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ORIGINAL CONTRIBUTION

Sang Eun Shim
Sunhye Yang
Myung-Jong Jin
Yoon Ho Chang
Soonja Choe

Effect of the polymerization parameters on the morphology and spherical particle size of poly(styrene-*co*-divinylbenzene) prepared by precipitation polymerization

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S. E. Shim · S. Yang · M.-J. Jin
Y. H. Chang · S. Choe (✉)
Department of Chemical Engineering,
Inha University, 253 Yonghyundong,
402–751 Namgu, Incheon, South Korea
E-mail: sjchoe@inha.ac.kr
Tel.: +82-32-860-7467
Fax: +82-32-872-0959

Abstract Poly(styrene-*co*-divinylbenzene) microspheres having a diameter range of 3.0–4.5 μm were synthesized by precipitation polymerization under various conditions, then the effects of the polymerization parameters such as monomer and initiator concentration, and used cosolvents on the characteristics of the final particles were compared with those in dispersion polymerization. It was found that precipitation polymerization is more sensitive to polymerization conditions than dispersion polymerization, and that precise control of polymerization parameters is therefore essential for individually stable spherical particles. Monomer and initiator concentration, and the use of cosolvents significantly vary the morphology and the size of the final particles. However, the uniformity of the microspheres is not greatly affected by the polymerization parameters.

Keywords Precipitation polymerization · Microsphere · Styrene · Divinylbenzene · Stability

Introduction

Polymer colloids have received much attention due to their vast application areas including conventional and recently emerged electronic and biotechnology fields such as coatings, adhesives, inks, toner binders, immunoassay and so forth [1, 2, 3]. Their applications are dominated by the chemical and/or physical properties of the polymers and one of the most important physical properties is the size and size distribution of the final particles.

In particular, one of the most frequently studied systems is micrometer-sized crosslinked polystyrene (PS) beads, due to properties such as superior thermal and mechanical resistance, applicability of surface modification, adaptability in a wide pH range, and susceptibility to deposition of inorganic materials on the surface [4, 5] etc.

The aforementioned properties enable PS microspheres to be used in ion exchangers, various chromatographic instruments, polymer-supported catalysis, and medical and chemical applications as absorbents [6, 7] etc. Therefore, the copolymerization of styrene and divinylbenzene system using various polymerization techniques has been extensively studied by many researchers [8, 9].

There are several methods for preparing a wide range of sizes using different particle formation mechanisms. In synthesizing polymer colloids, it is quite important to endow stability on individual particles to prevent coagulation among the particles. In general, individually stable, spherical polymer beads are obtained by electrostatic stabilization in emulsion polymerization [10], steric stabilization in suspension, dispersion and seeded polymerization [11], and self-stabilization by crosslinking in precipitation polymerization [12].

Spheres of less than 1 μm are readily obtained through macro- (conventional), mini-, and micro-emulsion polymerization [10], whereas, dispersion polymerization is used to simply produce 1–10 μm-sized microspheres [13]. In addition, Shirasu porous glass (SPG) membrane emulsification with a subsequent polymerization, which is a modified suspension polymerization technique, can prepare polymer microspheres in the range of 1–60 μm in a single step [14, 15]. As another alternative, precipitation polymerization has shown that fully crosslinked polymer microspheres having a similar particle size to that from dispersion polymerization can be obtained by a simple method without additional apparatus or process. Upon the discovery of precipitation polymerization in organic media, a variety of monomers including methacrylate, maleic anhydride, and chloromethylstyrene were copolymerized with divinylbenzene as the crosslinkable monomer using this technique [12, 16, 17].

Although precipitation polymerization yielding microspheres shares many polymerization characteristics with dispersion polymerization, its uniqueness stems from the absence of polymeric stabilizer which is a key element in dispersion polymerization for achieving spherical, stable particles. Thus, the particle formation mechanism in precipitation is different from that in dispersion polymerization. The uniqueness in precipitation polymerization lies in the high degree of crosslinking compared with dispersion polymerization, whereas the concentration of crosslinkable monomer such as divinylbenzene in dispersion polymerization is generally below 0.5%, based on the main monomer, for stable spherical micrometer-sized polymer particles [18, 19].

In this study, poly(styrene-*co*-divinylbenzene) microspheres were synthesized by precipitation polymerization and characterized in terms of the polymerization parameters, including, monomer and initiator concentration in polymerization media, and the use of co-solvents. In addition, the properties of the microspheres obtained under different conditions were characterized.

