

Synthesis of Monodisperse Crosslinked Poly(styrene-*co*-divinylbenzene) Microspheres by Precipitation Polymerization in Acetic Acid

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ABSTRACT: Poly(styrene-*co*-divinylbenzene) microspheres with size ranging from 1.6 to 1.8 μm were prepared in acetic acid by precipitation polymerization. The particle size and particle size distribution were determined by laser diffraction particle size analyzer, and the morphology of the particles was observed with scanning electron microscope. Besides, effects of various polymerization parameters such as initiator and total monomer concentration, divinylbenzene (DVB) content, polymerization time and polymerization temperature on the morphology and particle size were investigated in this article. In addition, the yield of

microspheres increased with the increasing total monomer concentration, initiator loading, DVB concentration and polymerization time. In addition, the optimum polymerization conditions for synthesis of monodisperse crosslinked poly(styrene-*co*-divinylbenzene) microspheres by precipitation polymerization in acetic acid were obtained. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3799–3806, 2012

Key words: precipitation polymerization; poly(styrene-*co*-divinylbenzene); crosslinked polystyrene microspheres; crosslinked microspheres

INTRODUCTION

Monodisperse cross-linked polymeric microspheres, as a kind of functional polymer materials, had been widely applied in electronic information, medical treatment and medicine, instrument calibration standards and chromatographic support materials,^{1–8} especially in some high top-end fields, such as liquid-crystal display, drugs, and catalyst carriers. Cross-linked polystyrene microspheres used as a framework of monodisperse functional microspheres offered many advantages, such as excellent hydrophobic property and nonbiodegradable performance, large specific area and high surface reaction capability, good heat stability, and chemical stability, convenience for raw materials availability and industrial

manufacture and so on.⁹ At present, increasing attention had been focused on the research of the material, which induces various polymerization methods.

There were several polymerization methods adopted to produce monodisperse microspheres, including emulsion polymerization,^{10,11} dispersion polymerization,¹² suspension polymerization,^{13,14} and precipitation polymerization. Among these methods, precipitation polymerization in organic solvent, introduced by Li and Stöver¹⁵ for preparation of polymer microspheres with uniform particle size, had been attached so much importance as soon as it was put forward. Compared with other polymerizations, precipitation polymerization can give rise to highly crosslinked microspheres with suitable particle sizes, clean surfaces and uniform particle size without using stabilizers or surfactants. The polymerization system was comprised of solvent, monomer, crosslinker, and initiator. With swinging and heating, expected product could be obtained in a single step.

The mechanism of the precipitation polymerization was that monomer, crosslinker, and initiator dissolve in the solvent while the product cannot dissolve in the solvent and precipitates from the solvent. For this reason, the selection of the solvent was of crucial importance. The most commonly used solvent in precipitation polymerization was acetonitrile due to its excellent miscibility with various solvents and monomers, as well as its proper ability to solubilize the resulting polymers. However, acetonitrile

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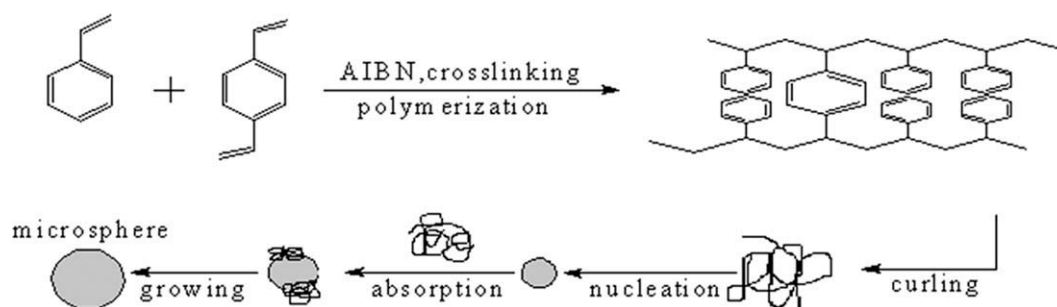


Figure 1 The procedure of the precipitation polymerization.

was a harmful substance for human health and environment. Then finding a new solvent, which is innocuous or less toxic and more eco-friendly, is a new issue that we have to confront with.

