# Synthesis of Narrow or Monodisperse Poly(divinylbenzene) Microspheres by Distillation−Precipitation Polymerization

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ABSTRACT: Highly cross-linked narrow or monodisperse poly(divinylbenzene) (PDVB) microspheres were prepared by distillation−precipitation polymerization as a novel polymerization technique in acetonitrile with 2,2′-azobis(2-methylpropionitrile) (AIBN) as initiator. The polymeric microspheres were formed simultaneously through a precipitation polymerization manner during the distillation of acetonitrile off the reaction system. Narrow or monodisperse particles with spherical shape and smooth surface were prepared with diameters between 1.10 and 3.41 $\mu$m without any stabilizers. The particle size and size distribution depended on the reaction conditions. The maximum particle size of 2.14 $\mu$m with size distribution index of 1.058 was attained at cross-linking degree of 64%, and the size distribution became narrower with increasing cross-linking degree. The particle sizes increased with increasing monomer and initiator concentration. A series of polymer particles with diameter between 1.99 and 3.41 $\mu$m were obtained by multi-semibatch mode with successive introduction of a mixture of the designed amount of AIBN and divinylbenzene containing 80% divinylbenzene (DVB80) in acetonitrile into the distillation−precipitation polymerization, and the size distribution index was kept around 1.02. Furthermore, the conversion increased from 31% for the first aliquot to 76% for the sixth aliquot. All of the resulting microspheres were characterized with SEM.

## Introduction

Polymer microspheres and microcapsules with internal structures are attractive for a wide number of applications, including supporting phases for separation science,[1,2] biomedical devices,[3] casting additives,[4] and controlled release reservoirs.[5,6] The Horvath group reported one-step dispersion polymerization of glycidyl methacrylate−divinylbenzene microspheres in acetonitrile and their application in the capillary electrochromatography of macrolide antibodies.[7]

Precipitation polymerization is unique to prepare microspheres of uniform size and shape, which can lead to narrow disperse microspheres free of any added surfactant or stabilizer.[8−17] This technique starts as homogeneous mixtures of monomer, initiator, and optional solvents.[17−19] During the polymerization, the growing polymer chains phase-separate from the continuous medium by enthalpic precipitation, or entropic precipitation, in cases where cross-linking prevents the polymer and solvent from freely mixing.[20]

Recently, Stöver et al. reported the monodisperse cross-linked core−shell polymer microspheres by precipitation polymerization[21] and quantitative compositional mapping of such particles by soft X-ray spectromicroscopy.[22] We also succeeded in obtaining narrow disperse polymeric microspheres with active hydroxyl groups with a dense core and a lightly cross-linked functional shell through a two-stage precipitation polymerization in the absence of any stabilizer.[23]

We are particularly interested in entropic precipitation polymerization, which was carried out in the presence of a cross-linker and a solvent for the polymer. In good solvents, these polymerizations form turbid macroscopic gels, largely depending on original monomer concentration.[24−27] In poor solvents, precipitation polymerizations normally produce micrometer-sized particles.[14−17,19] Here, we intend to report distillation−precipitation polymerization as a novel polymerization technique to produce narrow disperse polymer microspheres, which was formed simultaneously through a precipitation−polymerization manner during the distillation of acetonitrile solvent from the reaction system.

## Experimental Section

**Chemicals**. Both divinylbenzene (DVB80, 80% divinylbenzene isomers) and styrene were supplied as technical grade by Shengli Chemical Technical Factory, Shandong, China. Both of them were washed with 5% aqueous sodium hydroxide and water and then dried over anhydrous magnesium sulfate prior to use, while the styrene was purified further by vacuum distillation before polymerization. 2,2-Azobis(2-methylpropionitrile) (AIBN) (analytical grade, available from Chemical Factory of Nankai University) was recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagents II Co.) was dried over 4 Å molecular sieves and purified by distillation before use. The other reagents were also analytical grade and used as received without any further purification.