Materials and methods

Materials Styrene (Junsei, Japan) and divinylbenzene (55% mixture of isomers, Aldrich, USA) were purified using an inhibitor removal column (Aldrich) and stored at −5 °C prior to use. As an initiator, analytical grade 2,2-azobisisobutyronitrile (AIBN) (Junsei) was used without further purification. Acetonitrile (Junsei), 2-methoxyethanol (Junsei), 2-propanol (Kanto, Japan), benzene (Junsei), and toluene (Oriental Chemical, Korea) used as the polymerization media were of analytical grade.

Polymerization procedure The polymerization ingredients consist simply of medium, monomer mixture composed of 50:50 mol% of styrene and divinylbenzene, and AIBN. The total amount of monomer was varied from 2 to 15 vol.% for the medium. The concentration of AIBN was increased from 2 to 8 wt% with respect to total amount of monomers. After charging 18 mL of polymerizing ingredient mixture in a scintillation vial, it was purged for 15 min with nitrogen and sealed. The vials containing solvent, monomer, and initiator were immersed in ultrasound bath and homogenized for 3 min. Polymerization was carried out in a shaking water bath working with an agitation speed of 30 rpm at 70 °C for 24 h. After completion of the polymerization, the resultant particles were obtained by centrifugation and washed with methanol repeatedly.

Characterizations Scanning electron microscopy (SEM) (Hitachi S-4300) was used to study the morphology of poly(styrene-*co*-divinylbenzene) particles. Number-average diameter (D_n), weight-average diameter (D_w), and the uniformity (D_w/D_n) were achieved using Scion Image Analyzer software by counting 100 individual particles from SEM microphotographs. The particle size distribution and circularity of the microspheres was instantaneously measured using the Flow Particle Image Analyzer (FPIA)-2100 (Sysmex, Japan) by flowing approximately 5 mL of particle-suspended sheath reagent through a flat sheath flow cell. The yield of the polymerization was determined gravimetrically.

Results and discussion

Stability of the microspheres

Figure 1a, b shows two representative SEM microphotographs indicating the instability and stability of the microspheres obtained during the precipitation polymerization of monomers composed of styrene and divinylbenzene. As briefly mentioned earlier, the formation of stable microspheres in precipitation polymerization is strongly influenced by the degree of crosslinking, and the existence of crosslinkable monomer in high concentration is therefore essential [20]. Since no stabilizing agents such as surfactants or steric stabilizers are used in precipitation polymerization, it is expected that the stability of the final particles would be significantly affected by polymerization parameters such as the concentration of monomer in the medium, the concentration of initiator, and the solvent used, which are examined in detail in the following sections.

Concentration of polymerization ingredients

A uniqueness of the precipitation polymerization compared with the conventional heterogeneous radical polymerizations is the low monomer concentration. In the dispersion polymerization of styrene, the monomer is charged up to 40 vol.% relative to the polymerization medium without resulting in a coagulation [21, 22, 23]. However, according to the results of Stöver's group on precipitation polymerization, it was reported that the stable spherical particles were obtained only up to 5 vol.% in the case of divinylbenzene [12] and only 2 vol.% of monomer mixture consisting of chloromethylstyrene and divinylbenzene [17] was added to the polymerization medium. Above this concentration, coagulated particles were obtained. However, we have obtained results which are not in accordance with theirs.

In Fig. 2a b, the microspheres prepared by the precipitation polymerization of 50:50 mol-% styrene and

