

Synthesis of Monodisperse Crosslinked Polystyrene Microspheres via Dispersion Copolymerization with the Crosslinker-Postaddition Method

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ABSTRACT: Monodisperse crosslinked polystyrene microspheres were prepared by the dispersion copolymerization of styrene and divinylbenzene in a mixed solvent of ethanol and H₂O. 2,2'-Azobisisobutyronitrile and poly(*N*-vinyl pyrrolidone) were used as the initiator and steric stabilizer, respectively. The crosslinker-postaddition method was adopted through a slow addition of a crosslinking agent into the dispersion system at a certain time after the beginning of the polymerization. The effects of the postaddition recipe, postaddition beginning time, postaddition velocity, and agitation rate on the particle size,

size distribution, and morphology were discussed. The resulting polymer microspheres were characterized with scanning electron microscopy and laser particle analysis. Crosslinked polystyrene microspheres with a narrow size distribution and a 12.0% crosslinker level were obtained with a size of 1.0 μm through the crosslinker-postaddition method. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3909–3916, 2008

Key words: crosslinking; kinetics (polym.); particle size distribution; polystyrene

INTRODUCTION

Recently, monodisperse polymer microspheres have received much attention because of their vast application areas, including conventional and recently emerging electronic and biotechnology fields such as coatings, instrument calibration, liquid chromatography, template polymerization, biomedical analysis, and information storage materials.^{1–5}

Crosslinked polystyrene (PS) microspheres, because of their superior thermal and mechanical resistance, susceptibility to chemical modification, and adaptability in a wide pH range, have been used in ion exchangers,⁶ reversed-phase high-performance liquid chromatography fillers,⁷ medical and chemical applications as absorbents,^{8,9} polymer-supported ca-

lysis,¹⁰ and so forth. Therefore, the copolymerization of styrene (St) and divinylbenzene (DVB) systems with various polymerization techniques has been extensively studied by many researchers.^{11,12} Various methods can be used to prepare polymer particles, such as suspension polymerization, emulsion polymerization, dispersion polymerization, and seeded emulsion polymerization. Polymer particles prepared by suspension polymerization¹³ have a particle size larger than 100 μm and a broad size distribution. Emulsion polymerization can produce polymer particles with a uniform size in the submicrometer (0.1 μm) range,^{14,15} whereas seeded emulsion polymerization can produce monodisperse polymeric particles of micrometer size in the range of 0.2–1.5 μm.^{16,17}

In recent years, dispersion polymerization has attracted much attention^{18,19} because it can produce polymer particles of 1–10 μm with a narrow particle size distribution via a single step. However, in a one-shot dispersion polymerization of crosslinked PS particles with DVB as a crosslinking agent, broad size distributions, oddly shaped particles, and coagulum are commonly observed^{20,21}; however, the amount of DVB added is very low (< 0.35%). Thomson et al.²² suggested that the incorporation of DVB makes the reaction of lining the poly(*N*-vinyl pyrrolidone) (PVP)–PS chains to the PS–DVB phase of the bulk particle irreversible. When the amount of incorporated DVB is very low, the crosslinked PS particles obtained in a one-shot dispersion polymeriza-

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tion steadily have poor mechanical properties, and their application is restricted in many fields. Otherwise, the morphology of the particles is sensitive not only to the absolute level of the crosslinker but also to the time and duration of the delivery addition of reactive materials.²³ Song et al.²⁴ reported that crosslinked monodisperse PS particles could be prepared by the addition of the crosslinking agent being delayed until after the end of the nucleation stage of the dispersion polymerization. However, their reaction conditions allow one to incorporate at most up to 3 wt % DVB based on St in the synthesis of crosslinked particles with a narrow size distribution.²⁵

In this study, to prepare monodisperse crosslinked PS microspheres having excellent mechanical properties, a crosslinker-postaddition method was adopted through a slow addition of crosslinking agents into the dispersion system at a certain time after the beginning of the polymerization. Optimal reaction conditions allow one to incorporate up to 12.0 wt % DVB in the synthesis of PS microspheres with a narrow size distribution. The effects of the concentration of DVB, postaddition method, and agitation rate on the particle size, size distribution, and morphology were examined. Finally, the polymerization kinetics were preliminarily investigated, and a dispersion polymerization mechanism for St and DVB in ethanol/H₂O at 70°C was proposed.

EXPERIMENTAL

Materials

Both styrene (St) and polyvinylpyrrolidone (PVP) (Mr = 10,000) (Tianjin Regent Chemicals Co., Ltd., Tianjin, China) were supplied as analytical grade. St was purified by vacuum distillation before polymerization, while PVP was used as received. Analytical grade 2,2'-Azobisisobutyronitrile (AIBN; analytical grade; Tianjin Fuchen Chemical Reagents Factory, Tianjin, China) was recrystallized from ethanol. Divinylbenzene (DVB) (80% mixture of meta and para isomers; Aldrich, St. Louis, MO) was used as received. The other reagents were also analytical grade and used as received without any further purification.