**Distillation−Precipitation Polymerization.** A typical procedure for the distillation−precipitation polymerization: AIBN (0.184 g, 1.12 mmol, 2 wt % relative to the total monomer) and DVB80 (10 mL, 9.2 g, 70.7 mmol, 2.5 vol % relative to the reaction medium) was dissolved in 400 mL of acetonitrile in a dried clean 500 mL two-necked flask, attaching with a fractionating column, Liebig condenser, and a receiver. The flask was submerged in a heating mantle, and the reaction mixture was heated from ambient temperature to the boiling state within 30 min, and then the solvent began to be distilled. The initially homogeneous reaction mixtures became milky white after boiling for 15 min. The reaction was ended after 200 mL of acetonitrile was distilled from the reaction system within 1.5 h. After the polymerization, the resulting PDVB80 microspheres were separated by vacuum filtration over a G-5 sintered glass filter and washed successively three times with THF, acetone, and ether. The polymeric

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particles were dried at 50 °C in a vacuum oven until constant weight to afford 2.85 g of polymer microspheres with 35% yield.

The procedures for the other distillation−precipitation polymerization were much similar as that for the typical one by altering either AIBN initiator concentration, or DVB concentration, or cross-linking degree of DVB and styrene comonomers. The initially homogeneous reaction mixture became milky white after boiling for 10−50 min, which depended on the reaction conditions. The treatment for these samples was also the same as the typical one.

**Multi-Semibatch Mode with Successive Introduction of AIBN Initiator and the Designed Amount of DVB Monomer**. The polymerization for the first aliquot was carried out as described above as in a typical procedure. After distillation of 200 mL of acetonitrile off the reaction system, 5 mL of the reaction mixture was sampled and treated as the typical procedures for SEM characterization. For the second aliquot of the polymerization, a mixture of 0.184 g (1.12 mmol) of AIBN initiator in 200 mL of the distilled acetonitrile from the reaction system was added to the residual reaction system after the first cycle polymerization. The polymerization was continued under the distillation conditions as the first aliquot. After distillation of 200 mL of acetonitrile off the reaction system, 5 mL of the reaction mixture was sampled and treated as the typical procedure for SEM characterization. For the third aliquot polymerization, a mixture of 0.184 g (1.12 mmol) of AIBN initiator and 5 mL (4.6 g, 35.5 mmol) of DVB monomer in 200 mL of the distilled acetonititrile was added to the residual reaction system after the second aliquot polymerization. The polymerization was continued under the distillation conditions as the first aliquot. After distillation of 200 mL of acetonitrile off the reaction system, 5 mL of the reaction mixture was sampled and treated as a typical procedure for SEM characterization.

Then a mixture of AIBN and the designed amount of DVB monomer in 200 mL of the distilled acetonitrile was added to the residual reaction system successively after each aliquot polymerization. The polymerization was continued under the distillation conditions as above with a multibatch mode. Such a process was repeated for a total of six aliquots as described in Table 5.

All the yields of microspheric particles were determined by gravimetry. The reproducibility of the results was confirmed through several duplicate and triplicate experiments.

**Particle Size Analysis.** The particle size and size distribution were determined by scanning electron microscopy (SEM) using a scanning electron microscope (Philips-XL-30). All of the SEM size data reflect the averages about 100 particles each, which are calculated by the following formula:

$$U = D_{\mathrm{w}}/D_{\mathrm{n}} \qquad D_{\mathrm{n}} = \sum_{i=1}^{k} n_i D_i \Big/ \sum_{i=1}^{k} n_i$$

$$D_{\mathrm{w}} = \sum_{i=1}^{k} n_i D_i^4 \Big/ \sum_{i=1}^{k} n_i D_i^3$$

where $U$ is the polydispersity index, $D_{\mathrm{n}}$ is the number-average diameter, $D_{\mathrm{w}}$ is the weight-average diameter, $N$ is the total number of the measured particles, and $D_i$ is the particle diameters of the determined microspheres.

## Results and Discussion

In our previous work,[23] divinylbenzene was precipitation polymerized in acetonitrile as the solvent with AIBN as the initiator which resulted in narrow disperse particles. Such results were also reported by Stöver et al.[28] for the synthesis of divinylbenzene−maleic anhydride microspheres using precipitation polymerization. Apparently, acetonitrile meets the solvency conditions required for the narrow or monodisperse particle formation: that is, it dissolves the monomer but precipitates the forming polymer. Acetonitrile is a nonsolvent for poly(divinylbenzene) (PDVB) as indicated by comparison of their solubility $\delta$ parameters: 11.9 (cal/cm$^3$)$^{1/2}$ for $CH_3CN$ vs 9.1 (cal/cm$^3$)$^{1/2}$ for PDVB.[29,30] The preparation of PDVB80 microspheres by distillation−precipitation polymerization, in which the DVB80 monomer is polymerized and precipitated during the distillation of acetonitrile solvent from the reaction system, presents a modified and more convenient opportunity to form the narrow or monodisperse polymeric microspheres. The effects of various reaction conditions on the formation of the polymer particles during the distillation−precipitation polymerization were studied.