Yan et al.¹⁶ reported the characteristics of acetic acid to substitute acetonitrile as solvent. In the report, monodisperse crosslinked PDVB-55 particles were prepared by precipitation polymerization in acetic acid. Besides, the process of the polymerization includes two modes as follows: the mechanism of nucleation and the growth of particles. Moreover, the collision among the soluble oligomer leads to a lower dissolvability and particles separating from the homogeneous. This process is called nucleation, and the particles are the active centers. In the growth of particles, surface vinyl groups capture soluble oligomer radicals from the solution for further polymerization. Furthermore, the solvent effect on the particle morphology during a precipitation polymerization in acetic acid and monodisperse poly-(St-co-DVB-55) microspheres by precipitation polymerization in acetic acid with good or poor cosolvent was also investigated.^{17,18}

In this work, neat acetic acid without any cosolvent was chosen as the medium in precipitation polymerization for the preparation of monodisperse crosslinked poly(St-co-DVB) microspheres with clean and smooth surface. In addition, the effects of various polymerization parameters such as initiator and total monomer concentration, DVB content, polymerization time and polymerization temperature on the morphology and particle size were investigated in detail in this article, which would probably be helpful for the industrial production or further scientific research.

EXPERIMENTAL

Materials

Styrene (St, A.R. grade, Regent Chemical, Tianjin, China) used in this study was purified by vacuum distillation before polymerization. Divinylbenzene (DVB, mixture of isomers: $\geq 80 - \leq 82\%$, Ethylstyrene 18%, 4-tert-Butylpyrocatechol $\leq 0.12\%$, Diethylbenzene $< 0.5\%$, Sigma-Aldrich) was used as

received. 2,2'-Azobisisobutyronitrile (AIBN, A.R. grade, Fuchen Chemical, Tianjin, China) was recrystallized from alcohol. Acetic acid (A.R. grade, Shuangshuang Chemical, Yantai, China) was used as received. Anhydrous Alcohol (A.R. grade, Regent Chemical, Tianjin, China) and was used without further purification.

Polymerization

In a typical precipitation polymerization procedure, acetic acid (50 mL), monomer, DVB and AIBN were charged as recipe to a 100 mL glass conical flask with cover. Purged with nitrogen gas for 15 min to remove oxygen and the glass conical flask was sealed and kept in a water-bathing constant temperature vibrator at designed temperature for desired time, 70 rounds per minute. At the end of the polymerization, the resulting particles were separated from the solvent by centrifugation, washed three times with anhydrous ethanol, and dried in vacuum at 50°C overnight. The procedure of the precipitation polymerization was shown in Figure 1.

Characterization

A scanning electron microscope (SEM; JEOL, JSM5610LV) was used to examine the morphology of the poly(styrene-co-divinylbenzene) particles. The vacuum-dried polymer microspheres were mounted by placing them on an aluminum stud via a double-sided carbon conductive tape. Then they were coated with a gold/palladium alloy using a sputter-coater for 90 s at 15 mA to prevent charging.

The particle size and particle size distribution were measured by a laser diffraction particle size analyzer (Beckman Coulter, LS13320). The samples were dispersed in alcohol under ultrasonic prior measurement. Uniformity (U) of the microspheres was calculated by the following formula:

$$U = D_v/D_n$$

where D_v is volume-average diameter, D_n is number-average diameter. The yields and percentage conversions of the monomer were determined gravimetrically.