Conventional dispersion polymerization of St and DVB

Polymerizations were carried out in a 250-mL, three-necked flask equipped with a gas supply, a Liebig condenser, and a stirrer (double-bladed, Teflon). The flask was suspended in a water bath maintained at 70°C by an immersion circulator. In a typical procedure, PVP was dissolved in the medium (ethanol and water) initially. Then, nitrogen was injected into

TABLE I
Standard Recipe for the Dispersion Polymerization of St and DVB

Ingredient	Weight (g)
St	15.88
PVP	1.102
AIBN	0.159
DVB	1.826
Ethanol	67.15
H ₂ O	15.00

The conditions were as follows: 70°C, 24 h, and 15.7 wt % St on the basis of the total weight. The concentrations of PVP (6.94 wt %), AIBN (1.0 wt %), and DVB (11.5 wt %) were all based on the weight of St.

the reaction system at room temperature for 30 min before batch addition of the monomeric solution (St, DVB, and AIBN). The polymerization was carried out under stirring for 24 h before cooling; latexes containing coagulum were filtered through cheesecloth. The crude product latex was centrifuged for 6 min at 4000 rpm. The supernatant was then decanted, and the remaining precipitate was repeatedly washed by four centrifugations and dried *in vacuo* at the ambient temperature overnight. All ingredients used are summarized in Table I.

Crosslinker postaddition method

All the monomer (St), stabilizer (PVP), and initiator (AIBN) and 95% of the ethanol and H₂O were added to a 250-mL, three-necked flask equipped with a gas supply, a Liebig condenser, and a stirrer (double-bladed, Teflon). After a homogeneous solution formed at room temperature, nitrogen was injected into the reaction system at room temperature for 30 min. Then, the flask was suspended in a 70°C water bath and stirred at 120 rpm. DVB was dissolved in the remaining ethanol and H₂O. After DVB had dissolved and the polymerization reaction had run for 2 h, the DVB solution was added slowly to the reaction system over 2.5 h. The treatment of the crude product was the same as that described previously.

Characterization

The particle diameter was measured with scanning electron microscopy (SEM; JSM-5610LV, JEOL, Tokyo, Japan). The samples were sputter-coated with Au film before the examination. About 100 individual particle diameters were measured from SEM photographs, and the average was taken. The polydispersity index (PDI) was obtained as follows:²⁶

$$D_n = \frac{\sum_{i=1}^n d_i}{\sum_{i=1}^n n_i}; \quad D_w = \frac{\sum_{i=1}^n d_i^4}{\sum_{i=1}^n d_i^3}; \quad \text{PDI} = D_w/D_n$$

where D_n is the number-average diameter, D_w is the weight-average diameter, n_i is the number of particle i , and d_i is the diameter of particle i .

The D_n and size distribution coefficient values of the particles were measured with a laser particle size analyzer (LS13320, Beckman Coulter, Los Angeles, CA). The samples were dispersed in ethanol under ultrasonic vibrations before measurement.

Fractional conversions were determined with the conventional gravimetric method. Polymer colloids (2 mL) were extracted from the reaction system through a liquid sampler and added to a weighing bottle. Promptly, after the addition of a drop of a 5% hydroquinone solution, the weighing bottle was quenched in ice water. Each sample was then dried *in vacuo* at the ambient temperature until the weight change was less than 0.001 g. The conversion was calculated as follows:²⁷

$$C_v = \frac{M - M_1 \times (w_2 + w_3)}{M_1 \times w_1}$$

where C_v is the calculated fractional conversion, M_1 is the weight of the sample before drying, M is the weight of the sample after drying, w_1 is the weight percentage of the monomers (St monomer and DVB), w_2 is the weight percentage of the stabilizer, and w_3 is the weight percentage of the initiator.

The crosslinking degree (CD) was measured with the solvent extraction method. The purified dry particles were transferred to the Soxhlet extraction apparatus for reflux extraction in toluene for 24 h and then were dried until the weight change was less than 0.001. CD (%) was calculated with the following expression:

$$\text{CD}(\%) = w_2/w_1$$

where w_1 is the weight before extraction and w_2 is the weight after extraction.

RESULTS AND DISCUSSION

Effect of the DVB concentration on the particle size and size distribution

Crosslinked PS microspheres were prepared through the crosslinker-postaddition method with the variation of the concentration of DVB from 7 to 15 wt % in an ethanol/water solution at 70°C for 24 h. The effects of the concentration of DVB on the particle size, size distribution, and CD are shown in Table II.