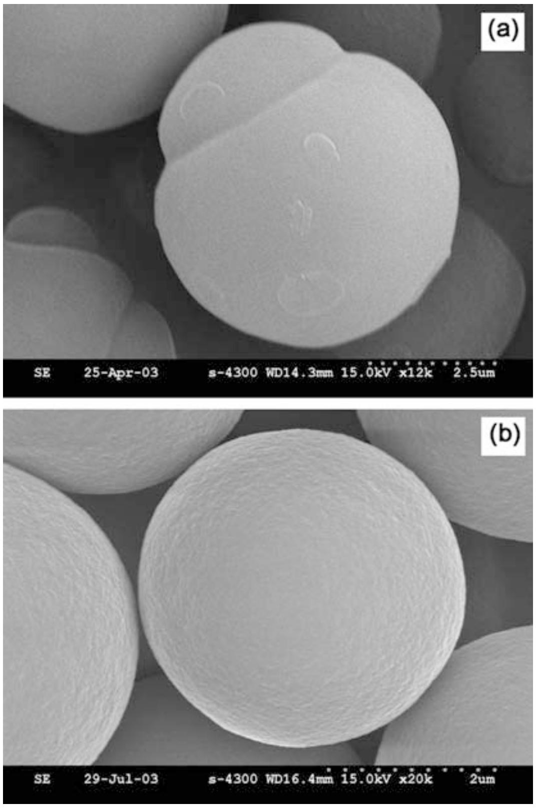

Fig. 1a, b Representative scanning electron micrososcopy microphotographs of **a** coagulated, and **b** stable microsphere particles formed during precipitation polymerization

divinylbenzene with varying concentration of monomer from 2 to 15 vol.% relative to acetonitrile are shown. Individually stable particles were obtained at all concentrations of monomer; however, it should be noted that at higher than 15 vol.% monomer, partially coagulated particles resulted.

Figure 3 represents the change in the final particle size and its uniformity with respect to the concentration of total monomers (styene and divinylbenzene) in the medium. It is seen that the particle size increases with the monomer concentration, while the uniformity remains intact. The D_n of 2.8 μm at 2 vol.% styrene increases to 3.9 μm at 15 vol.% styrene. A similar trend is also observed in the dispersion polymerization of styrene [21] owing to the change in the solvency of the medium resulting from increased amount of monomer.

In order to study the stability of the microspheres, the circularity concept was used. The circularity of the particles is defined as the ratio of the circumference of a circle of equivalent area to the particle and the perimeter of the particle itself as follows:

$$Circularity = \frac{Circle\ circumference}{Perimeter\ of\ projected\ particle\ image} \quad (1)$$

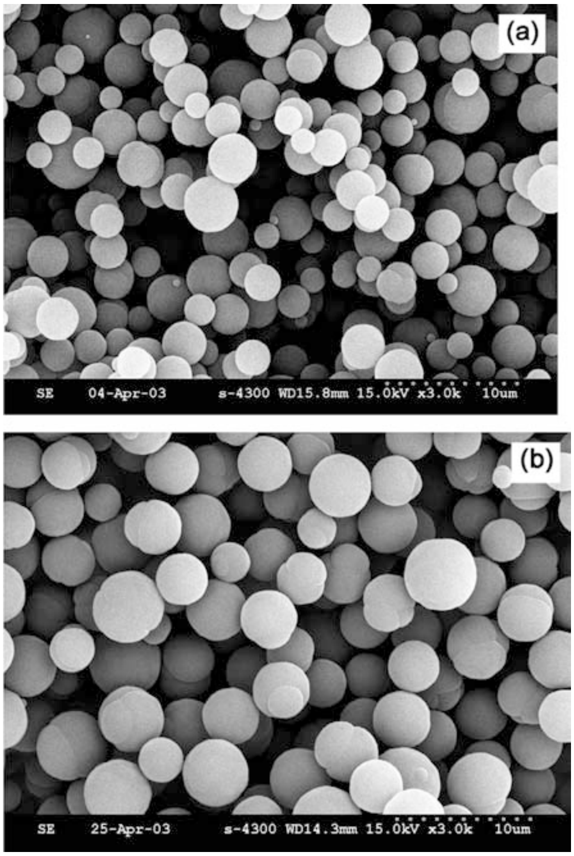

Fig. 2 Effect of the total concentration of monomer in polymerization medium with 4 wt% 2,2-azobisisobutyronitrile (AIBN) in acetonitrile at 70 °C for 24 h. **a** 2 vol.%. **b** 15 vol.%

