Kinetics of Polymerization and Particle Stabilization Mechanism on Dispersion Copolymerization of Styrene and Divinylbenzene

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ABSTRACT: Monodisperse highly crosslinked microspheres were prepared by dispersion copolymerization of styrene and divinylbenzene in an ethanol/water medium using poly(N-vinylpyrrolidone) (PVP) as the stabilizer. The locus of polymerization and growth of particles were investigated. The polymerization kinetics, average particle diameter (D_n), polydispersity index (PDI), and numbers of particles (N_p) were presented. When the initial styrene concentration is below 20%, the results indicate that the polymerization occurs in the particles, and the particles grow to their final size by the diffusion of monomer and oligomer into the existing particles. The polymerization rate can be described by the equation $R_p = k[l]^{0.87} ([St]^{1.91} + [DVB]^{0.09}) (1 + [PVP]^{0.01}) \exp(-45.35/RT)$. The data from infrared spectroscopy demonstrated that the graft stabilizer was present. The dissolution experiments show that the crosslinking reaction occurred irregularly in batch dispersion polymerization. Using the postaddition approach, up to 3% divenylbenzene (DVB) was successfully incorporated in the synthesis of coagulum-free substance, and monodisperse crosslinked 5 μm microspheres with a superior resistance to solvents have been prepared. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 2230–2238, 2002

Key words: polystyrene, radical polymerization, kinetics of copolymerization, particle nucleation, stabilization, dispersion copolymerization

INTRODUCTION

As conventional polymer support material, polystyrene resins have been used in the solid-phase synthesis of biomedical, insecticidal, and organic chiral molecule. Commercial polystyrene resins used to be produced by suspension polymerization with a broad size range of 0.2–2 mm and porous structure, which results in a low reaction efficiency of rigid organic chiral molecules in the polymer reagent.[1] In contrast with the traditionally sized ion-exchange resins, micron-sized monodisperse crosslinked polystyrene microspheres (MCPS) have the following advantages: (1) Higher specific surface area can increase the capacity of functional groups on the polymer supports, especially of the rigid molecules; and (2) The solid structure, called the "unfold framework," has no steric hindrance and can increase the use ratio of functional group on the supports.[2] However, little attention was paid to the preparation of the MCPS 5–10 μm size for these applications.

There are several routes to prepare the MCPS 0.2–10 μm size range, including emulsion poly-

merization, suspension polymerization, and dispersion polymerization. However, traditional emulsion polymerization commonly produces particles in the submicron size range. Multistep seeded emulsion polymerization can obtain MCPS of the micron size, but this approach is time-consuming and requires multiple steps. And tight control on polymerization conditions is required for the success of this technique in case of coagulum and/or the generation of a second crop of particles.[3] Suspension polymerization is an ineffective method for achieving monodisperse particles because of the inherent nonuniform in the mechanic disperse systems.[4]

Monodisperse microspheres in the size range of 20–30 μm was obtained by microgravity suspension in the space, but the product is very expensive. Professor He Bing-Lin proposed an improved microsuspension technique to prepare microsize microspheres of polystyrene (PS), but the size distribution was not monodisperse.[5] Dispersion copolymerization is an unique method for forming monodisperse microspheres in the size range of 0.1–10 μm with a single step. And these particles were used for the applications such as coating, ink, dry toner, supports for chromatography, biomedical, and organic chiral reagent.[6,7] Different types of particles such as crosslinked particles,[8–10] core/shell particles,[11] and monodisperse particles having functional groups,[12] have been prepared by this technique.

However, few studies on dispersion copolymerization of styrene and divinylbenzene have been reported in the literature. One reason is that dispersion polymerization is highly sensitive to the even subtle changes of the various reaction parameters involved in the process, and the behavior of polymerization may change with the variety of the comonomer.[13] Another reason is that the crosslinking reaction is complicated and seems to occur on the surface of the formed particles, as proposed by Ober.[14] Thus, it is importance to identify the polymerization behavior of DVB in the process and increase the amount of DVB incorporated into the particles.