As shown in Table II, there was a narrow size distribution when polymerization was carried out with a moderate concentration of the crosslinking agent. The particle size increased with the crosslinking

TABLE II
Effect of the DVB Concentration on the Particle Size and PDI

Run	W_{DVB} (wt %)	D_n (μm)	PDI	CD (%)
A1	7.0	0.988	1.227	75.46
A2	9.0	0.515	1.126	86.44
A3	10.0	0.818	1.103	92.01
A4	12.0	0.923	1.248	90.66
A5	15.0	0.593	1.097	88.94

The basic recipe was as follows: St = 15.88 g, AIBN = 0.158 g, PVP = 1.59 g, and solvent (85 : 15) = 100 mL. The conditions were as follows: beginning time = 2.0 h and adding time = 2.5 h. WDV B is the weight percentage of DVB based on styrene.

agent concentration increasing, but the variation was very small. As a comonomer, more DVB was used, and larger particles were obtained; this is similar to conventional dispersion polymerization. However, the amount of DVB based on St was so small that it had little effect on the particle size. However, when the DVB concentration was increased to 15.0 wt %, smaller particles with narrow size distributions were obtained eccentrically. This result indicates that a high DVB concentration leads to the formation of a highly crosslinked network on the surface of the particles. This makes it difficult for the monomers and oligomer radicals to diffuse from the solution to the particles.

From Table II, we can also see that it is not the more DVB used, the higher CD is. When the amount of DVB was 10.0 wt % based on St, the highest CD was obtained.

Figure 1 shows SEM photographs at each concentration of DVB based on the St monomer weight (9.0, 10.0, and 12.0 wt %). Up to the DVB concentration of 12.0 wt %, stable particles could be obtained around the size range of 1.0 μm . This proves that the stability of the dispersion system is improved in the case of the postaddition of the crosslinker. Although the amount of DVB reaches 12.0%, monodisperse crosslinked PS microspheres are still prepared by dispersion polymerization when the postaddition of the crosslinking agent is carried out at an appropriate addition beginning time and addition velocity.

Effect of the postaddition recipe on the particle size and size distribution

As shown in Table III, the particle size distribution decreased with the DVB concentration of the postaddition recipe decreasing. With the same beginning time, adding time, and total amounts of DVB, the adding velocity increased as the total volume of the postaddition recipe increased. When the postaddition was finished, the concentration of monomers in

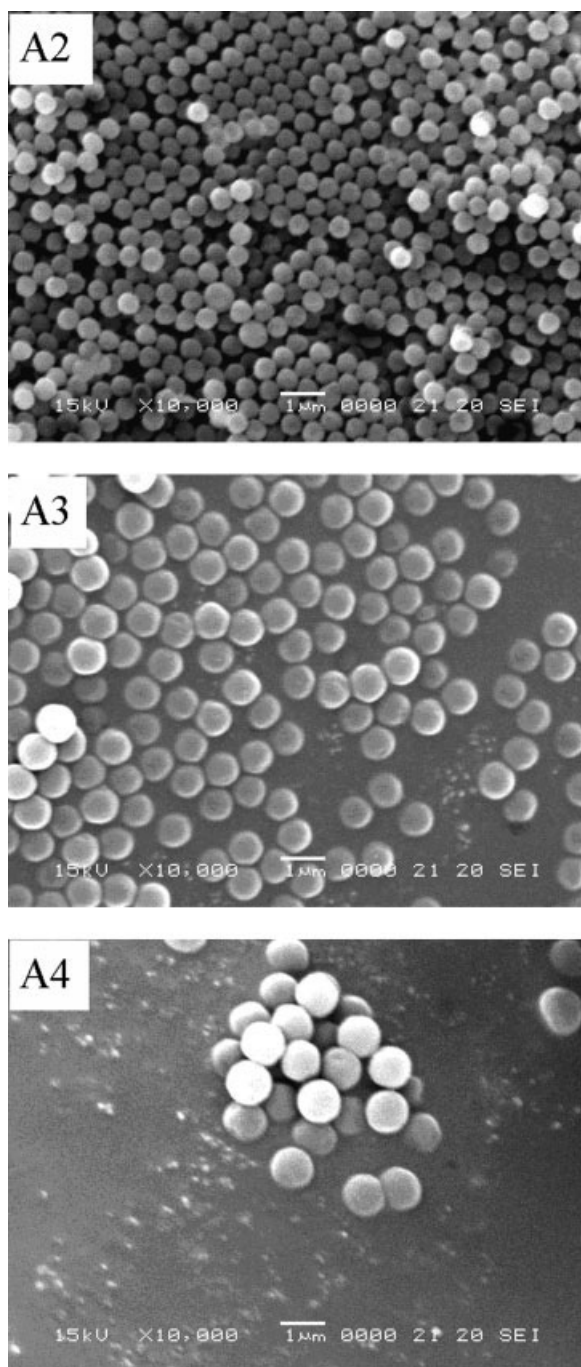


Figure 1 SEM photographs of the microspheres with different DVB concentrations at 70°C for 24 h: (A2) 9.0, (A3) 10.0, and (A4) 12.0 wt % (on the basis of the St weight).

the solution became smaller. Therefore, the opportunity of the oligomeric radicals to nucleate new particles was reduced, and this resulted in a narrow size distribution. However, it is shown in Table III that the particle sizes did not change regularly when the volume of ethanol in the postaddition recipe varied from 2.01 to 18.01 mL. Because the nucleation stage had been complete before the addition of the crosslinker, the number of particles did not change too much until the end of the polymerization.