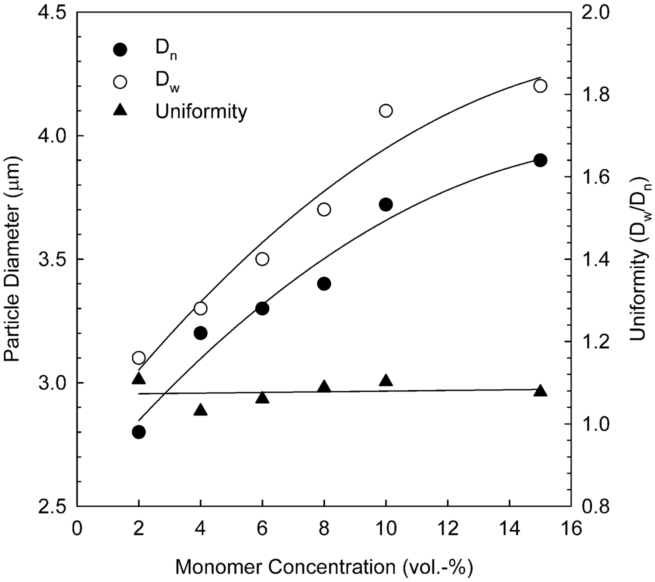

Fig. 3 Effects of the monomer concentration on the particle size and its uniformity of the microspheres prepared by precipitation polymerization with 4 wt% AIBN in acetonitrile at 70 °C for 24 h. D_n Number-average diameter, D_w weight-average diameter

Circularity is a measure to specify the shape of particles. The more spherical the particle, the closer is its circularity to unity, and the more elongated the particle, the lower the observed circularity. The circularity of the microspheres as a function of the concentration of monomer was instantaneously measured with FPIA-2100. The particle number density (N_p) as the particle number of unit quality was calculated as follows:

$$N\mathrm{p} = 6\frac{MY}{\pi r^3 \rho} \qquad (2)$$

where, M is the monomer added, Y is the yield of the polymerization, r is the number average-radius of the microsphere, and ρ is the density of the polymer. The density (ρ) was taken to be that of amorphous polystyrene (i.e. $\rho = 1.065$ g/cm^3) [24].

As seen in Fig. 4, the circularity decreased from 0.985 for 2 vol.% of monomer mixture to 0.942 for 15 vol.%, implying that fewer particles are coagulated owing to the improved stability of individual particles at low monomer concentration. It is natural that higher particle number density in medium would lead to a higher possibility of collision among particles. This observation is also confirmed from the SEM microphotographs in Fig. 2.

The final diameter and uniformity of the microspheres with respect to the concentration of initiator is investigated in detail in Fig. 5. The corresponding increase in size of the microspheres with the initiator concentration from 2 to 8 wt% relative to monomer resembles that of dispersion polymerization [25, 26]. Again, it is seen that the uniformity is not influenced by the concentration of initiator. In dispersion polymerization, the increase in monomer and initiator concentration with the same concentration of other ingredients respectively gives larger particles with broadened particle size distribution [27]. The constant uniformity in precipitation polymerization would be owing to the different mechanism of particle formation. Compared to dispersion polymerization, in which polymeric stabilizer initially dissolved in the polymerization medium causes the formation of nuclei [28], the nuclei formation in precipitation polymerization is solely attributed to the crosslinked polymer molecules having a chain length greater than the critical limit which can not be further dissolved in the medium. Once the nuclei are formed, they grow to particles by continuously adsorbing the monomer or oligomeric species on the particle surface. Since no giant molecule such as the polymeric stabilizer used in dispersion polymerization exists in the polymerization medium, the low molecular weight species are readily adsorbed onto the particle surface, which minimizes the formation of secondary particles. Thus, the particle size distribution would not be much influenced by changes in the concentration of monomer or initiator.

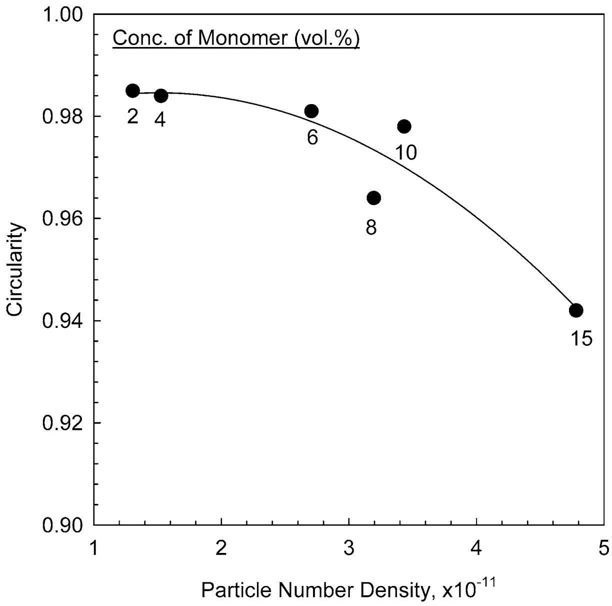

Fig. 4 Circularity vs. particle number density in polymerization medium with the concentration of monomer in the range 2–4 vol.% and with 4 wt% AIBN in acetonitrile at 70 °C for 24 h. The *numbers* indicate the concentration of monomer in vol.%

