

Highly Crosslinked Poly(styrene-*co*-divinylbenzene) Microspheres Prepared by Precipitation Polymerization: Effects of the Polymerization Parameters on the Characteristics of the Particles

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Received 5 September 2007; accepted 27 September 2008

DOI 10.1002/app.29380

Published online 11 December 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Highly crosslinked poly(styrene-*co*-divinylbenzene) microspheres with a 1.0–2.5- μm diameter were prepared by precipitation polymerization in neat acetonitrile. The effects of various polymerization parameters such as the monomer and initiator concentration, comonomer composition, and cosolvents on the properties of the resulting particles were studied. The particle diameter increased with the monomer concentration, whereas the particle size distribution remained almost constant. The

resulting yield of the particles reached 41.1% when 6 wt % 2,2'-azobisisobutyronitrile (based on the total monomer) was used as the initiator. The styrene fraction in the monomer composition and toluene fraction in the solvent mixture also significantly affected the morphology and size of the resulting particles. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 3144–3149, 2009

Key words: copolymerization; crosslinking; polystyrene

INTRODUCTION

Monodisperse polymer microspheres have attracted increasing attention in many fields not only for their commercial and industrial importance but also for the requirements of scientific research. Their application areas developed from conventional fields such as instrument calibration, coatings, adhesives, catalyst supports, and chromatographic packing materials as well as recently emerged fields such as information technology and biomedical science and chemistry.^{1–5}

As we all know, highly crosslinked monodisperse polymer microspheres are superior to linear ones in terms of heat and solvent resistance, pH adaptability, and mechanical strength.^{6,7} However, the preparation of such polymer particles is technically difficult because of the introduction of a crosslinker. Therefore, it is necessary to develop a simple technique to synthesize highly crosslinked monodisperse polymer microspheres to satisfy the needs of various applications. Monodisperse polymer colloids with a size of less than 1 μm can be prepared by emulsion polymerization techniques with water as the reaction medium. Dispersion polymerization simply gives monodisperse polymer particles in the size range of 1–15 μm in an organic solvent. Supramicrometer-sized polymer microbeads (20–2000 μm) are usually prepared by suspension polymerization but lack uniformity. Vanderhoff's successive seeding method and Ugelstad's two-stage swelling method are also used to prepare polymer particles ranging from 1 to 15 μm with a narrow size distribution.^{8–11} Obviously, both approaches are rather complicated and time-consuming. Various novel techniques have been developed because the conventional polymerization methods cannot prepare highly crosslinked microspheres in a single step. Shirasu porous glass membrane emulsification with subsequent polymerization, which is a modified suspension polymerization technique, can simply produce crosslinked polymer microspheres in the range of 1–60 μm .^{12,13}

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Contract grant sponsor: Applied Project of Yantai City; contract grant number: 2005227.

Contract grant sponsor: Youth Science Foundation of Shandong Province; contract grant number: 2005BS11010.

Contract grant sponsor: Natural Science Foundation of Shandong Province; contract grant numbers: Q2006F05 and Y2005F11.

Contract grant sponsor: Natural Science Foundation of Ludong University; contract grant numbers: L20062901, 032912, and 20052901.

Contract grant sponsor: Applied Project of the Educational Bureau of Shandong Province; contract grant numbers: J05D03 and J04B02.

During the past 2 or 3 years, Huang's group has introduced a new method to synthesize highly crosslinked polymer beads with clean surfaces in the micrometer size. Such polymer microspheres are formed simultaneously through precipitation during the distillation of acetonitrile off the reaction system.^{14,15} This technique follows a precipitation mechanism; that is, particles are formed through the aggregation of soluble oligomers and continue to grow by adsorbing particles or soluble oligomeric species from the medium. Several monomers, including glycidyl methacrylate,¹⁶ acrylonitrile,¹⁷ chloromethylstyrene,¹⁸ and (meth)acrylic acid,¹⁹ have been copolymerized with either divinylbenzene (DVB) or ethylene glycol dimethacrylate as a crosslinker by precipitation polymerization or distillation-precipitation polymerization, and this has resulted in microspheres. Poly(methacrylic acid) microspheres can also be prepared by distillation-precipitation polymerization in the absence of any crosslinker through an internal contraction mechanism.²⁰