In this article, highly crosslinked (DVB = 4%) polystyrene particles were synthesized by dispersion polymerization in an ethanol/water medium with aqueous poly(N-vinylpyrrolidone) as the stabilizer, by postaddition approach. The relations between polymerization conversion, polymerization rate (R_p), average particle diameter (D_n), and number density of particle (N_p) with the reaction conditions were investigated. The composition of

the polymer was measured by infrared (IR) spectroscopy. The morphology of the particles was characterized by transmission electron microscopy (TEM). The resistance of microspheres to solvents was determined by a solvency experiment.

EXPERIMENTAL

Reagents

Styrene and DVB were distilled under reduced pressure after washed with a 10% sodium hydroxide solution. Azobisisobutylnitrile (AIBN) was recrystallized from ethanol. The other reagents were used as received, including methanol (MeOH), ethanol (EOH), ethyl acetate (EA), toluene (MB), tetrahydrofufan (THF), poly(N-vinylpyrrolidone) (PVP, MW = 40,000) and hydroquinone.

Batch Dispersion Polymerization

The polymerization was carried out in a 250 mL four-necked flask equipped with a condenser, a stirrer, and a nitrogen inlet. The EOH/H$_2$O solution of PVP was introduced into the flask, then the solution of St, DVB, and AIBN was added slowly under stirring. After purging with N_2 for more than 30 min, the flask was immersed in a thermostatic bath maintained 73°C for 24 h before cooling and filtering the dispersion through cheesecloth.

In a typical experiment, monodisperse PS particles of 4.17 μm diameter were formed by introducing a solution containing 25 g of St, 2 g of PVP, 0.125 g of DVB, 0.75 g of AIBN, and 82.125 g (95%) of EOH/H$_2$O into a reaction flask.

Postaddition Dispersion Polymerization

With the aim of increasing the particle size and crosslinking density, a charge of EOH/H$_2$O solution of St containing 2% DVB (wt/wt of total St) is added slowly (about 0.8 mL/min) into the reaction system containing an initial solution for 4 h after polymerization starts. The composition of the initial solution is the same as the typical recipe given above. The polymerization continued 24 h under the same conditions as the batch procedure. An example recipe of the charge is given: 5 g of St, 1.00 of DVB, 44.525 g (60/40) of EOH/H$_2$O.

Solvency Experiment

The microspheres were washed by repetitious centrifugation cycle with ethanol and then with water. The particles were then dried in a low temperature (−5°C) under vacuum. A set of samples was taken; each sample was immersed into 50 mL of solvent. The solvent used were MeOH, EA, MB, and THF. After 24 h, the samples were withdrew and dried at 70°C under vacuum until the weight was constant.

Monomer Conversion and Polymerization Rate

The conversion (C) was determined gravimetrically. And the polymerization rate (R_p, mol L^{-1} min^{-1}) was calculated as follows, which was proposed by LIU Jin-Hui[15]:

$$R_p = dc/dt \times [M]$$

where dc/dt is the slope of the conversion-time curve and $[M]$ is the initial concentration of St (mol/L), of the medium volume in the recipe.

Particle Diameter and Size Distribution

The particles were observed by transmission electron microscopy (TEM-100SX). The particle diameter (D_n) and polydispersity index (PDI) were calculated as previously reviewed.[16]

Particle Number Density

The particle number density (N_p) is defined as the particle number of unit quality and calculated as follows:

$$N_p = 6 \times S/(\pi r^3 \rho)$$

where S is the solid quantity of the dispersion, r is the radius of particles, and ρ is the density of polymer, which is defined as 1.05 g/cm^3.
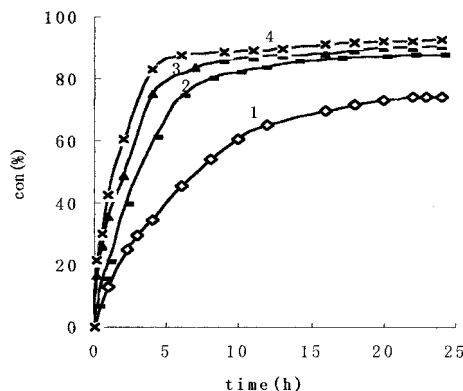
FTIR Spectroscopy

The IR spectrum was characterized by IR spectrum-one (PE).