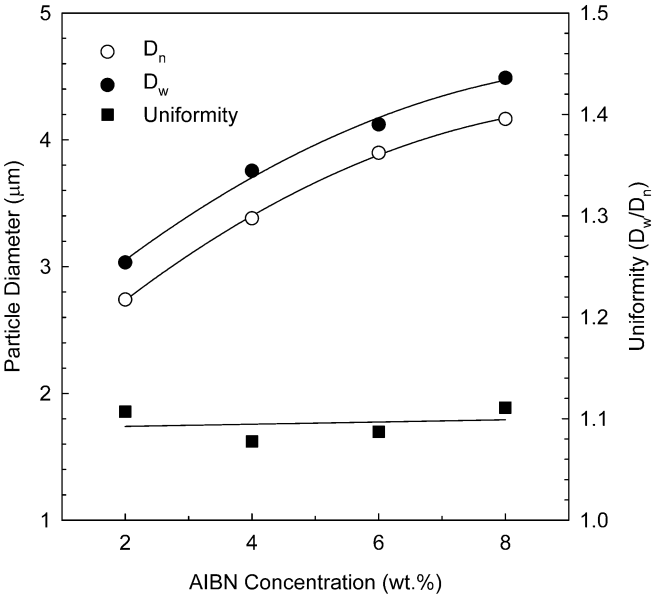

Fig. 5 Particle size diameter and the uniformity of the microspheres prepared by precipitation polymerization of 50/50 styrene and divinylbenzene with various concentrations of *AIBN* at 70 °C for 24 h

The yield of polymerization in acetonitrile with changing concentrations of monomer and AIBN at 70 °C is depicted in Fig. 6. Since the resultant polymerized species in precipitation polymerization are separated in medium-soluble sol and insoluble gel [17], the

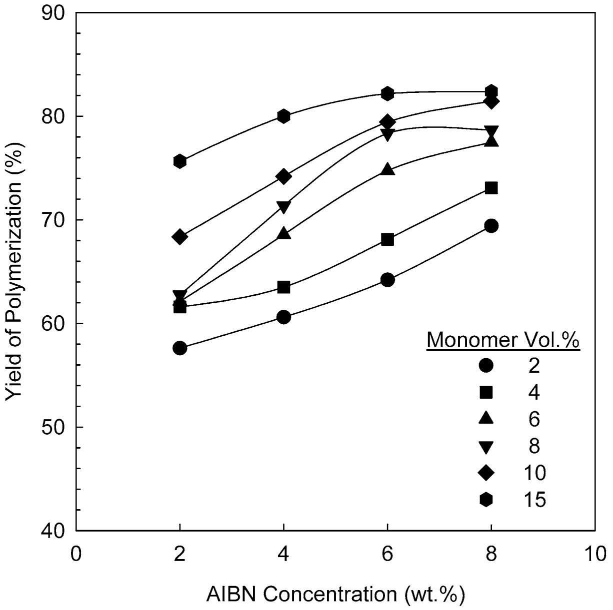

Fig. 6 Yield of polymerization with respect to the concentration of initiator for several monomer concentrations at 70 °C for 24 h

yield of the polymerization indicates the amount of monomer converted to microspheres. Since acetonitrile is not a good solvent for PS, oligomeric chains with a low degree of polymerization would favor being dissolved in acetonitrile due to the poor solubility with polymerized species; thus, they are separated from the medium and finally adsorbed by the growing particles. As seen in Fig. 6, the yield of the polymerization increases with the concentration of initiator and the amount of monomer in the medium. This may be due to the fact that the higher initiator and monomer concentrations would lead to the easy access of polymerization species in the unreacted state or active polymerizing radicals in the medium. Therefore, the lowest yield in polymerization was obtained at the lowest monomer concentration along with the lowest initiator concentration, and vice versa.