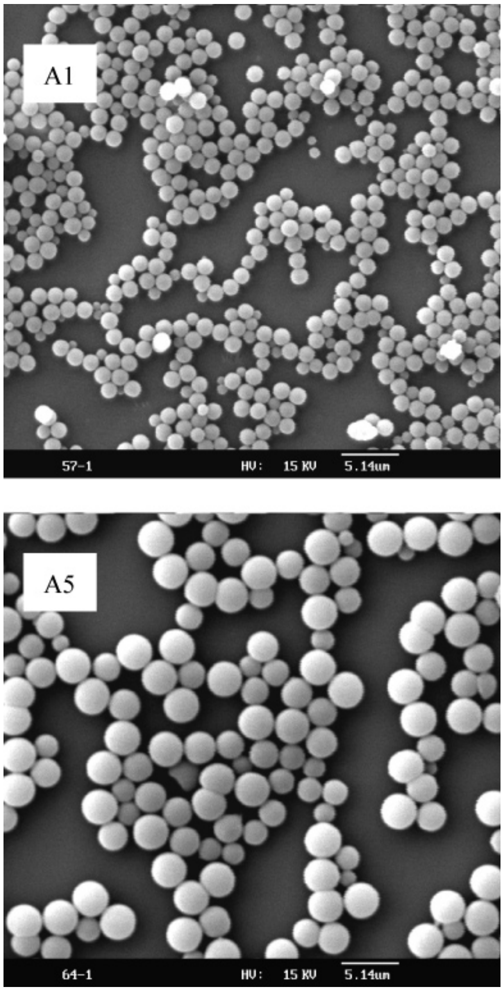

**Figure 1.** SEM micrographs of PDVB80 microspheres with different AIBN initiator concentrations in the range of 1.0 and 5.0 wt % (relative to DVB monomer): A1, 1.0 wt %; A5, 5.0 wt %.

**Effect of Initiator Concentration.** A series of experiments were initially designed to investigate the effect of the initiator concentration on the particle synthesis, while the DVB80 monomer was fixed at 2.5 vol % (relative to the whole reaction medium). An important standard for the choice of a suitable initiator concentration is that it can offer a suitable initiation rate in the polymerization to afford the polymer microspheres with narrow disperse. A short nucleation is necessary but not sufficient to obtain regular microspheres free of agglomerates and of narrow size distribution.[31,32] The SEM images of the prepared PDVB80 particles with different initiator concentrations are shown in Figure 1 (only with A1 and A5 as the samples). It demonstrated that the resulted microspheres had spherical shape with a smooth surface.

**Table 1. Size and Size Distribution and the Yield of the Polymeric Microspheres with Different AIBN Initiator Concentrations**[a]

| | | microsphere | | | |
|---|---|---|---|---|---|
| entry | AIBN (wt %) | $D_n$ ($\mu$m) | $D_w$ ($\mu$m) | $U$ | yield (%) |
| A1 | 1.0 | 1.42 | 1.48 | 1.042 | 25 |
| A2 | 2.0 | 1.99 | 2.03 | 1.019 | 31 |
| A3 | 3.0 | 2.26 | 2.34 | 1.036 | 35 |
| A4 | 4.0 | 2.64 | 2.76 | 1.045 | 39 |
| A5 | 5.0 | 2.83 | 3.02 | 1.068 | 45 |

[a] Reaction conditions: 2.5 vol % (relative to the whole reaction medium) of DVB monomers in 400 mL of acetonitrile. AIBN: 2,2-azo(bis(2-methylpropionitrile), wt % relative to divinylbenzene (DVB) monomer.