Resistance of Polymer Particle to Solvents

The resistance of particles to solvents was characterized with the weight loss (WL), which defined as follows:

$$WL = (W_1 - W_2)/W_1 \times 100\%$$

Figure 1 The conversion-time curve of dispersion copolymerization under different [St]. (1) 10%, (2) 20%, (3) 30%, (4) 40%. DVB/St = 0.01, PVP/St = 0.08, AIBN/St = 0.03, EOH/H_2O (95/5).

where W_1 is the initial weight of samples, and W_2 is the weight of sample after soaking.

RESULTS AND DISCUSSION

Kinetics Character of Dispersion Polymerization

Figure 1 shows the variations of the conversion with reaction time where the St monomer concentration [St] varies from 10 to 40% (wt/wt, of the total). The overall polymerization rate increased with the increasing St concentration. There is no pronounced "autoacceleration phenomenon" when [St] is 10%, as shown in Curve 1, which indicates that polymerization occurs predominantly in the continuous phase (the medium). While [St] is up to 20%, there is a sharp increase in conversion in Curves 2–4. The polymerization rate (R_p) and acceleration rate (R_A) curves were calculated from the conversion of Curves 1–3, and given in Figure 2. The R_p in Curve 1 do not change notably throughout the process, which is similar to dilute solution polymerization. This predicates that there is no the period in which the acceleration rate increases in the R_A Curve 1. Only the homogeneous polymerization (namely polymerization in the medium) can explain the phenomenon. However, the R_p Curve 2 and 3 increase in the early period.
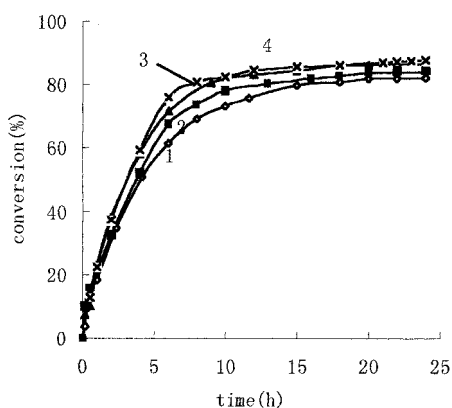
Then the R_p decreases as the polymerization proceeds. It is obvious that, in correspondence to the R_A curve, R_A increases with reaction time in the early period. The accelerating rate is increased and R_p increases more quickly with increasing the St concentration. These results indi-
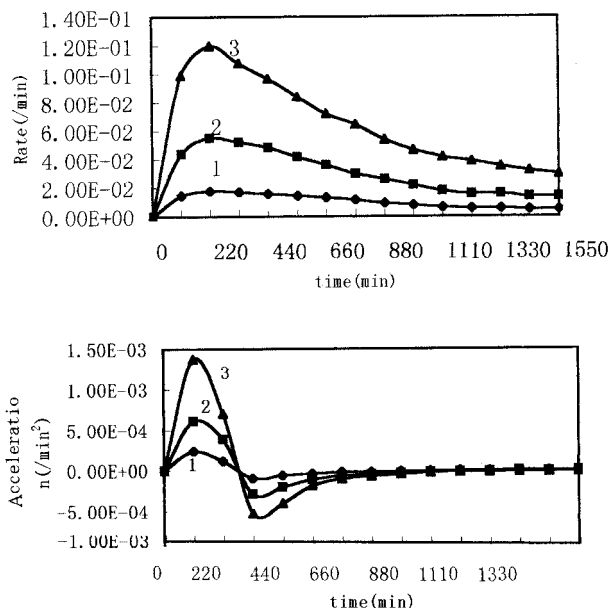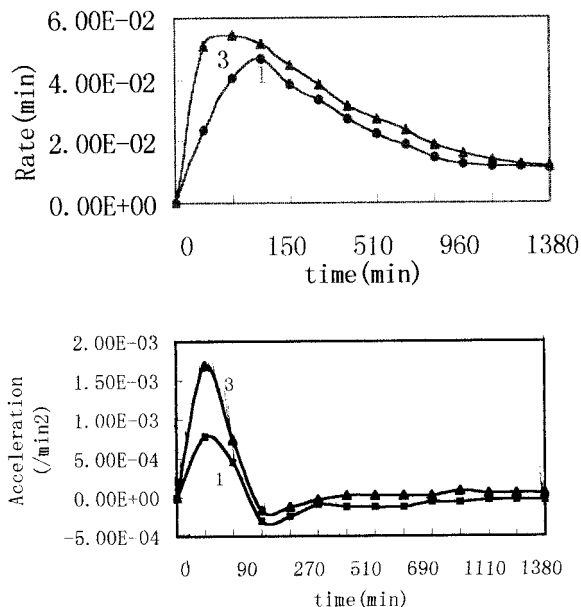
Figure 2 The plot of polymerization rate and acceleration rate under different [St]. (1) 10%, (2) 20%, (3) 40%. DVB/St = 0.01, PVP/St = 0.08, AIBN/St = 0.03, EOH/H$_2$O (95/5).