It is noted that the final yield in the precipitation polymerization is lower than that usually obtained in the dispersion polymerization (usually higher than 85%). Since the yield is calculated as the ratio of the total amount of particles to the initial amount of monomer, the difference in the reactivity ratio between styrene and divinylbenzene would be related to the final yield of the precipitation polymerization. The *m*-divinylbenzene (r_2) has the same reactivity ratios (0.58) as styrene (r_1), but the *p*-divinylbenzene ($r_2 = 1.18$) ratio is 4.5-fold higher than r_1 ($= 0.26$) [29]. Therefore, it is expected that divinylbenzene would be consumed faster than styrene during the polymerization. Indeed, we have found that divinylbenzene did not exist in the sol part separated after the completion of the precipitation polymerization examined based on ^{1}H-NMR spectra [30]. In order to obtain individually spherical particles in the precipitation polymerization, the existence of crosslinkable monomer is essential. When divinylbenzene was not added, the precipitation polymerization of styrene did not proceed [30]. In dispersion copolymerization of styrene and divinylbenzene, the increased amount of divinylbenzene also accelerates the polymerization rate (R_p), i.e. $R_p = [\mathrm{DVB}]^{0.13}$; however, the difference in the final conversion is marginal, that is, only within 5%[23]. Therefore, the notable difference in the yield in the precipitation polymerization with respect to the change in the polymerization ingredients is characteristic of the precipitation polymerization.

Effect of cosolvent

Several solvents with a wide range of the solubility parameter (δ), from 8.6 to 14.5 (cal/cm^3)$^{1/2}$, were employed as the polymerization medium as listed in Table 1.

Firstly, all solvents were used as the main medium without mixing with others. However, it was found that acetonitrile was the only solvent with which the microspheres were obtained. At present, it is not clearly understood why only acetonitrile works for preparing stable spherical beads. Although the total solubility parameters (δ), and each component of the solubility parameter in terms of dispersive (δ_d), polar (δ_p), and

Table 1 Solubility parameters [32] of various solvents used and particle shape of the resulting polymer when used with acetonitrile

Solvent	δ^a	δ_d	δ_p	δ_H	Particle shape
		(cal/cm^3)$^{1/2}$	(cal/cm^3)$^{1/2}$	(cal/cm^3)$^{1/2}$	
Acetonitrile	11.9	7.5	8.8	7.5	Spherical
Methanol	14.5	7.4	6.0	10.9	Coagulum
Ethanol	12.7	7.7	4.3	9.5	Coagulum
2-Methoxyethanol	12.1	8.0	4.5	7.0	Spherical
2-Propanol	11.5	7.7	3.0	8.0	Spherical
Benzene	9.2	9.0	0	1.0	Spherical
Toluene	8.9	8.8	0.7	1.0	Spherical
Diethyl oxalate	8.6	-	-	-	Coagulum
Styrene	9.3	9.1	0.5	2.0	-

$^a\delta = (\delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2)^{1/2}$

hydrogen bonding (δ_H) for 2-methoxyethanol and 2-propanol are quite close to those of acetonitrile, the resulting particles were coagulated when 2-methoxyethanol or 2-propanol were solely used as a medium. Therefore, the polymerization was conducted using mixtures of acetonitrile as the main solvent and others as the cosolvent with various compositions. The stable microspheres having a unimodal distribution measured by FPIA-2100 were obtained in acetonitrile/2-methoxyethanol, acetonitrile/2-propanol, acetonitrile/benzene, acetonitrile/toluene systems as seen in Fig. 7. The D_ns obtained at the various acetonitrile/cosolvent systems were 3.39 μm measured by FPIA-2100 (3.43 μm measured by Image analyzer), 3.62 μm (3.58 μm), 4.05 μm (3.92 μm), and 4.41 μm (4.43 μm), respectively. There was no big difference in the particle sizes measured between the FPIA-2100 and Image analyzer from the SEM micrographs.

Some cosolvents which were successful in the precipitation polymerizations have similar solubility parameters to those of acetonitrile. The total solubility parameters (δ) are close to that of styrene, 9.3 (cal/cm^3)$^{1/2}$, ranging from 9.3 to 12.1 (cal/cm^3)$^{1/2}$. The dispersion terms (δ_ds) are in the narrow range of 8.0 to 9.0 (cal/cm^3)$^{1/2}$. However, no information was found from the polar (δ_p) and hydrogen bonding (δ_H) terms since they are distant values. Therefore, it is believed that the formation of stable microspheres depends on the total solubility parameter (δ) and its dispersion term (δ_d) rather than its polar (δ_p) and hydrogen bonding (δ_H) terms.