We are particularly interested in precipitation polymerization, which can produce highly crosslinked polymer microspheres in a single step without an additional apparatus or process.²¹⁻²⁶ To keep the uniformity and stability of the resulting particles, the dispersion polymerization technique and other traditional techniques generally adopt polymeric stabilizers or surfactants, neither of which are used in precipitation polymerization. The uniformity and stability stem from the use of low monomer loadings and marginal solvents.²⁷ Otherwise, a crosslinkable monomer is also required to prevent coagulation among particles by the formation of a highly crosslinked gel layer on the surface of the polymer microspheres.^{28,29}

In this article, we describe the use of this precipitation polymerization process to form highly crosslinked, stable poly(styrene-*co*-divinylbenzene) [poly(St-*co*-DVB)] copolymer microspheres with diameters ranging from about 1.0 to 2.5 μm . Effects of various polymerization parameters such as the monomer and initiator concentrations, comonomer composition, and use of cosolvents on the particle diameter, particle size distribution (PSD), and yield of particles were investigated.

EXPERIMENTAL

Materials

Styrene (St; 98.0%; Regent Chemicals, Tianjin, China) was purified by vacuum distillation before polymerization. DVB (a mixture of isomers, $\sim 80\%$; Sigma-Aldrich, St. Louis, MO) was used as received. 2,2'-Azobisisobutyronitrile (AIBN; 99.9%; Fuchen Chemical, Tianjin, China) was recrystallized from ethanol. Analytical-grade acetonitrile (99.9%; Regent Chemi-

cals) was used as a solvent and purified by distillation before use. Organic solvents such as acetone (99.5%; Regent Chemicals), ethanol (99.7%; Regent Chemicals), methanol (99.5%; Regent Chemicals), toluene (99.5%; Regent Chemicals), and tetrahydrofuran (THF; 99.0%; Regent Chemicals) were analytical-grade and were used without further purification.

Polymerization

The polymerization ingredients consisted of a medium, various compositions of St/DVB comonomer mixtures, and AIBN. The total amount of the monomers was varied from 0.5 to 3.5 vol % with respect to the medium. The concentration of AIBN was increased from 0.5 to 5 wt % with respect to the total amount of the monomers. After 100 mL of the polymerizing mixture was charged into a conical flask, nitrogen was purged for 15 min, and then the flask was sealed. Polymerization was carried out in a shaking water bath with an agitation speed of 30 rpm at 70°C for 24 h. At the end of the reaction, the particles were separated from the reaction medium by filtration or centrifugation, successively washed three times each with THF, acetone, and methanol, and then dried *in vacuo* at 50°C overnight.

Characterization

A scanning electron microscope (SEM; JSM 5610LV, Jeol, Tokyo, Japan) was used to examine the morphology of the poly(St-*co*-DVB) particles. The vacuum-dried polymer microspheres were mounted by placement on an aluminum stud with double-sided carbon conductive tape. Then, they were coated with a gold/palladium alloy with a sputter coater for 90 s at 15 mA to prevent charging.

The uniformity of the microspheres was expressed as D_v/D_n , where D_v is the volume-average diameter and D_n is the number-average diameter. The D_v and D_n values were measured with a laser diffraction particle size analyzer (LS13320, Beckman Coulter,

TABLE I
Effects of the Total Monomer Loading on the Particle Size, Size Distribution, and Yield

Total monomer loading (vol %)	D_n (μm)	D_v/D_n	Yield (%)
1	1.46	1.64	4.17
2	1.88	1.58	30.89
3	2.03	1.56	39.06
4	2.15	1.66	42.37
5	2.27	1.62	44.61
6	2.35	1.63	47.58

The AIBN concentration was 2 wt % with respect to the monomer, and the monomer composition was 50 : 50 vol % St/DVB.