The size and size distribution of the resulted microspheres are shown in Table 1 with different AIBN initiator levels. Both the size of the particles and the yields of the microspheres increased dramatically with increasing AIBN initiator concentration. As the initiator concentration increased, the diameters of the resulted particles increased from 1.42 $\mu$m for AIBN of 1 wt % (relative to DVB monomer) (entry A1) to 2.83 $\mu$m (entry A5) for AIBN of 5 wt % (relative to DVB monomer). The yield of the microspheres also increased from 25% (entry A1) to 45% (entry A5). All of the afforded polymeric particles had narrow dispersion size with a polydispersity index at around 1.02−1.07. The narrowest distribution was obtained at AIBN of 2 wt % with the diameter of 1.99 $\mu$m and the polydispersity index of 1.019 (entry A2). The other initiator concentrations with more or less AIBN produced the particles with broader distributions. At lower initiation level (1 wt %, entry A1), the initiator might not be able to initiate enough oligomers, and the microspheres cannot precipitate from the solution in a short stage to extend the nucleation stage. Therefore, the narrow disperse microspheres ($U$ = 1.042) was obtained with diameter of 1.42 $\mu$m. As seen in Table 1 and Figure 1, an increase in AIBN initiator concentration (more than 2 wt %, entries A3−A5) led to larger particles with a broader size distribution, which occurred as expected. It may be explained by the fact that an increase of the number of free radicals resulted in the concentration of growing oligomers, and thus fewer mature nuclei were formed, which led to larger particles. Furthermore, larger particles are possible to capture nuclei or oligo-radicals from the continuous phase due to the lower surface area, which resulted in the retardation of the nucleation stage to bring a broader size distribution.

**Effect of DVB80 Concentration.** To understand the effect of DVB monomer concentration on the polymerization, the DVB concentration was varied from 1.25 to 7.5 vol % (relative to the total reaction medium) in the reaction system. All other components including the initiator level at 2 wt % (relative to DVB monomer) and the distillation rate of acetonitrile were held constant. The SEM images of the prepared PDVB80 particles with different DVB80 concentrations are shown in Figure 2 (only with B1, B3, and B6 as samples). All SEM micrographs showed that all the final PDVB80 microspheres had spherical shapes with a smooth surface. Such results demonstrated that DVB80 in such a range of concentration could be polymerized to form stable microspheres in the absence of any stabilizer by distillation−precipitation polymerization.

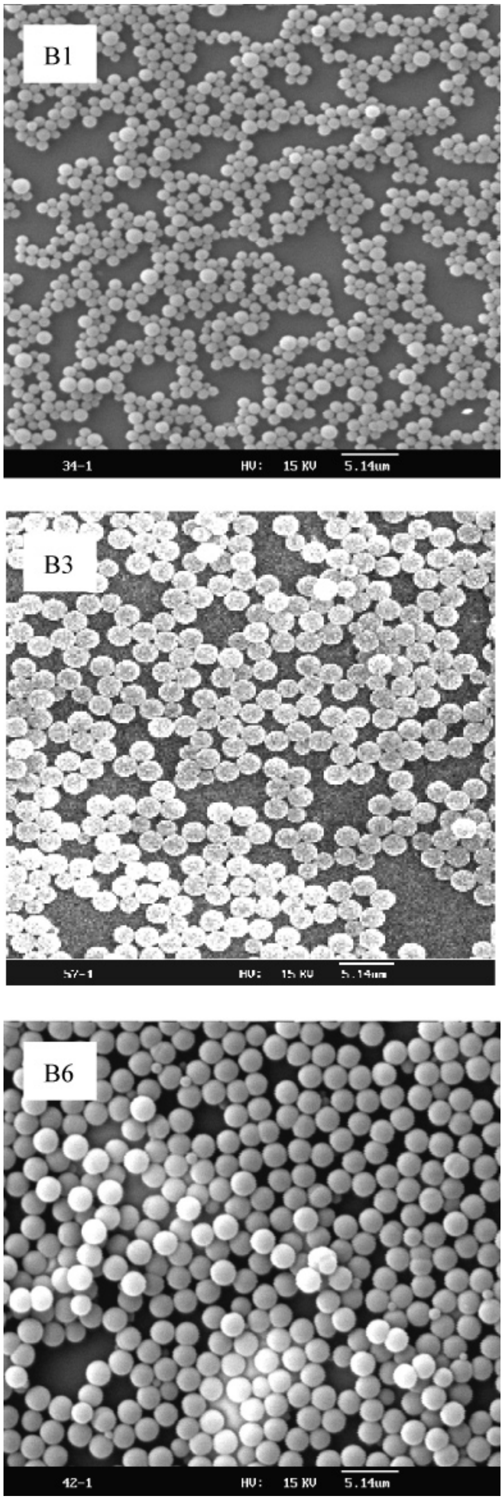

**Figure 2.** SEM micrographs of PDVB80 microspheres with different DVB80 monomer concentrations in the range of 1.25 and 7.50 vol % (relative to the total reaction medium): B1, 1.25 vol %; B3, 2.50 vol %; B6, 7.50 vol %.