Figure 4 The plot of polymerization rate and accelerate rate under different [DVB] (wt%). (1) 0, (3) 1%. [St] = 20%, PVP/St = 0.08, AIBN/St = 0.03, EOH/H$_2$O (95/5).

cate polymerization mostly occurs in the formed particles when the St concentration is less than 20%. Polymerization in the particles results in the "gel effect," which causes increase of the R_A.

Figure 3 shows the variation of conversion with reaction time for certain polymerization using different amount of DVB. It can be seen that the polymerization rate increases with increasing DVB concentration. This is due to the higher reactivity of DVB, which reduces the activation en-

Figure 3 The conversion-time curve of dispersion copolymerization under different (DVB) (wt%). (1) 0, (2) 0.5%, (3) 1%, (4) 1.5%. [St] = 20%, PVP/St = 0.08, AIBN/St = 0.03, EOH/H$_2$O (95/5).

ergy of polymerization. But it seems that the influence is not distinct while DVB concentration varies from 0.5 to 1%, and a large amount of coagulum yields. In the same way, the variation of polymerization rate and accelerate rate in the process is given in Figure 4. There are two reaction systems, one without DVB, the other with 1% DVB, which are shown in Curves 1 and curve 3 of R_p, respectively. The initial R_p in Curve 1 is lower than that in Curve 3. This is due to the acceleration of DVB.

In the same way, the variations of polymerization conversion with the reaction temperature (T), and the concentration of PVP and AIBN, were also obtained. From these experimental results, the plots of logR_p vs log[St], logR_p vs log[DVB], logR_p vs log[PVP], logR_p vs log[I] and logR_p vs 1/T are given. An equation demonstrating the relation of R_p and these reaction parameters were obtained as follows:

$$R_p = k[I]^{0.83}([St]^{1.91} + [DVB]^{0.13})$$

$$\times (1 + [PVP]^{0.01}) \exp(-E/RT)$$

where R_p is the polymerization rate, k is the polymerization constant, [St], [DVB], [PVP], and [I] are the concentration of St, DVB, PVP and AIBN, respectively. T is the reaction temperature. E is
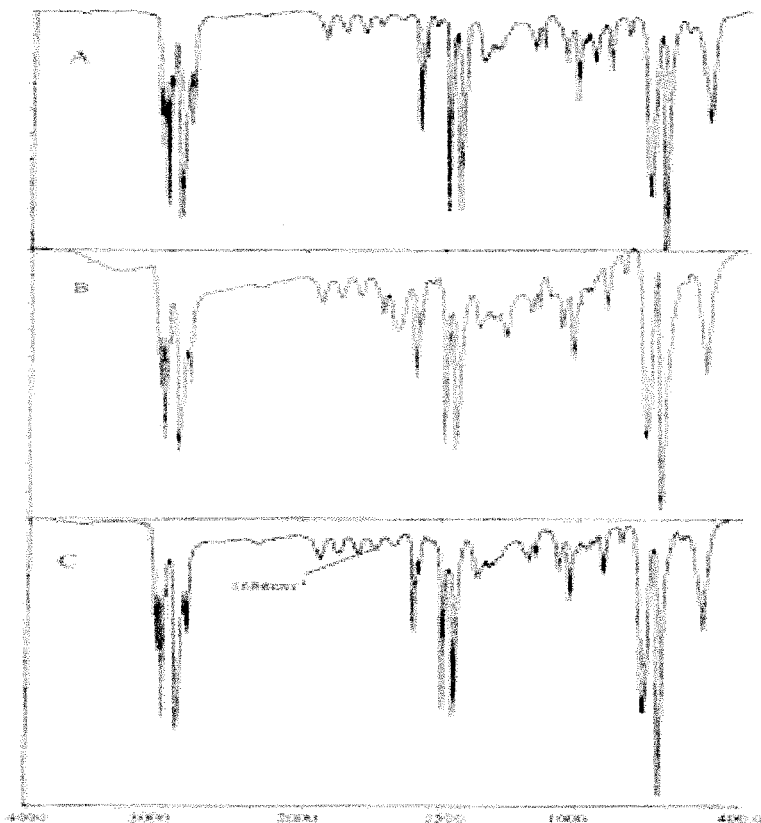
Figure 5 FTIR spectra of PS sample with different treatment. (A) PS standard; (B) PS particle unwashed; (C) PS particle washed.

the activation energy of copolymerization, whose value is −45.96 KJ/mol.

The polymerization rate is dependent principally on [St] and [I]. PVP concentration has no remarkable influence on the polymerization. This can be explained by the fact that the graft polymerization of PVP has completed in the early polymerization process, and the amount of PVP has no pronounced effects on the number of stabilized particles. Thus the effect of [PVP] on R_p is not distinct. R_p is dependent on $[DVB]^{0.13}$, whose effect is much lower than that of $[St]^{1.91}$. This is due to two reasons. One is the lower concentration of DVB; the other is the quicker consumption of DVB in the polymerization, which causes the rapid decrease of DVB.

Mechanism of PVP Stabilization

There are several stabilization mechanisms on dispersion polymerization. Furusawa and Kimura consider that the stabilizer is adsorbed to the surface of particles, which is similar to emulsifier in emulsion polymerization.[17] Others propose that the stabilizer is grafted into the formed polymer chain and it is the graft polymer that stabilizes the particles in the reaction system.[18] The latter mechanism is called "mechanism of graft stabilization." However, the experimental proofs for this mechanism have been rather limited.

To identify the existence of the PVP-PS polymer, the IRspectroscopy was performed. Figure 5 shows the IR spectroscopy of three samples: PS standard, unwashed particles, and particles washed with ethanol and water. In Figure 5 there are distinct differences among the spectra of the three samples. At about 1688 cm^{-1}, the peak of each sample shows here in the three spectra. However, the peak of PS standard sample is weaker than that of the other two samples due to the increase of the carbonyl group from PVP molecules.

Furthermore, the peak in the unwashed sample is stronger than that in the washed sample due to decrease of the PVP in the sample washed with ethanol or water. These results indicate that not only there are PVP-PS graft copolymers in the

Table I The D_n, PDI, and N_p Under Different St Concentrations

	Run 1	Run 2	Run 3	Run 4	Run 5	
[St] (wt%)	10	20	25	30	40	T = 73°C, DVB/St = 0.5%,
D_n (μm)	2.45	3.98	4.38	4.60	5.12	PVP/St = 8%, AIBN/St = 3%, EOH/H$_2$O = 95/5
PDI	1.21	1.07	1.04	1.11	1.42	(all the ratios are weight percentage) Runs 1–5 by
N_p (10^9/g)	11.33	6.36	6.92	6.142	6.05	batch

particles, but also PVP absorbed onto the particles. In the previous section, the PVP concentration has little effect on the polymerization rate.