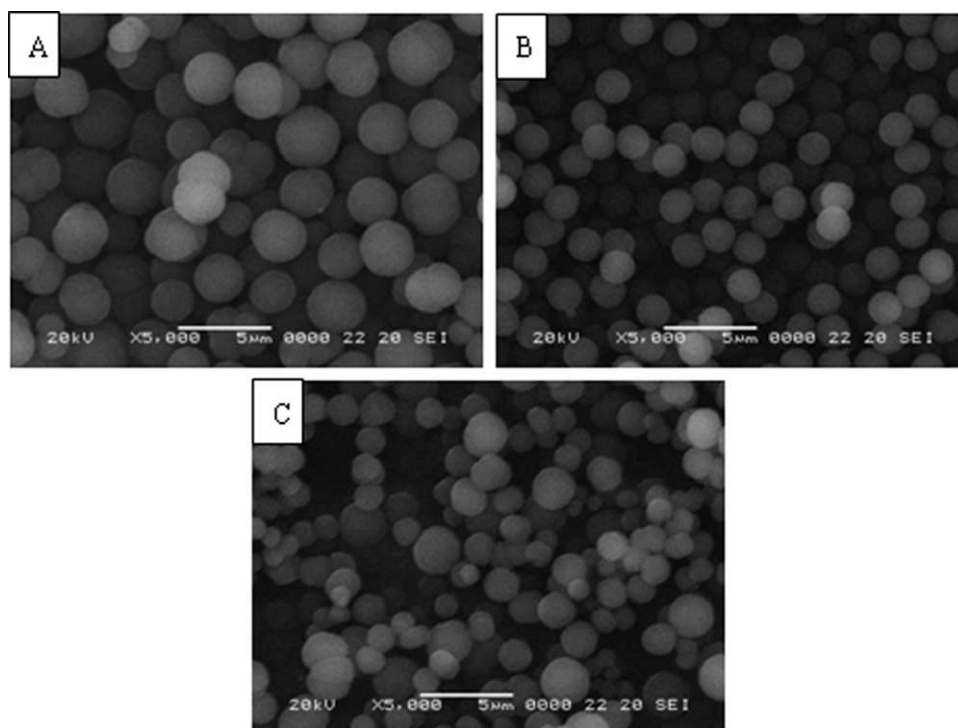


Figure 2 SEM photographs of poly(St-co-DVB) microspheres prepared by precipitation polymerization with various concentrations of total monomer (1 : 1 St : DVB) at 70°C for 24 h: (A) 0.75 vol %, (B) 1.0 vol %, and (C) 2.0 vol %.

RESULTS AND DISCUSSIONS

With no stabilizer or emulsifier, polymer microspheres were produced by the stabilization of the polymerizing system. As a result, the growth procedure of the polymer microspheres was sensitive to reaction conditions. There would be significant impact on morphological structure and particle size distribution of the product by changing monomer concentration, the ratio of monomer and cross linker, or initiator loading.

Effect of the total monomer concentration

Figure 2 displayed the effect of the total monomer loading on the precipitation polymerization (with the total monomer loading from 0.75 to 2 vol %, AIBN loading 1 wt % with respect to the total monomer, the ratio of St and DVB was 1 : 1, 70°C, 24 h), and the yield as well as diameter variation were shown in Table I. It can be observed that monodisperse microspheres were successfully obtained when the total monomer loading was below or equal to 1 vol %. As the total monomer loading increasing, doublet- or triplet-shaped coagulated particles appeared. For a total monomer loading of 2 vol %, a secondary nucleation was observed. These results were logical, since a higher particle concentration in the medium should lead to a higher possibility of collision among the particles.¹⁹ When the total monomer' loading was very high, the system was

crowded with oligomers in the solvent. The higher concentration of total monomer was able to increase the solubilizability of the system, since St was a good solvent for the polymers. In this way, the nucleation period was prolonged, resulting in a secondary nucleation.

Effect of ratio of monomer to crosslinker

The SEM micrographs in Figure 3 displayed the effect of ratio of monomer to crosslinker on the precipitation polymerization. Table II portrayed that the particle yield increases with the DVB loading from 10 to 50% of the total monomer, while the diameter decreased from 2.56 to 1.61 μm. For a fixed solvent concentration, the solubility of the initial nuclei in acetic acid would become poor with the concentration of DVB increasing, and then the final particle size would become smaller because of the larger number of nuclei formed in the initial stage.²⁰ Besides, the higher the DVB loading, the lower was

TABLE I
Effect of Total Monomer Concentration on Yield and Diameter of Poly(St-co-DVB) Microspheres

Sample	Concentrations of total monomer (vol %)	D_n (μm)	U	Yield (%)
A	0.75	2.15	1.23	12.56
B	1.0	1.61	1.04	18.79
C	2.0	1.15	1.40	24.13