TABLE III

Effect of the Postaddition Recipe on the Particle Size and PDI

Run	DVB/ethanol (v/v)	D_n (μm)	PDI	Yield (%)
B1	1.99 : 2.01	1.100	1.754	54.88
B2	1.99 : 4.01	0.792	1.551	82.43
B3	1.99 : 8.01	1.237	1.412	76.98
B4	1.99 : 14.01	0.717	1.114	52.54
B5	1.99 : 18.01	1.066	1.096	58.57

The conditions were as follows: beginning time = 2.0 h and adding time = 2.5 h. The basic recipe was as follows: St = 15.88 g, AIBN = 0.16 g, PVP = 1.27 g, and solvent (85 : 15) = 100 mL.

Effect of the postaddition beginning time on the particle size and size distribution

The time to carry out postaddition is an important factor in influencing the properties of the resulting particles. To investigate the effect of this factor, the postadditions were carried out for 0, 0.5, 1.5, 2.5, and 3.5 h after primary seeded polymerization. As shown in Table IV, the particle size increased slightly, but the PDI value decreased with the delay of the point to carry out postaddition within 3.5 h after initial polymerization. When the postadditions were carried out 0 and 0.5 h after the beginning of polymerization, stable monodisperse particles could not be obtained. This indicates that the nucleation stage was not completed within 0.5 h. As the polymerization proceeded, the concentration of radicals in the solution declined, and this decreased the crosslinking rates and uniform crosslinking in the particles. However, primary particles are formed through the exclusion of PVP-PS chains from the solvent during the initial polymerization. Therefore, the primary particles do not crosslink anymore, and this leads to the resulting heterogeneous crosslinking particles. Because of these two contradicting

TABLE IV

Effect of Postaddition on the Particle Size and PDI

Run	Beginning time (h)	Adding time (h)	D_n (μm)	PDI
C1	0	2.5	Coagulum	—
C2	0.5	2.5	3.496	4.218
C3	1.5	2.5	1.036	1.125
C4	2.0	2.5	1.141	1.084
C5	3.5	2.5	1.193	1.096
C6	2.0	0.75	2.547	2.341
C7	2.0	1.5	1.783	1.629
C8	2.0	3.5	1.236	1.127
C9	2.0	4.5	1.052	1.104

The basic recipe was as follows: St = 23.96 g, AIBN = 0.24 g, PVP = 0.72 g, and solvent (85 : 15) = 100 mL. The postaddition recipe was as follows: DVB/ethanol (3 : 3) = 6 mL.

TABLE V
Effect of the PVP Concentration on the Particle Size and PDI

Run	W_{PVP} (wt %)	D_n (μm)	PDI
D1	6.0	Coagulum	—
D2	8.0	0.792	1.551
D3	9.0	0.746	1.069
D4	10.0	0.601	1.088
D5	11.0	0.324	29.30

The conditions were as follows: beginning time = 2.0 h and adding time = 2.5 h. The basic recipe was as follows: St = 15.88 g, AIBN = 0.16 g, solvent (85 : 15) = 100 mL, and agitation rate = 120 rpm. The postaddition recipe was as follows: DVB/ethanol (1.99 : 4.01) = 6 mL. WPVP is the weight percentage of PVP based on styrene.

factors, the later the postaddition is carried out, the larger the primary particles are with narrow size distributions.

Effect of the postaddition velocity on the particle size and size distribution

As shown in Table IV, the particle size and size distribution decreased with the postaddition velocity decreasing (the adding time increasing). The sharp polymerization of DVB and St may not take place with the adding velocity decreasing. The polymer crosslinking becomes more uniform, and the effect of crosslinking becomes better. Briefly, to prepare crosslinked PS particles with larger sizes and narrow size distributions, the crosslinker-postaddition method is superior to the batch method.

Effect of the stabilizer concentration on the particle size and size distribution

As shown in Table V, the particle diameter decreased with the concentration of the stabilizer increasing, and this is similar to the results presented in refs. 19 and 28–30. During the nucleation period, the PVP molecules with a grafted structure act as a skeleton for particle growth. The higher the concentration is of PVP, the more widespread the graft formation and adsorption are, and therefore the larger the surface area is that can be protected. Thus, the number of forming nuclei increases with the stabilizer concentration increasing, and this leads to more particles but of a smaller size.