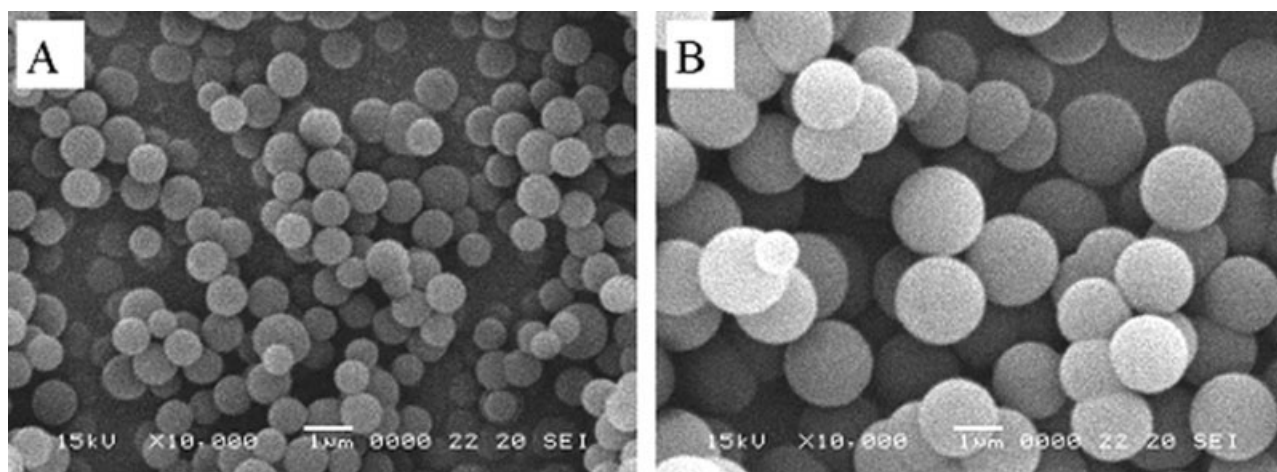


Figure 1 SEM microphotographs of particles prepared with different total monomer loadings: (A) 1 and (B) 6 vol %.

Los Angeles, CA). A polarization intensity diffraction system was used to measure the particle diameters in the range of 0.04–0.4 μm . The samples were dispersed in ethanol under ultrasound before the measurement.

PSD was calculated as follows:

$$\text{PSD}(\%) = \delta/D_n$$

where δ is the standard deviation of the particle diameter.

The yield of the polymerization was determined gravimetrically.

RESULTS AND DISCUSSION

Effects of the monomer concentration on the particle size and size distribution

Table I shows the results for poly(St-co-DVB) microspheres prepared by the precipitation polymerization of 50 : 50 vol % St/DVB with the concentration of the monomer increasing from 1 to 6 vol % with respect to acetonitrile. Individually stable particles were obtained at all monomer concentrations in the region of the conditions studied experimentally. However, partially coagulated particles resulted with more than 6 vol % monomer. This may indicate that the chance of aggregation or coagulation between primary particles increased with the monomer concentration increasing. No particles were obtained when less than 1 vol % monomer was used; they remained in a transparent solution after 24 h of polymerization. The yield of the polymerization increased with the concentration of the total monomer, and this is common for radical polymerization. Scanning electron microscopy (SEM) microphotographs of particles prepared with a 1 or 6 vol % total monomer loading are shown in Figure 1.

Figure 2 displays the variation in the particle size and size distribution with respect to the concentration of the total monomer loading in the medium. The particle size increased with the monomer concentration, whereas the size distribution remained almost constant. The D_n value of 1.46 μm at a 1 vol % monomer loading increased to 2.35 μm at a 6 vol % monomer loading. These results indicated that St could be polymerized with DVB to form stable microspheres even in the absence of any stabilizer. It seems that the growing poly(St-co-DVB) microspheres were stabilized against coagulation by their highly crosslinked, rigid surfaces. In Table I, a more detailed experimental recipe and the results for the particle size and uniformity are presented.

Effects of the initiator concentration on the particle size, size distribution, and yield

The yield of particles prepared in neat acetonitrile with an increasing concentration of AIBN at 70°C is

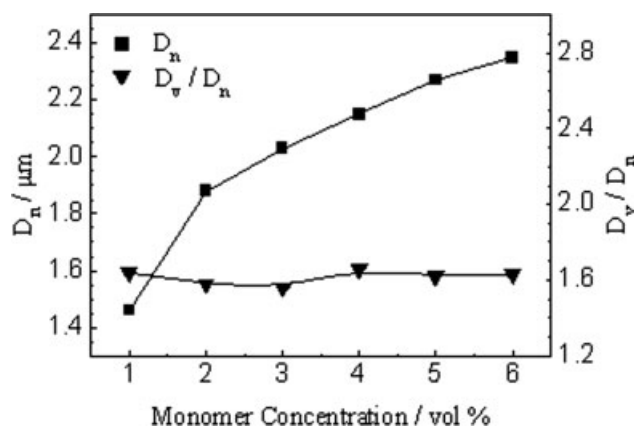


Figure 2 Particle size diameter and size distribution of the microspheres prepared through the precipitation polymerization of 50 : 50 St/DVB with various total monomer loadings.