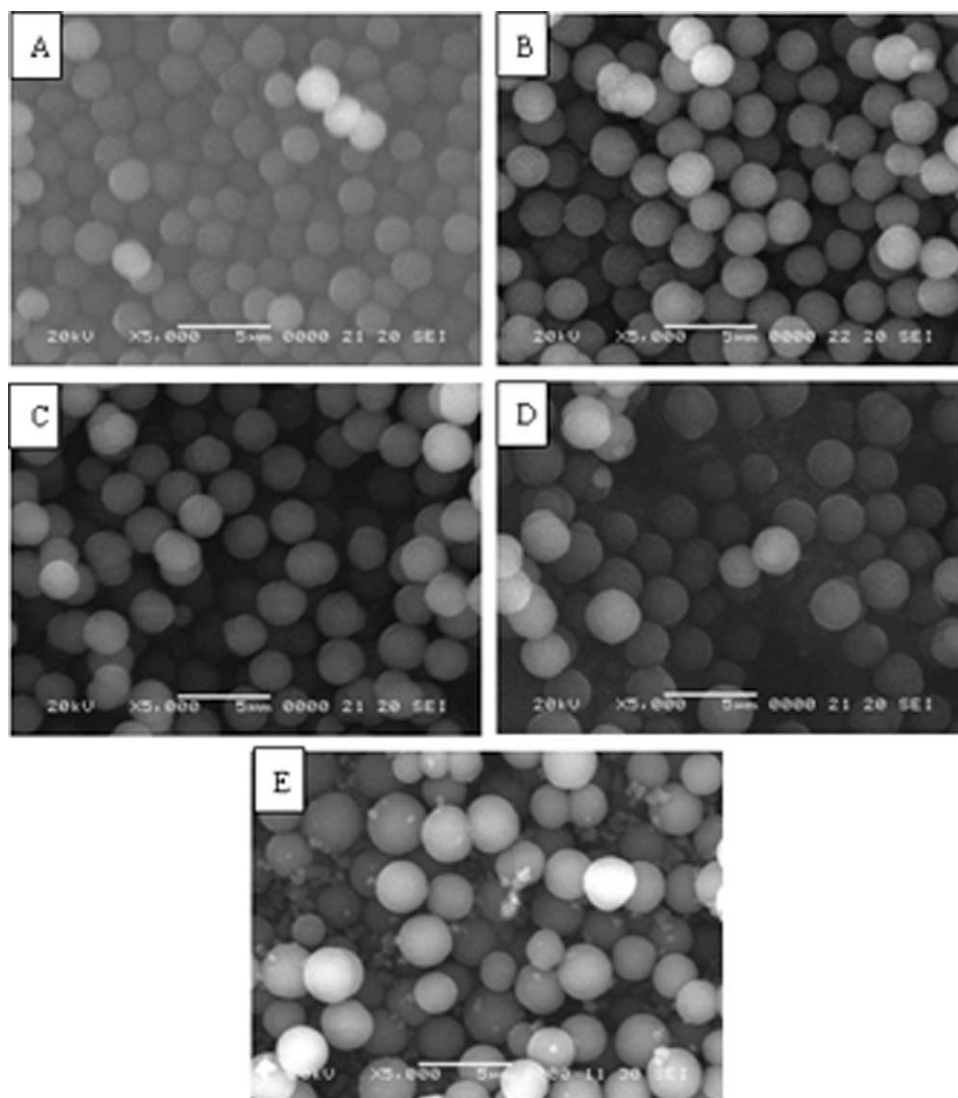


Figure 3 SEM photographs of poly(St-co-DVB) microspheres prepared by precipitation polymerization with different ratio of monomer to crosslinker at 70°C for 24 h and with total monomer at 1.0 vol %. (A) 1 : 1, (B) 6 : 4, (C) 7 : 3, (D) 8 : 2, and (E) 9 : 1.

the fraction of dissolved oligomers with respect to PS. Thus, more PS was able to precipitate, resulting in the increase of the yield, and no particles were obtained when the monomer was totally St, remaining in a transparent solution after 24 h of polymerization. Compared with products using DVB-55 as cross linker, microspheres produced in neat acetic

acid with DVB-80 as crosslinker were a little smaller in size (2.8 to 1.61 μm).

Effect of the initiator loading

Figure 4 was the SEM micrographs of PS particles obtained after polymerization with various AIBN loadings (AIBN loading from 0.5 to 3 wt %, DVB loading 1 vol %, 70°C and 24 h). The experiment results were shown in Table III. The micrographs displayed that there were no significant differences in the morphology of the particles. When acetic acid was used as the solvent, monodisperse crosslinked PS microspheres were observed. In the nucleation period, an increased amount of initiator (from 0.5 to 3 wt %) resulted in a higher polymerization rate. Thus, during the nucleation period, many small particles were formed in a short time and then

TABLE II
Effect of Ratio of Monomer to Crosslinker on Yield and Diameter of Poly(St-co-DVB) Microspheres