As shown in Figure 2, when the concentration of PVP decreases to 6%, a large amount of coagulum is produced. When the particles are crosslinked with DVB, larger amounts of stabilizers are needed to prohibit the coalescence between particles. However, too much PVP easily leads to smaller particles that cannot satisfy the demands in many fields. Accord-

ing to the SEM photograph in Figure 2(D2), a lot of particles with small dimples on their surfaces were obtained because some of the stabilizer chains became physically linked to one another via the bulk-particle PS–DVB phase, provided that they had a pendant vinyl group in their PS arm.³¹ In this situation, radial growth cannot be sustained indefinitely, and the particles must either distort in some way to counter the effect of the linked PVP chains or begin to destabilize. Therefore, monodisperse crosslinked PS microspheres can be produced with a higher stabilizer concentration (see D4 in Fig. 2).

Effect of the agitation rate on the particle size and size distribution

SEM photographs of microspheres at different agitation rates are shown in Figure 3. The relation between the size and size distribution of the microspheres and agitation rate is shown in Table VI. Although dispersion polymerization is less sensitive to the agitation rate than suspension polymerization and emulsion polymerization, the proper agitation rate and agitation method should be selected to re-

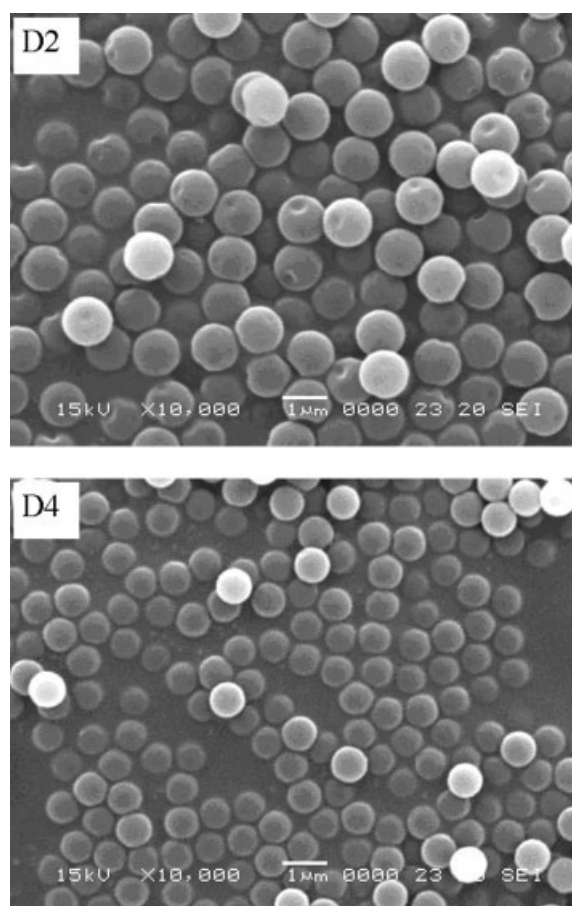


Figure 2 SEM photographs of the microspheres at different PVP concentrations: (D2) 8.0 and (D4) 10.0 wt %.