Figure 8 shows the number-average particle diameter of microspheres prepared using acetonitrile and various cosolvents as the media at 70 °C. Generally, the size of microspheres depends on the solubility parameter of the cosolvent used in dispersion polymerization [28]. The better solvent for synthesized polymer gives a larger particle size, since a smaller number of nuclei is produced in the nucleation stage. This trend is also seen in Fig. 8. When 2-propanol, having a solubility parameter similar to that of acetonitrile, was added at various concentrations, the final size of the microsphere hardly changed. When toluene and benzene were used with acetonitrile, the size of microspheres increased with the concentration of cosolvents from 3.35 to 3.97 μm and from 3.34 to 3.50 μm, respectively. This phenomenon was more pronounced for toluene, whereas the size of the microspheres accordingly decreased from 3.09 to 2.47 μm as the concentration of 2-methoxyethanol, which has a solubility parameter of 12.1 (cal/cm^3)$^{1/2}$ increased from 15 to 50 vol.% relative to acetonitrile.

In Table 2, more detailed experimental results of the particle size and uniformity are presented. As seen in Fig. 8, the size of the microspheres increases with the addition of good solvents for PS i.e., toluene and benzene, remains unaffected with the addition of 2-propanol, and decreases with the addition of poor solvent, i.e., 2-propanol. It is noted that coagulation among particles

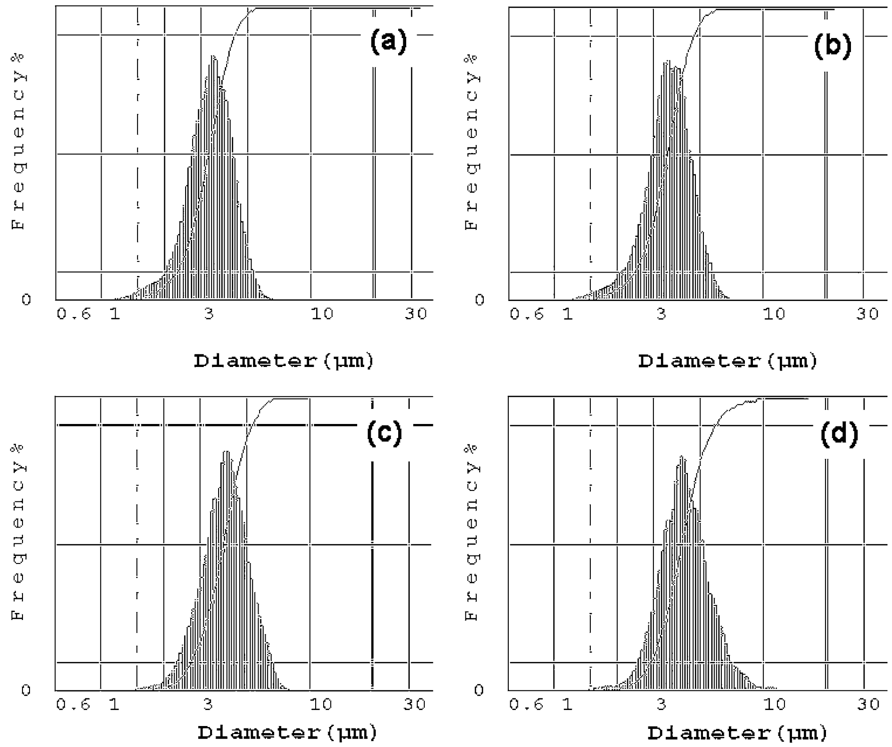

Fig. 7a–d Particle size distribution of the microspheres prepared by 50/50 styrene/divinylbenzene monomer composition in 2/1 (v/v) various cosolvent/acetonitrile mixtures with 4 wt% AIBN at 70 °C. **a** 2-Methoxyethanol. **b** 2-Propanol. **c** Benzene. **d** Toluene