Sample	St : DVB (vol.)	D_n (μm)	U	Yield (%)
A	1 : 1	1.61	1.13	19.51
B	6 : 4	2.04	1.15	16.84
C	7 : 3	2.41	1.09	16.36
D	8 : 2	2.48	1.05	13.76
E	9 : 1	2.56	1.09	9.37

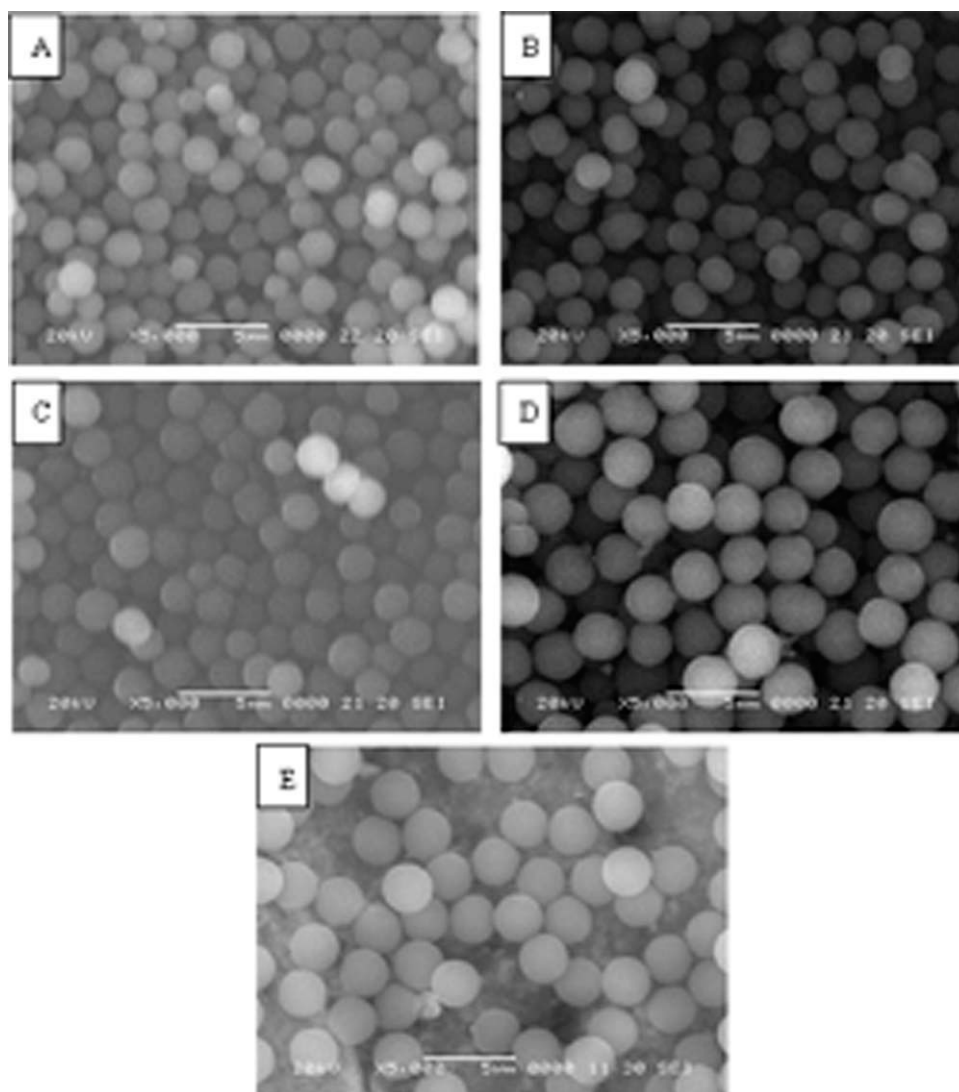


Figure 4 SEM photographs of poly(St-co-DVB) microspheres prepared by precipitation polymerization with various AIBN loadings at 70°C for 24 h: (A) 0.5 wt %, (B) 0.75 wt %, (C) 1.0 wt %, (D) 1.5 wt %, and (E) 3.0 wt %.

aggregated before the swollen surface could reach the proper thickness. This explained why an increased AIBN loading induced increased particle diameter. This result was meaningful since the polymerization rate, which is directly related to the yield in the same reaction time, increased with the concentration of free radicals.²¹ Thus, the higher yield could be obtained by

increasing the initiator loading, and the initiating efficiency could also be promoted.