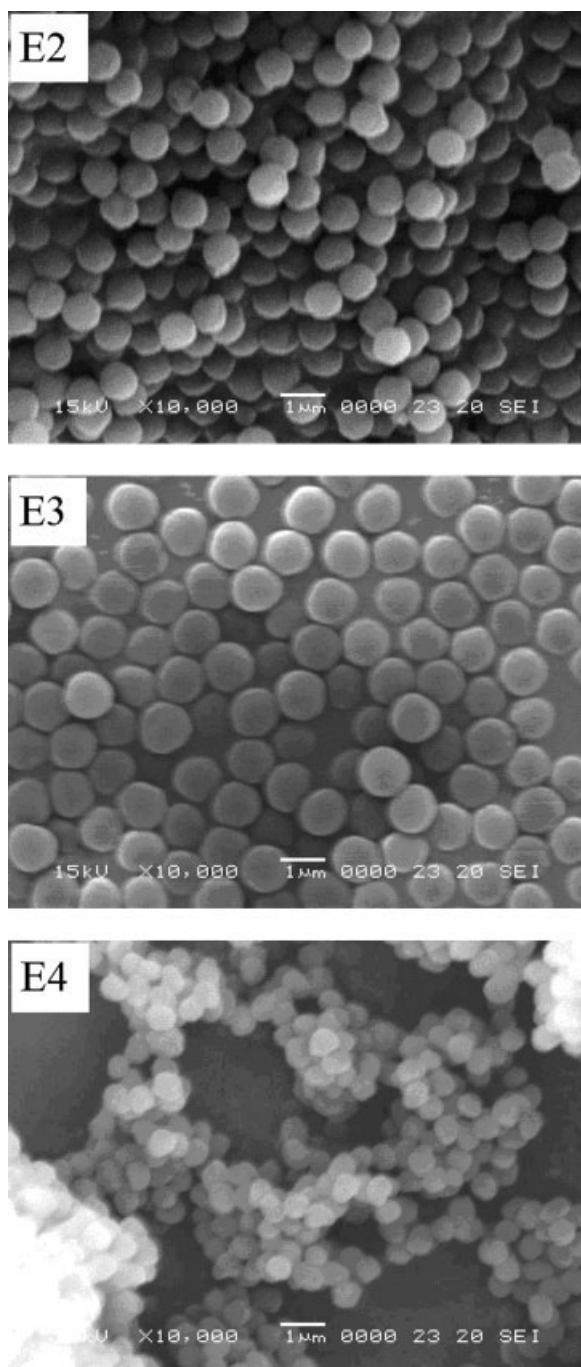


Figure 3 SEM photographs of the microspheres at different agitation rates: (E2) 90, (E3) 120, and (E4) 140 rpm.

duce the coacervation effect. As shown in Table VI, the particle diameter increases and then decreases when the agitation rate varies from 60 to 180 rpm. Particles prepared at the agitation rate of 120 rpm are monodisperse and 1.0 μm in size. When the agitation rate is quite low, the mobility and self-round rate of microspheres are also low. In this case, monomers more easily approach microspheres, and this will result in coagulum between nuclei. However, when the agitation rate is too high, the formation

TABLE VI
Effect of the Agitation Rate on the Particle Size and PDI

Run	Agitation rate (rpm)	D_n (μm)	PDI
E1	60	2.311	3.425
E2	90	0.858	1.330
E3	120	1.087	1.070
E4	140	2.039	4.079
E5	180	0.340	7.238

The conditions were as follows: beginning time = 2.0 h and adding time = 2.5 h. The basic recipe was as follows: St = 17.24 g, AIBN = 0.17 g, PVP = 1.72 g, and solvent (85 : 15) = 100 mL. The postaddition recipe was as follows: DVB/ethanol (2.16 : 3.84) = 6 mL.

and growing process of microspheres will be disturbed because the steric stabilization of PVP is seriously destroyed by the fierce agitation.²⁴ This will result in nonuniform primary nuclei and agglomeration between microspheres at the later stage of nucleation.

Polymerization kinetics in the dispersion polymerization of St and DVB

Figure 4 shows the fractional conversion for cross-linked PS microparticles with different DVB concentrations (9.0 and 12.0 wt %) as a function of the polymerization time at 70°C in ethanol/H₂O. As shown in Figure 4, the polymerization rate and final conversion increased with the concentration of DVB increasing. Because the solubility of St and DVB in an ethanol/H₂O solution is lowered with an increase in the DVB concentration, an increased number of nuclei are finally generated. This indicates that the total surface area is increased. Therefore, the equilib-

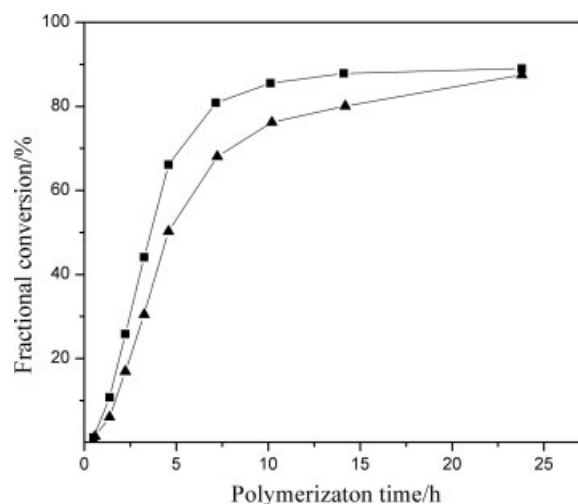


Figure 4 Fractional conversion/polymerization time curves for crosslinked PS particles with different DVB concentrations at 70°C in ethanol/H₂O: (▲) 9.0 and (■) 12.0.