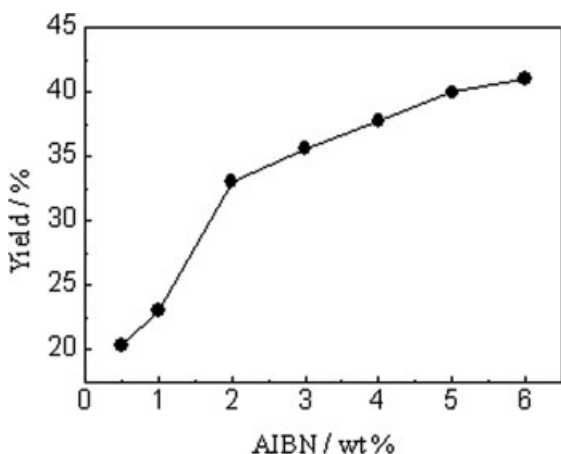


Figure 3 Yield of particles prepared with a 50 : 50 St/DVB monomer composition and various concentrations of AIBN at 70°C for 24 h.

depicted in Figure 3. The yield of particles means the amount of the monomer converted to particles. The other monomer is partially converted to a medium-soluble sol left in the medium. Acetonitrile is called a marginal solvent because it dissolves oligomeric polydivinylbenzene (PDVB).²³ Thus, the oligomeric species are separated from the medium and adsorbed by the growing particles because of their internal desolvation. As shown in Figure 3, the yield of particles increased with the concentration of the initiator. When the AIBN concentration was 6 wt % with respect to the total monomer, a 41.1% yield was obtained at the end of polymerization. The low yield of particles was due to the low monomer and initiator loading. A moderate proportion of the monomer-converted oligomers was left in the medium or just remained unreacted until the end of polymerization. At such a low monomer loading (2 vol % with respect to the solvent) in the reaction me-

TABLE II
Experimental Conditions and Results for Different Comonomer Compositions

St (mL)	DVB (mL)	D_n (μm)	D_w/D_n
0.1	0.9	—	Coagulum
0.2	0.8	0.66	2.23
0.4	0.6	1.07	1.64
0.6	0.4	1.35	1.55
0.8	0.2	1.77	1.36
0.9 ^a	0.1	0.11	55.09

The AIBN concentration was 2 wt % with respect to the monomer, and the total monomer loading was 2 vol % with respect to the reaction medium.

^a St (0.9 mL) and 0.1 mL of DVB in 50 mL of acetonitrile yielded a cloudy solution at the end of the polymerization.

dium, a considerable number of the initiator radicals may have self-terminated before escaping from their solvent cage.

Effects of the comonomer composition on the particle size and size distribution

Copolymerizations of St with DVB in neat acetonitrile were carried out with a 2 vol % total monomer loading with respect to the reaction medium and with 2 wt % AIBN with respect to the total monomer. In these experiments, the St fraction in the comonomer composition was varied from 0.1 to 0.9. The experimental conditions for these precipitation polymerizations and some of the results are summarized in Table II.

Narrowly disperse copolymer microspheres of poly(St-co-DVB) were formed with St volume fractions ranging from 0.5 to 0.8. As the St fraction increased, the particle size became larger, and the PSD became narrower. At even higher St fractions, cloudy solutions containing only a small amount of the precipitated polymer were observed.