Effect of the polymerization temperature

The polymerization temperature, which determined the radical formation rate, played an important role in affecting the physical property of the final product. Figure 5 depicted the microspheres prepared at the different polymerization temperature by precipitation polymerization with a total monomer concentration of 1 vol % for 1 : 1 St : DVB and an AIBN concentration of 1 wt % in acetic acid for 24 h (Table IV). The final yield of this reaction at 60°C was the lowest. From Figure 5, we can observe the effect of the polymerization temperature on the morphology of the particles. The lower temperature thus produced larger particle while small ones were formed at a high temperature. The effect of the polymerization

TABLE III
Effect of AIBN Loading on Yield and Diameter of Poly(St-co-DVB) Microspheres

Sample	AIBN loading (wt %)	D_n (μm)	U	Yield (%)
A	0.50	1.40	1.21	8.45
B	0.75	1.63	1.09	12.63
C	1.0	1.61	1.10	19.02
D	1.5	2.17	1.18	23.14
E	3.0	2.37	1.12	27.58

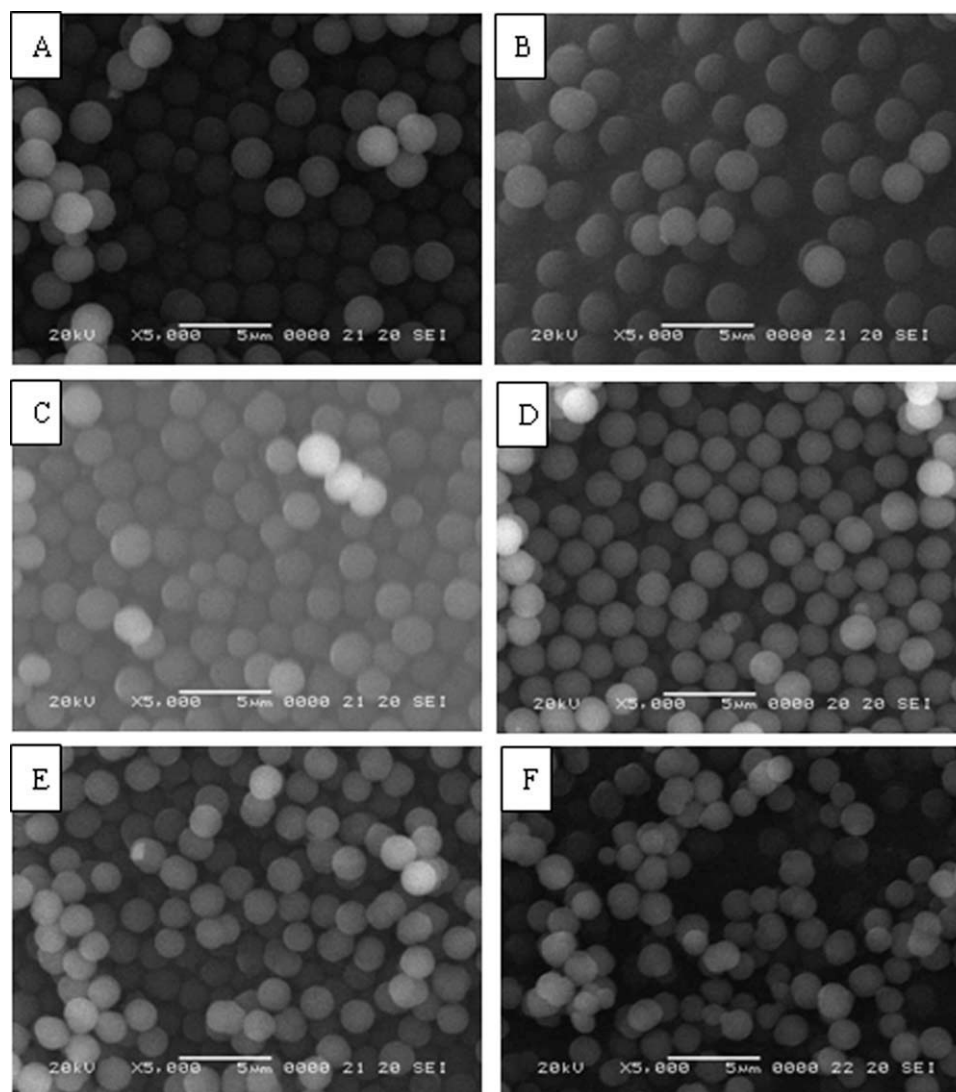


Figure 5 SEM micrographs of poly(St-co-DVB) prepared by precipitation polymerization with total monomers (St : DVB 1 : 1) at 1.0 vol % and AIBN at 1.0 wt % at different polymerization temperature for 24 h: (A) 60°C, (B) 65°C, (C) 70°C, (D) 75°C, (E) 80°C, and (F) 85°C.