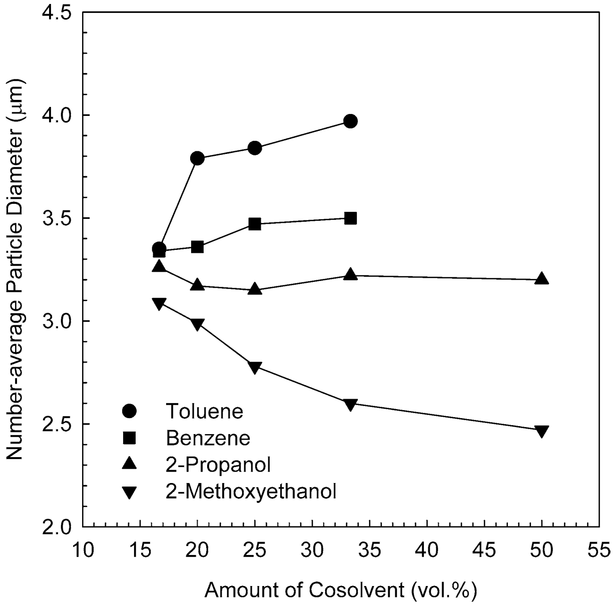

Fig. 8 The effect of cosolvents on the size of microspheres prepared using acetonitrile and various concentrations of cosolvents for 50/50 styrene/divinylbenzene monomer composition with 2 wt% AIBN at 70 °C

is observed when the concentration of good solvents exceed a 3/1 (v/v) ratio of acetonitrile/(toluene or benzene). In addition, the particle size distribution is seen not to be affected by the presence of cosolvents.

The influence of the cosolvents on the final particle size in the precipitation polymerization is similar to that in the dispersion polymerization: a good solvent system gives larger particles. In good cosolvent systems, the critical chain length increases and the adsorption rate of the oligomers onto the particles is suppressed, thereby decreasing rates of nuclei formation and adsorption of the oligomers, followed by the formation of larger particles [31].

Conclusions

Poly(styrene-*co*-divinylbenzene) microspheres having a diameter range of 3.0–4.5 μm were synthesized by precipitation polymerization under various conditions, and the effects of the polymerization parameters on the polymerization and the final particles were studied and compared with dispersion polymerization. Important similarities between precipitation polymerization and dispersion polymerization in the synthesis of microspheres can be summarized as follows:

-1. The particle formation is obtained by nucleation and growth stages from the solution stage in the beginning of the polymerization.
-2. The final particle size is in the same range.
-3. The final particle sizes are affected by the concentration of the polymerization ingredients: the higher the monomer and initiator concentrations, the larger are the microspheres are obtained.
-4. The solubility parameter plays a significant role in determining success in the formation of microspheres and the size of the resulting polymer particles.

In addition, major dissimilarities can be summarized as follows:

-1. The mechanism for the formation of stable microspheres is different since no stabilizer is present in the

Table 2 The size and uniformity of the microspheres synthesized using mixtures of acetonitrile and various solvent as the polymerization media with 2 wt% AIBN at 70 °C

Cosolvent	Concentration of cosolvent (v/v)	D_n (μm)	D_w (μm)	Uniformity
2-Methoxyethanol	5/1	3.09	3.57	1.15
	4/1	2.99	4.23	1.42
	3/1	2.78	2.96	1.06
	2/1	2.60	2.74	1.06
	1/1	2.47	2.80	1.13
2-Propanol	5/1	3.26	3.61	1.11
	4/1	3.17	3.37	1.06
	3/1	3.15	3.42	1.08
	2/1	3.22	4.18	1.33
	1/1	3.20	3.65	1.14
Benzene	5/1	3.34	4.04	1.21
	4/1	3.36	3.76	1.09
	3/1	3.47	3.78	1.09
	2/1	3.50	3.98	1.14
	1/1	Coagulum	-	-
Toluene	5/1	3.35	3.74	1.12
	4/1	3.79	3.95	1.04
	3/1	3.84	4.47	1.17
	2/1	3.97	4.20	1.06
	1/1	Coagulum	-	-

precipitation polymerization. Therefore, precipitation polymerization is more sensitive to the polymerization conditions.

-2. The yield of precipitation polymerization is lower than that of dispersion polymerization since the polymerized species are divided into gel and sol, and it is significantly affected by the reactivity ratios of the monomers.
-3. Generally, monomer concentration is kept lower in order to prevent coagulation in precipitation polymerization.
-4. The uniformity of the final particle in the precipitation polymerization is little influenced by the change in the concentration of ingredients.
-5. Precipitation polymerization is more sensitive to the solvency of the medium. Therefore, the successful formation of microsphere is limited to a few select solvents although they have the similar solubility parameters.
-6. The particle size control is more difficult than in dispersion polymerization since maintaining the stability of the microspheres in the precipitation polymerization is difficult due to the absence of stabilizer.

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