in the initial period of polymerization was of two molecular weight distributions: one at higher M_w , another at low M_w . As the polymerization proceeds further, the major peak shifts gradually to the higher M_w region and finally covers the higher M_w peak generated in the initial period. For the same reason observed by Chen and Lee,¹⁷ a broad distribution of M_w was obtained.

CONCLUSION

Emulsifier-free emulsion polymerization of St and copolymerization of St and 4VP were carried out by using APS as an initiator. For the St-4VP system, the copolymer rich in 4VP could act as an emulsifier; the number of the particles increased, and the diameter of the particles decreased as 4VP increased. Thus, the polymerization rate of the St-4VP system was higher than that of St system, and the rate of polymerization increased with the increase of 4VP. The emulsifier-free emulsion polymerization of the St-4VP system behaved in three stages the same as the conventional emulsion polymerization. For the St system, because the particles were stabilized only by the oligomer with sulfate group produced from APS, the rates of nucleation and polymerization were relatively low, but a bigger diameter of this

particle (ca. 850 nm) was obtained. Bimodal distributions of particle size and M_w were found at 33.2% of conversion. Monodispersed P(St-co-4VP) latices could be prepared. The particles' diameter and the M_w of the polymer can be easily controlled by the amount of 4VP in the polymerization system.

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