temperature on the particle morphologies could be explained by the stabilization mechanism of precipitation polymerization,²² where the solvent swollen gel layer at the particle surface acted as a steric stabilizer. When at a lower temperature, the solubilizability of acetic acid was reduced and the solvent-

swollen gel layer was not thick enough to prevent the aggregation of small particles, since acetic acid was not a marginal solvent for styrene polymers. The solubility of acetic acid was enhanced with the polymerization temperature increasing, which caused an increase in the thickness of the layer. Therefore, particles could be well stabilized in the acetic acid.¹⁷ However, increasing the temperature

TABLE IV
Effect of Polymerization Temperature on Yield and Diameter of Poly(St-co-DVB) Microspheres

Sample	Polymerization temperature (°C)	D_n (μm)	U	Yield (%)
A	60	2.12	1.17	10.23
B	65	2.13	1.15	14.55
C	70	1.61	1.10	18.92
D	75	1.52	1.12	19.21
E	80	1.42	1.18	21.59
F	85	1.38	1.24	25.34

TABLE V
Effect of Polymerization Time on Yield and Diameter of Poly(St-co-DVB) Microspheres

Sample	Polymerization time (h)	D_n (μm)	U	Yield (%)
A	8	1.43	1.08	5.48
B	10	1.45	1.15	9.82
C	16	1.63	1.21	14.74
D	18	1.62	1.10	17.37

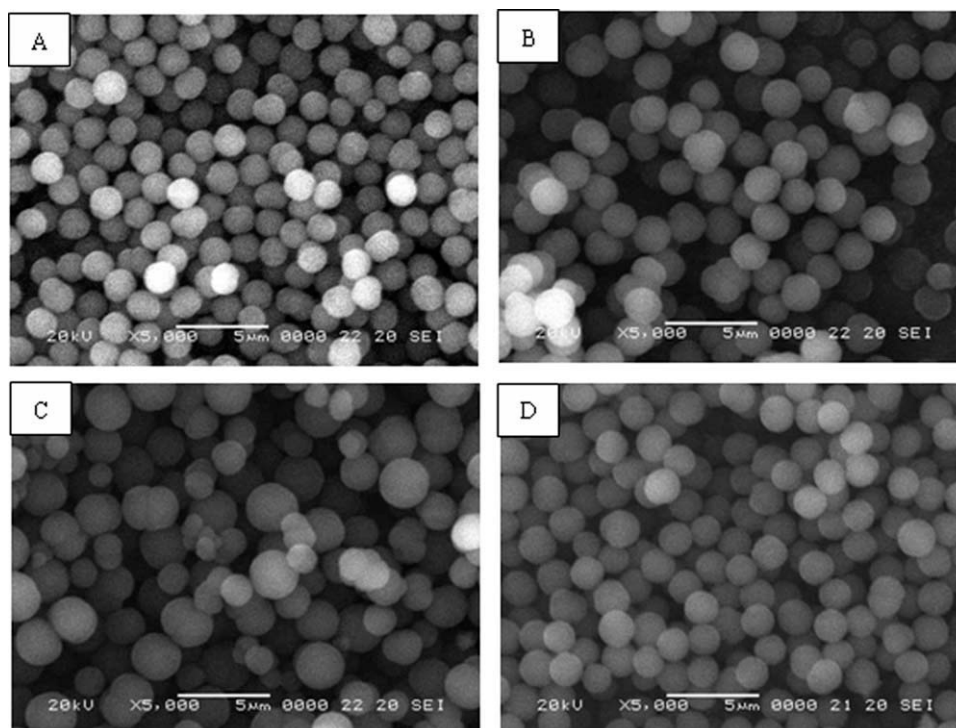


Figure 6 SEM micrographs of poly(St-co-DVB) microspheres obtained at different polymerization time with total monomers (St : DVB 1 : 1) at 1.0 vol % and AIBN at 1.0 wt % at 70°C: (A) 8 h, (B) 10 h, (C) 16 h, and (D) 18 h.

apparently led to an increase in the decomposition rate of the initiator, and results in the increase of the number of free radicals and microspheres. As a result, the increase in the number of microspheres reduced their sizes.