The size and size distribution of the resulting particles and the conversion of monomer in the polymerization with different DVB80 concentrations in the range 1.25−7.50 vol % are shown in Table 2. The results show that all resulting microspheres are narrow disperse with a size distribution index around 1.02−1.06 without any coagulation. Polymerization started in the homogeneous phase, and the oligomers aggregated to form colloidal-stable particles. Such particles grew by capturing oligomers and monomers ultimately to form monodispersed, highly cross-linked particles with diameters between 1.10 and 2.68 $\mu$m. Both the size and the

**Table 2. Size and Size Distribution and the Yield of the Polymeric Microspheres with Different Monomer Concentrations**[a]

| | | microsphere | | | |
|---|---|---|---|---|---|
| entry | DVB (vol %) | $D_n$ ($\mu$m) | $D_w$ ($\mu$m) | $U$ | yield (%) |
| B1 | 1.25 | 1.10 | 1.17 | 1.065 | 8 |
| B2 | 2.00 | 1.76 | 1.88 | 1.068 | 25 |
| B3 | 2.50 | 1.99 | 2.03 | 1.019 | 31 |
| B4 | 3.75 | 2.49 | 2.53 | 1.018 | 35 |
| B5 | 5.00 | 2.68 | 2.73 | 1.020 | 42 |
| B6[b] | 7.50 | 2.53 | 2.61 | 1.009 | 30 |

[a] Reaction conditions: AIBN = 2 wt % of DVB monomers in 400 mL of acetonitrile. DVB = divinylbenzene monomer, vol % relative to the whole reaction medium. [b] The yield was obtained after distillation of 150 mL of acetonitrile off the system.

conversion of the DVB80 monomer increased with increasing monomer loadings. The size distribution index decreased from 1.065 ($C_{DVB}$ = 1.25 vol %, entry B1) to 1.009 ($C_{DVB}$ = 7.5 vol %, entry B6). Polydisperse microspheres were obtained probably because the particle nucleation extended with decreasing monomer concentration. At higher DVB80 concentration (7.5 vol %, entry B6), the bumping occurred in the reaction system when 150 mL of acetonitrile was distilled off the system due to the increasing viscosity of the reaction mixture with higher solid and oligomer loadings. However, the polymer microspheres were sampled to be monodisperse with an average diameter of 2.61 $\mu$m when 100 mL of acetonitrile was distilled off the system. At lower monomer concentrations, a substantial portion of the initiator radicals may self-terminate before escaping from the solvent cage. The low initiating efficiencies at low monomer concentrations led to the lower yield. The yields of the polymeric particles increased considerably from 8% at 1.25 vol % of DVB80 (entry B1) to 42% at 5 vol % of DVB80 (entry B5).

**Effect of Cross-Linking Degree.** Figure 3 shows the SEM micrographs (only with C1 and C3 as the samples and C5 the same as B3) of the polymer particles with different cross-linking degrees by distillation−precipitation polymerization in acetonitrile with AIBN initiator of 2 wt % relative to the total monomers. Styrene was used to give a series of comonomer systems labeled as from DVB80 to DVB16, which corresponded to different divinylbenzene cross-linking degrees referred to as vol % of DVB (v/v) relative to the total comonomer of DVB and styrene.

As seen in Figure 3, when the cross-linking degrees were 16% and 32%, doublet and triplet shaped particles were obtained. The spherical particles with a smooth surface were formed only with the cross-linking degree higher than 64%. Only with styrene were no particles obtained, and a latex mixture was obtained after distillation of 200 mL of acetonitrile from the reaction system. These results indicated that a high cross-linking degree was necessary to afford the microspheres with a better surface property.

The size and size distribution of the polymer particles and the yields of the polymers with different cross-linking degrees are shown in Table 3.