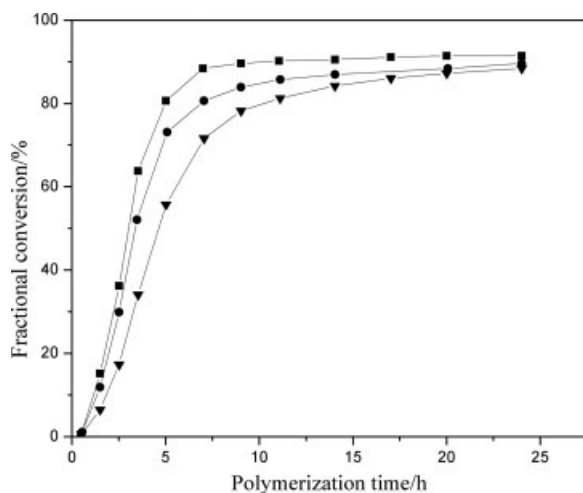


Figure 5 Fractional conversion/polymerization time curves for PS particles crosslinked with 11.5 wt % DVB (on the basis of the St weight) with various AIBN concentrations at 70°C in ethanol/H₂O: (▼) 0.5, (●) 1.5, and (■) 2.5 wt %.

rium distribution of the monomer toward the particle phase is more favorable, and this eventually results in a faster polymerization rate.³² However, the increasing trend becomes smaller and smaller when the polymerization proceeds. Because the crosslinking structure of the polymer is difficult for monomers to diffuse into, copolymerization follows the solution polymerization technique more. For this kind of polymerization, the polymerization rate decreases without any autoacceleration effects with the consumption of the monomers.

Figure 5 shows the fractional conversion for crosslinked PS microparticles with various initiator concentrations (0.5, 1.5, and 2.5 wt %) as a function of the polymerization time at 70°C in ethanol/H₂O. As shown in Figure 5, the polymerization rate increases with the increase in the initiator concentration in the low-conversion region. On the contrary, in the high-conversion region, the polymerization rate comes to be independent of the initiator concentration. This indicates that there is competition between the solution polymerization and heterogeneous polymerization. In the dispersion polymerization for the linear polymers, the polymerization rate is nearly independent of the initiator concentration, and this arises from the heterogeneous polymerization process being dominant over the polymerization process.^{10,19} Alternatively, then, for our polymerization system, it can be said that the heterogeneous polymerization could not dominate the whole polymerization process. Thus, it appears that, even though the crosslinked primary particles readily absorb the monomer from the medium, the hindrance caused by their crosslinked network structure still exists, and this also favors the solution polymerization process.

Mechanism for the dispersion polymerization of the crosslinked microspheres with the postaddition method

Figure 6 presents a schematic procedure for the particle nucleation and particle growth of the crosslinked PS particles with the postaddition method, which is proposed on the basis of this work and published studies in the literature.^{11,17–19} At the beginning of the process, the St monomer, stabilizer, and initiator exist homogeneously in the medium. Upon heating to the reaction temperature, the initiator decomposes, and the free radicals react with the St monomer to form oligomer radicals. When a critical chain length is reached, the oligomers precipitate to form the primary nucleus. The stable growing particles are formed through the coalescence of many nuclei and the adsorption of stabilizers on their surfaces. After primary polymerization, the crosslinking agents are added to the dispersion system. The crosslinking agents either react with the remaining radicals in the solution or are absorbed by the primary particles. Then, the crosslinked primary particles grow by both monomer absorption and oligomer radical adsorption until almost all monomers are consumed.^{33,34}

In conventional dispersion polymerization, crosslinked polymer particles are formed with broad size distributions and rough surfaces. When the particles are crosslinked with DVB, the broad size distribution of the DVB-crosslinked PS particles at high conversions is due to the long nucleation time and continuous second nucleation.³⁵ The main difference between the postaddition method and traditional batch method is the nucleation time in the first stage of the polymerization. The monodisperse primary particles with a noncrosslinked structure continue to grow on existing crosslinked microspheres with uniform sizes during the subsequent polymerization because of the short nucleation time. To obtain monodisperse crosslinked polymer particles in dispersion polymerization, the time for the formation of the primary particles should be manipulated regularly.

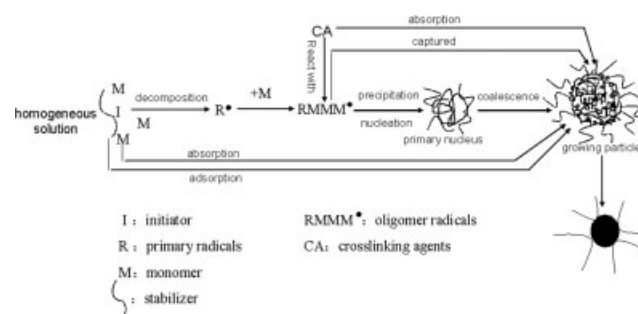


Figure 6 Schematic diagram for the particle nucleation and particle growth of the crosslinked PS particles with the postaddition method.

CONCLUSIONS

Monodisperse crosslinked PS microspheres were successfully synthesized by the dispersion copolymerization of St and DVB with a crosslinker-postaddition method in ethanol/H₂O when the concentration of DVB was varied from 7 to 12 wt % with respect to the St monomer. The postaddition beginning time and postaddition velocity had a serious effect on the particle size and size distribution. When the postaddition of DVB was carried out at 2 h after the beginning of the polymerization and the time of postaddition was 2.5 h, the best results were obtained. The particle diameter decreased with the increasing concentration of the stabilizer. The polymerization rate and final conversion increased with the increasing concentration of DVB and AIBN.