Thus, we may consider the stabilization to be attributable to graft copolymer but not to the adsorbed PVP; otherwise, with increase of the PVP quantity stability of the system will increase.

Effects of St Concentration on Particle Size and Number

Table I shows the variations of particle average diameter D_p, PDI, and particle number N_p with St concentration. With increase of St concentration, the particle diameter increases from 2.45 to 5.12 μm, PDI increases, too, while the particle numbers decreases rapidly. It can be seen that monodisperse microspheres were obtained in Run 3, where the St concentration is 25%. Whenever the concentration of St are higher or lower than 25%, distribution of the particle size broadens. The similar trend was reported in the literatures[19] about styrene dispersion polymerization. With increasing the St concentration, the solubility of polymer formed in the medium increases and thus the critical chain length of the oligomers increases. In addition, it increases the solvency of the graft copolymer formed *in situ* with the stabilizer. Consequently, initial nuclei with a large size yields, and the numbers of nuclei decreased as it is shown in Table I.

The variation of PDI can be explained in the following manner. (1) Under too low St concentration, polymerization rate is slow and the nucleation period is extended. Consequently, this yields initial nuclei with different sizes; thus the distribution of final size particles will broaden. (2) Under too high St concentration, the higher solvency of the medium to the polymer results in the sticky oligomers and small particles, which tend to agglomerate with each other to form the initial nuclei. Therefore, polydisperse particles were obtained. In addition, the limited solvency of the medium to the monomer results in the competition between "monomer droplet nucleation" and "homogeneous nucleation". The two effects can account for the variation of PDI. In addition only when the concentration range of St is narrow that highly monodisperse particles will be obtained.

Effects of PVP Concentration on Particle Size and Number

Table II shows the effects of PVP amounts on D_n, PDI, and N_p. It can be seen that with an increase of the PVP concentration, only the particle numbers increases, but not much. This result implies the graft copolymers are the real stabilizers, and the PVP absorbed on the particles is just as the costabilizers. Otherwise, the initial PVP concentration would seriously increase the particle numbers as emulsifiers did in the emulsion polymer-

Table II The D_n, PDI, and N_p Under Different PVP Concentration

	Run 2	Run 6	Run 7	Run 8	
[PVP] (wt %/St)	8	10	12	16	T = 73°C, St = 20% (wt % of
D_n (μm)	3.98	3.61	3.57	3.57	the mass), DVB/St = 0.5%, AIBN/St = 3%, EOH/H$_2$O
PDI	1.07	1.04	1.03	1.04	= 95/5 (all the ratios are
N_p (10^9/g)	6.36	7.25	8.82	8.79	weight percentage) Runs 6–8 by batch

Table III   The D_n, PDI, and N_p Under Different DVB Concentration

	Run 9	Run 10	Run 2	Run 11	
[DVB] (wt % St)	0	0.25	0.5	1	T = 73°C, St = 20% (wt % of the mass), St/PVP = 8%, AIBN/St = 3%, EOH/H$_2$O = 95/5 (all the ratios are weight percentage Runs 9–11 by batch
D_n (μ m)	3.65	3.76	3.98	4.17	
PDI	1.02	1.04	1.07	1.60	
N_p (10^9/g)	7.09	6.54	6.36	5.02	

ization. Table II demonstrates there is no remarkable influence of PVP concentration on the particle size and size distribution, which is due to the early completion of graft copolymerization and nucleation. But PVP concentration influences the stability of polymerization procedure. When the concentration of PVP decreases to 6%, a large amount of coagulum is produced because there are fewer PVP graft copolymers.