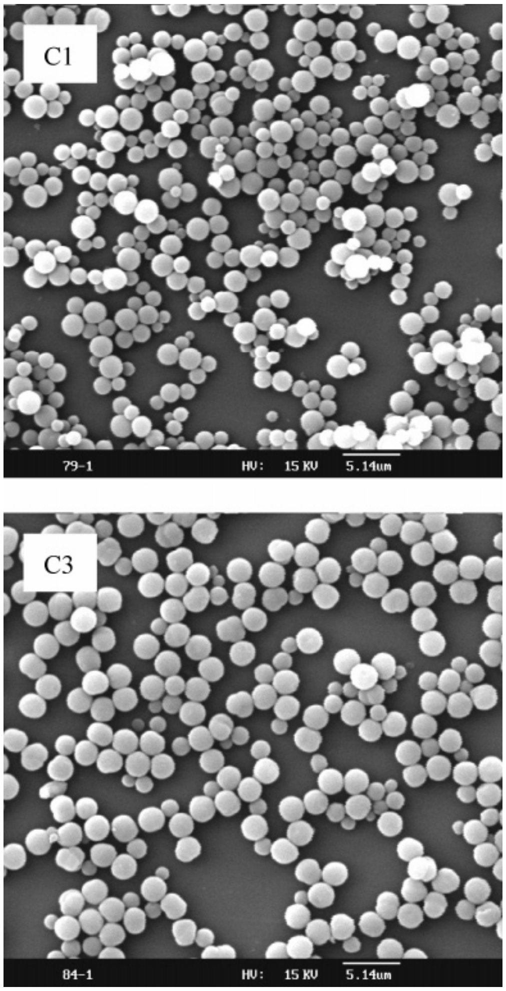

**Figure 3.** SEM micrographs of PDVB80 microspheres with different cross-linking degree from 16% to 80% for the copolymerization of DVB80 and styrene: C1, 16%; C3, 48%.

**Table 3. Size and Size Distribution and the Yield of the Polymeric Microspheres with Different Cross-Linking Degree for the Copolymerization of DVB and Styrene**[a]

| | | microsphere | | | |
|---|---|---|---|---|---|
| entry | cross-linking degree (%)[a] | $D_n$ ($\mu$m) | $D_w$ ($\mu$m) | $U$ | yield (%) |
| C1 | 16 | 1.64 | 1.88 | 1.146 | 6 |
| C2 | 32 | 1.83 | 2.01 | 1.098 | 9 |
| C3 | 48 | 2.13 | 2.26 | 1.061 | 15 |
| C4 | 64 | 2.14 | 2.26 | 1.058 | 30 |
| C5 | 80 | 1.99 | 2.03 | 1.019 | 31 |

[a] Reaction conditions: the total comonomers of 2 vol % relative to the whole reaction medium in 400 mL of acetonitrile and initiator of 2 wt % relative to total monomers. Cross-linking degree referred as vol % of divinylbenzene (total percent of *p*- and *m*-DVB) relative to the total monomer of DVB and styrene.

The average diameter increased significantly from 1.64 $\mu$m of 16% cross-linking degree to 2.14 $\mu$m of 60% cross-linking degree. The solubility parameters of the solvents played a significant role in disseminating the successful formation of a stable spherical shape as the same as in dispersion polymerization.[31,32] The solubility parameters of styrene, divinylbenzene, and acetonitrile are listed in Table 4. According to the “similar dissolve similar” principle, when acetonitrile was used as the medium, the solubility parameter of acetonitrile was closer to that of styrene. The final polymer particles were determined by the conversion of the monomers and the number of nuclei. As in good solvent, the oligomers can be dissolved well to retard the formation of nuclei for precipitation polymerization. The decrease of the number of the nuclei may be related to the formation of microspheres with larger size after completion of the polymerization. A larger number of nuclei were formed with the increasing cross-linking degree in the initial stage to have the tendency to decrease the particle size. However, as the cross-linking degree increased, the

**Table 4. Solubility Parameters ($\delta$) of Polymerization Ingredients[25,26]**

| entry | $\delta^a$ (cal/cm$^3$)$^{1/2}$ | $\delta_d$ (cal/cm$^3$)$^{1/2}$ | $\delta_p$ (cal/cm$^3$)$^{1/2}$ | $\delta_h$ (cal/cm$^3$)$^{1/2}$ |
|---|---|---|---|---|
| styene | 9.3 (8.7) | 8.2 (8.7) | 4.4 (0.5) | 0 (0) |
| divinylbenzene | (8.5) | (8.5) | (0.4) | (0) |
| acetonitrile | 12.1 | 5 | 5.4 | 9.6 |

[a] $\delta = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{1/2}$. [b] $\delta$ = total solubility parameters, $\delta_d$ = component due to dispersion forces, $\delta_p$ = component due to polar forces, $\delta_h$ = component due to hydrogen bonding. [c] The solubility parameters of divinylbenzene and styrene calculated from Hansen's group contribution method and given in parentheses.