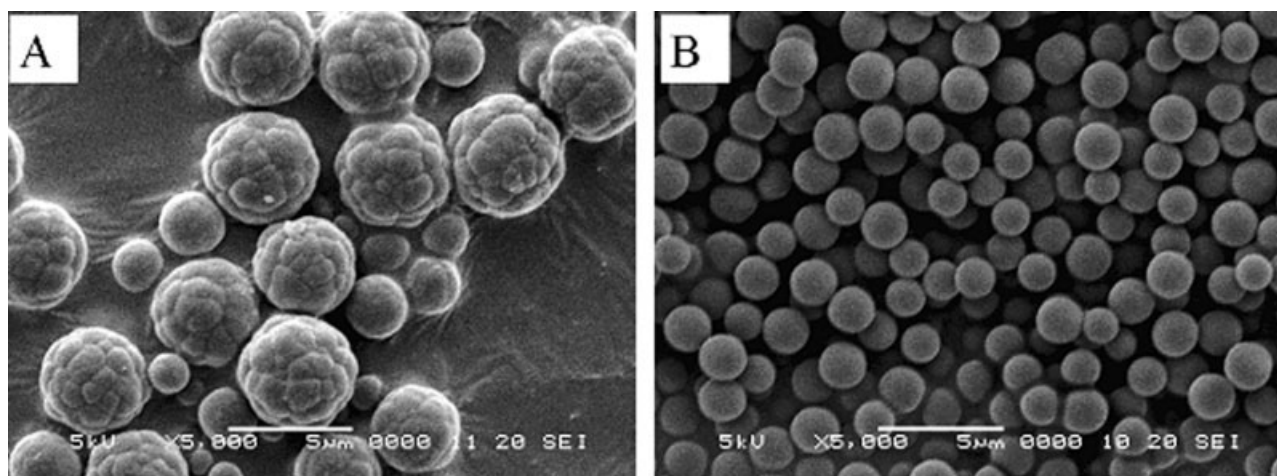


Figure 4 SEM microphotographs of particles prepared with different St fractions in the monomer composition: (A) 0.2 and (B) 0.8 St.

TABLE III
Solubility Parameters of Various Solvents Used with Acetonitrile and Resulting Products of the Reaction

Solvent	δ (MPa ^{1/2})	δ_d (MPa ^{1/2})	δ_p (MPa ^{1/2})	δ_h (MPa ^{1/2})	Observation
Toluene	18.21	18.04	1.43	2.045	Microspheres
2-Propanol	23.54	15.76	6.14	16.37	Microspheres
Methanol	29.62	15.17	12.27	22.29	Coagulum
Ethanol	26.55	15.81	8.79	19.43	Coagulum
Ethyl acetate	18.61	15.21	5.32	9.20	Gel
Acetone	19.93	15.50	10.43	6.95	Coagulum
Acetonitrile	24.43	15.34	18.0	6.14	

δ = Hildebrand solubility parameter [$\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$]; δ_d = dispersive Hansen parameter; δ_h = hydrogen-bonding Hansen parameter; δ_p = polar Hansen parameter.

Figure 4(A,B) shows SEM photographs of the copolymer particles prepared with St fractions of 0.2 and 0.8, respectively. The surfaces of the poly(St-co-DVB) particles were rough at the lower St fraction of 0.2 and became much smoother at the St fraction of 0.8. According to the mechanism of precipitation polymerization, the particles formed by the aggregation of oligomers and grew by a radical reaction with oligomers and monomers in the reaction medium. As the St fractions in the monomer composition decreased, the solubility of the oligomers in acetonitrile became poor, and then the final particle size became smaller because of the large number of oligomers formed in the initial stage, which also caused the slight reduction of D_w/D_n . Coagula obtained at even lower St fractions (<0.1) may have resulted from extended homocoagulation between the particles.

Effect of the cosolvent on the particle size and size distribution

The solvent plays an important role in preparing monodisperse particles in precipitation polymerization. In the synthesis of DVB or St/DVB particles, acetonitrile was the only single solvent that could obtain monodisperse microspheres.^{21,25} Apparently, acetonitrile meets the solvent conditions required for monodisperse particle formation; that is, it dissolves the monomer but precipitates the forming polymer. Up to now, it has not been distinctly known why only acetonitrile is appropriate for preparing stable microspheres. Frank et al.²³ considered acetonitrile to be a marginal solvent because it still dissolves oligomeric PDVB in the preparation of DVB particles.²³

Solubility parameters of several solvents used as polymerization media are listed in Table III. As shown in Table III, although the Hildebrand solubility parameter of 2-propanol is quite close to that of acetonitrile, only coagula were obtained when 2-propanol was individually used as a medium. Because the one-dimensional Hildebrand solubility parameter reflects only the overall solvent properties and does not differentiate between specific effects such as dipolar interactions, hydrogen bonding, and van der

Waals interactions,^{16,30} 2-propanol, although having a solubility parameter (23.54 MPa^{1/2}) similar to that of acetonitrile (24.43 MPa^{1/2}), did not produce particles. This is likely due to the hydrogen-bond-forming ability of 2-propanol (hydrogen-bonding Hansen parameter = 16.37 MPa^{1/2}).

Toluene, as a porogen, has been used in suspension polymerization and seeded swelling polymerization to prepare porous particles. The preparation of porous PDVB particles by precipitation polymerization was reported by Li and Stöver.²¹ In this article, we report the precipitation polymerization of St and DVB in toluene/acetonitrile solvent mixtures.