Effects of DVB Concentration on Particle Size and Number

Tables II, III illustrates the effects of the DVB concentration on D_n, PDI, and N_p of final particles. The D_n and PDI will increase with an increase of the DVB concentration. This means polydisperse particles with a larger average diameter yielded. One reason is that the crosslinking oligomers formed in the medium and thus nuclei with larger size was produced, and then nuclei grew to larger particles. The changes of PDI are due to the crosslinking reaction happening irregularly, which is ascribed to the different reactivity of the monomers involved in the reaction system, and in turn the nuclei with different

sizes is obtained. Figure 6 shows the TEM photographs of the particles prepared under different amounts of DVB and by different polymeric methods. From Figure 6, we can find that with increasing the DVB concentration, the particle size and the PDI increases.

When the DVB concentration increases to 2% (Photo B), more particles are connected by DVB crosslinking, and the shape of particles is irregular. This is due to the irregularity of crosslinking density in the different areas of the particles, which results in the different absorption quantity of monomer into the formed particles. Thus monodisperse PS particle with low crosslinking were obtained as shown in Photo A. But by postaddition, monodisperse highly crosslinked PS particle were obtained as shown in photo C.

All the results indicate the crosslinking reaction occurs in the particles and/or on the particles. Because of the different reactivity between styrene and divinylbenzene, the reaction in batch proceeds irregularly. Consequently, the polymer properties are ordinary in batch dispersion polymerization, especially the resistant to solvents is poor, which would limit the applications.
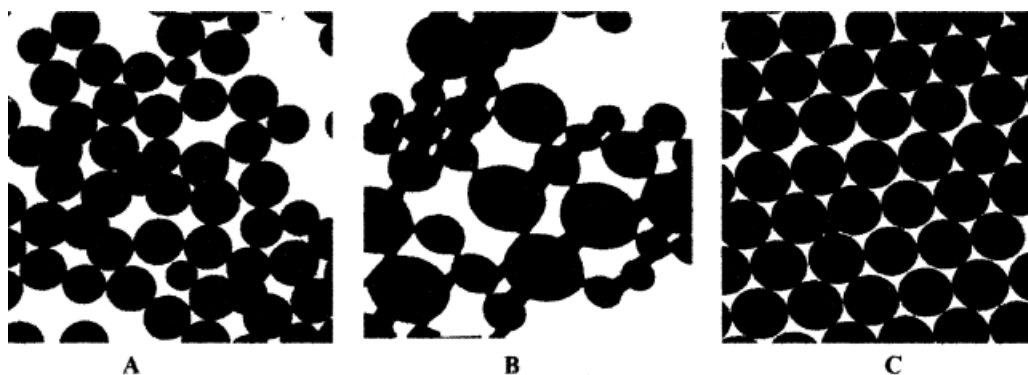
Figure 6   TEM photographs of PS microspheres ($\times$ 1200). (A) 0.5% DVB by batch; (B) 2% DVB by batch; (C) 3% DVB by post-addition

Table IV   The Weight Loss Probability (*WL*) Under Different Conditions[a]

	Run 9[b]	Run 10[b]	Run 2[b]	Run 11[b]	Run 12[c]	Run 13[c]	Run 14[c]	Run 15[c]
[DVB] %:	0	0.25	0.5	1	0.5	1	2	4
MeOH	9.8	2.1	1.0	0.5	0.3	—	—	—
EA	76.6	71.9	68.4	63.2	44.9	18.7	8.2	3.9
THF	66.8	53.1	38.6	30.5	24.7	10.3	5.3	2.1
MB	99.5	94.5	84.7	68.1	46.3	20.1	9.7	4.2

[a] The typical recipes are shown as in the experiment part.
[b] Batch procedures.
[c] Postaddition procedure; — without WL.