Effect of polymerization time

A set of time-dependent experiments were carried out in acetic acid as the solvent, where the samples toward different polymerization times were collected. Poly(St-co-DVB) microspheres obtained at different polymerization time with total monomers (St : DVB 1 : 1) at 1.0 vol % and AIBN at 1.0 wt % at 70°C were shown in Table V. The morphology and yields of each sample were examined at the same time by SEM. The results of the time-dependent experiments were displayed in Figure 6. It had become apparent that, with polymerization proceeding, the sizes of the particles became homogeneous. The oligomers were believed to be absorbed by the gel layer to grow to be more spherical in shape.

CONCLUSIONS

Precipitation polymerization was carried out in innocuous acetic acid to produce monodisperse crosslinked poly(St-co-DVB) microspheres. The yield of the microspheres increased with the increase of

monomer, initiator, and DVB concentration and the polymerization time. The optimum polymerization conditions were proposed as follows: St and DVB loading was 1 vol % with respect to the solvent, and the ratio of them was 1 : 1, AIBN concentration was 1 wt % of the total monomer weight, polymerization time was 24 h and polymerization temperature was 70°C. Poly(styrene-co-divinylbenzene) microspheres with size ranging from 1.6 to 1.8 μm were prepared under the optimum conditions.

References

1. Fudouzi, H.; Xia, Y. *Adv Mater* 2003, 15, 892.
2. Yang, X. Z.; Wu, X. L.; Zhu, X. L.; Zhang, L. *Macromol Rapid Commun* 2009, 30, 909.
3. Kawaguchi, H. *Prog Polym Sci* 2000, 25, 1171.
4. Tuncel, A.; Kahraman, A.; Piskin, E. *J Appl Polym Sci* 1994, 51, 1485.
5. Ellingsen, T.; Aune, T.; Ugelstad, J.; Hagen, J. *J Chromatogr* 1990, 535, 147.
6. Galia, M.; Svec, F.; Fréchet, J. M. J. *J Polym Sci Part A: Polym Chem* 1994, 32, 2169.
7. Ober, C. K.; Lok, K. P. *Macromolecules* 1987, 20, 268.
8. Coutinho, F. M. B.; Neves, M. A. F. S.; Dias, M. L. *J Appl Polym Sci* 1997, 65, 1257.
9. Wang, W. Q.; Zhang, Q. Y.; Liu, Y. Y.; Ma, M. L. *Chem Ind Eng Prog* 2009, 28, 93.
10. Koji, I.; Narihiro, T. *Polymer* 1996, 37, 1729.
11. Koji, I.; Masao, Y.; Ayako, I. *Polymer* 1997, 38, 5471.
12. Jose, M. S.; Jose, M. A. *J Polym Sci Part A: Polym Chem* 1996, 34, 1977.
13. Li, J. P.; Li, X. Y.; Li, C. Y.; Xu, H. F.; He, X. W. *Anal Chim Acta* 2001, 442, 105.

14. David, W.; Seitz, W. R.; Lavine, B. K. *Microchem J* 2003, 74, 121.
15. Li, K.; Stöver, H. D. H. *J Polym Sci Part A: Polym Chem* 1993, 31, 3257.
16. Yan, Q.; Bai, Y. W.; Meng, Z.; Yang, W. T. *J Phys Chem B* 2008, 112, 6914.
17. Yan, Q.; Zhao, T. Y.; Bai, Y. W.; Zhang, F.; Yang, W. T. *J Phys Chem B* 2009, 113, 3008.
18. Yan, Q. Synthesis of Monodisperse Functional Crosslinked Poly (divinylbenzene) Microspheres via Precipitation Polymerization in Acetic Acid [D]; Beijing University of Chemical Technology: China, 2009; p 120.
19. Shim, S.; Yang, S.; Jin, J.; Zhang, Y.; Choi, S. *J Colloid Polym Sci* 2004, 283, 41.
20. Shim, S. E.; Yang, S.; Choi, H. J.; Choi, S. *J Polym Sci Part A: Polym Chem* 2004, 42, 834.
21. Goh, E. C. C.; Stöver, H. D. H. *Macromolecules* 2002, 35, 9983.
22. Downey, J. S.; Frank, R. S.; Li, W. H.; Stöver, H. D. H. *Macromolecules* 1999, 32, 2838.