References

- Ma, G. H.; Su, Z. G. *Materials of Polymer Microspheres*; Chemical Industry Press: Beijing, 2005; Chapter 8.
- Fudouzi, H.; Xia, Y. *Adv Mater* 2003, 15, 892.
- Melamed, O.; Margel, S. *J Colloid Interface Sci* 2001, 241, 357.
- Chen, M.; Wu, L. M.; Zhou, S. X.; You, B. *Adv Mater* 2006, 18, 801.
- Park, J. G.; Kim, J. W.; Oh, S. G.; Suh, K. D. *J Appl Polym Sci* 2003, 87, 420.
- Denizli, A.; Kesencib, K.; Aricac, Y.; Piskinb, E. *React Funct Polym* 2000, 44, 235.
- Huber, C. G.; Kleindienst, G.; Bonn, G. K. *Chromatographia* 1997, 44, 438.
- Tuncel, A.; Tuncel, M.; Ergun, B.; Alagoz, C.; Bahar, T. *Colloid Surf A* 2002, 197, 79.
- Kawaguchi, H. *Prog Polym Sci* 2000, 25, 1171.
- Kawaguchi, S.; Mitchell, A. W. *Macromolecules* 1995, 28, 1159.
- Kiatkamjornwong, S.; Chientachakul, P.; Prasassarakich, P.; Damronglerd, S. *J Appl Polym Sci* 2001, 82, 1521.
- Ryu, J. H.; Kim, J. W.; Suh, K. D. *Colloid Polym Sci* 1999, 277, 1205.
- Maria, L. C.; Aguiar, M. R.; D'Elia, M. P.; Ferreira, L. O.; Wang, S. H. *Mater Lett* 2007, 61, 160.
- Matsumoto, A.; Kodama, K.; Aota, H.; Capek, I. *Eur Polym J* 1999, 35, 1509.
- Tobita, H.; Kumagai, M.; Aoyagi, N. *Polymer* 2000, 41, 481.
- Pang, X. S.; Cheng, G. X.; Lu, S. L.; Cheng, G. C.; Zhang, L. G. *React Funct Polym* 2005, 62, 69.
- Christopher, J. F.; Gregory, T. R.; Robert, G. G. *Polymer* 2002, 43, 6371.
- Lee, J.; Ha, J. U.; Choe, S.; Lee, C. S.; Shim, S. E. *J Colloid Interface Sci* 2006, 298, 663.
- Anthony, J. P.; Wayne, L.; James, M. *Macromolecules* 1990, 23, 3104.
- Jean, G. *J Polym Sci Part B: Polym Phys* 1998, 36, 325.
- Ober, C. K.; Lok, K. P. *Macromolecules* 1987, 20, 268.
- Thomson, B.; Rudin, A.; Lajoie, G. *J Appl Polym Sci* 1996, 59, 2009.
- Huang, J. X.; Zhang, H. T.; Hou, J. L.; Jiang, P. P. *React Funct Polym* 2002, 53, 1.
- Song, J. S.; Tronc, F.; Winnik, M. A. *J Am Chem Soc* 2004, 126, 6562.
- Song, J. S.; Winnik, M. A. *Macromolecules* 2005, 38, 8300.
- Lee, D. H.; Kim, J. W.; Suh, K. D. *J Mater Sci* 2000, 35, 6181.
- Ho, C. H.; Chen, S. A.; Amiridis, M. D.; VanZee, J. W. *J Polym Sci Part A: Polym Chem* 1997, 35, 2907.
- Lok, K. P.; Ober, C. K. *Can J Chem* 1985, 63, 209.
- Tseng, C. M.; Lu, Y. Y.; El-Aasser, M. S.; Vanderhoff, J. W. *J Polym Sci Part A: Polym Chem* 1986, 24, 2995.
- Sáenz, J. M.; Asua, J. M. *Macromolecules* 1998, 31, 5215.
- Thomson, B.; Rudin, A.; Lajoie, G. *J Polym Sci Part A: Polym Chem* 1995, 33, 345.
- Shim, S. E.; Yang, S. H.; Choe, S. J. *J Polym Sci Part A: Polym Chem* 2004, 42, 3967.
- Shen, S.; Sudol, E. D.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1994, 32, 1087.
- Downey, J. S.; Frank, R. S.; Li, W. H.; Stover, H. D. H. *Macromolecules* 1999, 32, 2838.
- Kim, J. W.; Kim, B. S.; Suh, K. D. *Colloid Polym Sci* 2000, 278, 591.