Resistance of Particles to Solvents

The solvency experiment was carried out for three types of samples: the PS particles without DVB, particles prepared by batch polymerization, and the particles prepared by using a postaddition procedure. Table IV shows the effects of the DVB concentration and the addition approach on the resistance to solvents. For most samples, the particles treated with methanol had no weight loss. When other solvents were used, the *WL* decreases with the increase of DVB concentration. And when the polarity of solvent was reduced, the solvency of the particles enhances. For the particles prepared by batch polymerization, the DVB content had no pronounced effects on the solvency of the particles. That can be seen from the results obtained in Run 10 and Run 11, which implies that the crosslinking reaction proceeded irregularly. This result coincides with the procedure above. On the other hand, for the particles prepared using postaddition, the effect of DVB concentration on the resistance to solvents is obvious. And the concentration of DVB can be up to 4% using the postaddition procedure, while the concentration of DVB is only 1% in the batch polymerization. Furthermore, the resistance to solvents of particles prepared by using postaddition is more prominent than that prepared by batch polymerization, which is shown in Run 11, Run 12, Run 13, and Run 14. These results indicate that the crosslinking reaction occurs throughout the polymerization procedure, and the crosslinkage is more regular with the use of postaddition than with the batch polymerization.

Effects of the Postaddition Rate on the Particle Size and Size Distribution

Table V demonstrates the variations of particle size and PDI with the rate of the postaddition. All the charges are introduced into the reaction flask after the initial solution has been initiated for 4 h. And the typical recipe of the charge is St 5 g, DVB 0.525 g, EOH 27.225 g, H_2O 18.2 g. For the conversion time curve, we know that the St concentration in the initial solution is about 10% when the polymerization has been carried out for about 4 h. So, it can be supposed that the polymerization will proceed with little change of the composition in the recipe if the consumption of monomers coincided with the introduction of the monomer. From the recipes of the charge and the initiator solution, it can be seen that the proportion of water in the medium is higher than in the latter. This increases the content of water in the

Table V   Variation of D_n and in the Postaddition Procedure

	Run 9[a]	Run 16[b]	Run 17[b]	Run 14[b]
Rate (mL/min)	—	5	2	0.8
$D_n(\mu m)$	3.65	5.23	5.98	5.53
PDI	1.02	1.89	1.32	1.06
N_p (10^9/g)	7.09	5.23	6.09	6.78

[a] The typical recipes are shown as in the experiment part.
[b] Batch procedures.

system, so it makes the St and DVB be absorbed into the formed particles. Thus the crosslinking reaction proceeds regularly.

Table V shows that the PDI is large in Run 16. This means that polydisperse particles were obtained and some coagulum is yielded with a fast addition rate. This result is due to the secondary nucleation and the agglomeration of particles in the part area in the medium. When the addition rate is too fast, a large amount of coagulum was produced and the polymerization could not continue as shown in Run 16. The slower the addition of the charge, the more stable the polymerization and the better the monodispersity of the particles. When the rate is slow enough, monodisperse particles were obtained and the particle prepared in Run 14 is larger than that in Run 9. And it also demonstrates that the resistance of these particles to solvents is better than that in Run 19 shown in Table IV. These results indicate that monodisperse microsphere with larger size and higher crosslinking were prepared by using the postaddition procedure.

CONCLUSIONS

Monodisperse copolymer particles with diameters from 2 to 5 μm were obtained by batch copolymerization of styrene and divinylbenzene in an ethanol–water medium. To enhance the crosslinking density, a postaddition procedure with a slow addition rate was carried out. And monodisperse particles with a larger diameter were produced.

To study the behavior of polymerization and crosslinking reaction, kinetics of polymerization and the variations of particle size, size distribution, and particle number under different conditions were investigated including the following variables: initial St concentration, PVP concentration and DVB concentration. The following was found (1) The change of the content of St and DVB can effect the final particle diameter and result in the particle size distribution broadens, but that of the PVP amount did not. (2) IR spectrum and the result of solvency experiment indicated that not only the PVP-PS grafting copolymer is incorporated into the particles, but also the PVP molecules were adsorbed onto particles, and the stabilization of particles is dependent on the

graft copolymers. (3) Polymerization mainly occurs in the medium to low St concentration, and the increase of St concentration changes the locus of polymerization. (4) Crosslinking reaction was completed in the early polymerization process and the DVB was irregularly incorporated into the PS chains in the batch polymerization. And the postaddition procedure can regularize the incorporation of DVB and obtain monodisperse particles with a larger size.

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