All the polymerizations were carried out with a 50 : 50 vol % St/DVB monomer composition, a 2 vol % total monomer loading, and a 2 wt % AIBN loading with respect to the monomer. The toluene content in the toluene/acetonitrile solvent mixture was varied from 15 to 50%, and the results are shown in Table IV. Narrowly disperse particles were obtained in the presence of 25–35 vol % toluene. The average particle diameter increased from 0.33 to 2.02 μm when the toluene content was varied from 15 to 25%, and then it decreased to 1.77 μm with 35 vol % toluene (Fig. 5). When the toluene content was higher (up to 50 vol %), the whole reaction mixture gelled. These results indicated that the solvency of the solvent mixture increased with the toluene content increasing. With the increasing solvency, the critical chain length increased, and

TABLE IV
Effects of the Toluene Content on the Particle Diameter, Size Distribution, and Yield

Toluene (vol %)	D_n (μm)	PSD	Yield (%)
15	0.33	1.46	31.67
20	0.49	1.39	32.65
25	2.02	0.57	41.26
35	1.77	0.85	34.74
50	—	Gel	—

The monomer concentration was 2 vol % with respect to the solvent mixture, the monomer composition was 50 : 50 vol % St/DVB, and the AIBN concentration was 2 wt % with respect to the monomer.

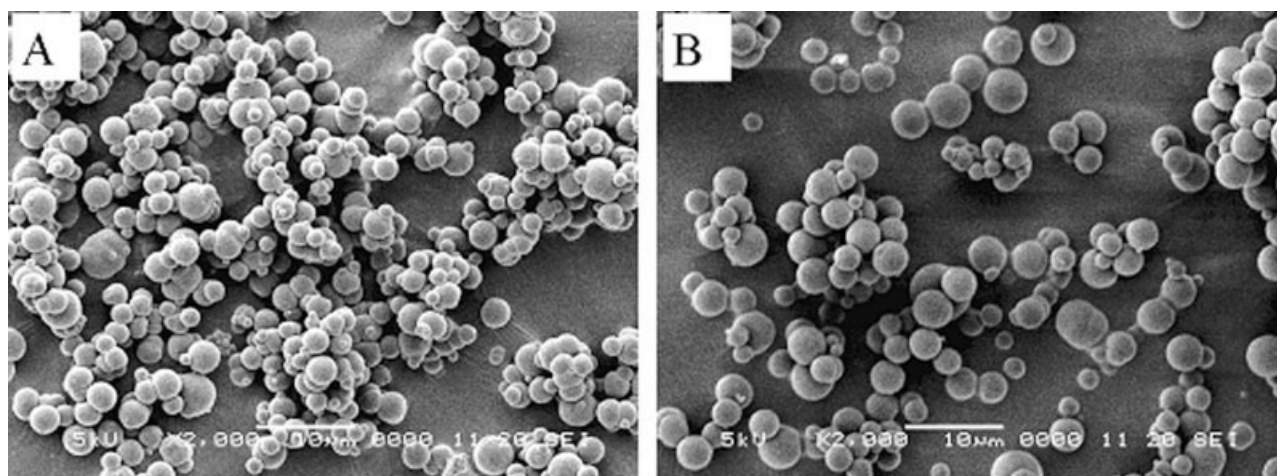


Figure 5 SEM microphotographs of particles prepared with different toluene contents in a toluene/acetonitrile solvent mixture: (A) 35 and (B) 25 vol % toluene.

the adsorption rate of the oligomers onto the particles was suppressed; this reduced rates of nucleus formation and adsorption of the oligomers, and the formation of larger particles followed. However, with even higher solvency, the polymer network could not collapse to form microspheres that were stabilized by the surface gel layer, and this led to the formation of polymer microgels.

CONCLUSIONS

This work reports the preparation of highly cross-linked, stable poly(St-co-DVB) microspheres by precipitation polymerization in neat acetonitrile. Particles in the range of 1.0–2.5 μm were synthesized with 50 : 50 vol % St/DVB and various total monomer loadings ranging from 1 to 6 vol % with respect to acetonitrile. The yield of particles was relatively low because of the low monomer and initiator loading. Narrowly disperse poly(St-co-DVB) microspheres were formed with St volume fractions ranging from 0.5 to 0.8. Acetonitrile was the most appropriate solvent for preparing styrenic microspheres. However, narrowly disperse particles could also be obtained with 25–35 vol % toluene in a toluene/acetonitrile solvent mixture.

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