conversion of the comonomers dramatically increased from 6% in entry C1 to 31% in entry C5. This might be due to the fact that the cross-linked oligomers can precipitate from the solution to the surface of the nuclei more easily. The resulting polymer particles were determined by these two competitive factors. The maximum particle size of 2.14 $\mu$m with the cross-linking degree of 64% and the minimum size of 1.88 $\mu$m with the cross-linking degree of 16% were obtained. The lower cross-linking degree delayed the formation of nuclei and the particle nucleation resulting in the particle size with a broader distribution.

**Effect of Successive Feedings of AIBN Initiator and Designed Amount of DVB Monomer with Multi-Semibatch Mode.** It has been confirmed by Stöver et al. that PDVB55 particles by precipitation polymerization contain more residual double bonds than those by suspension polymerization.[21] This was due to the poor solvent medium for polymer and the much lower monomer concentration used in the precipitation polymerization. The residual double bonds located on the surface of the particle favor the capture of the radical oligomers and monomers from the reaction solution phase to grow the particles. We have synthesized core−shell microspheres with active hydroxyl group on the surface by two-stage precipitation polymerization.[23]

During the distillation precipitation polymerization of PDVB80 with monomer loading of 2.5 vol % (relative to the whole reaction medium) and AIBN initiator of 2 wt % (relative to DVB80) in 400 mL of acetonitrile, the conversion of DVB80 reached only 31% (entry D1, the same entry as A2) after distillation of 200 mL of solvent off the reaction system due to the low monomer concentration and rigid cross-linked surface of the particle. There were many residual monomers and soluble oligomers in the reaction system. PDVB80 particles contained a lot of residual carbon−carbon double bonds on the surface, which can react further with either DVB80 or other monomers. Here, a mixture of AIBN initiator and designed amount of DVB80 in acetonitrile was successively introduced to the reaction system after 200 mL of acetonitrile was distilled off the system. Then the polymerization was continued under the distillation conditions by a multi-semibatch mode, and the unreacted DVB80 monomers and soluble oligomers in the solution were polymerized and captured by the previously formed PDVB80 particles.

A series of monodisperse PDVB80 particles with various diameters were prepared by the multi-semibatch mode. The SEM images of such polymeric microspheres are shown in Figure 4 (D1 the same as B3 and only with D2 and D6 as samples).

All SEM micrographs showed that all the final particles have spherical shapes with a smooth surface.

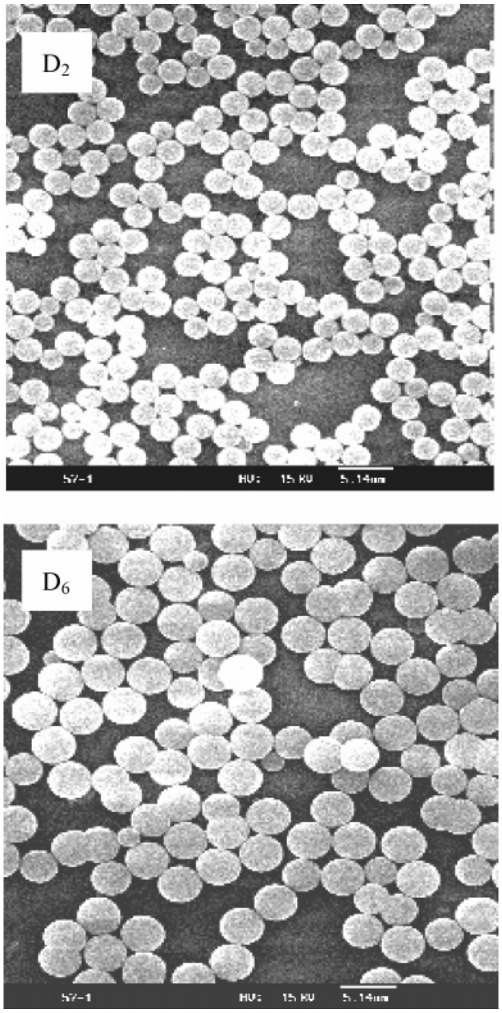

**Figure 4.** SEM micrographs of PDVB80 microspheres with a multibatch mode by alternative addition of AIBN initiator and the designed amount of DVB monomer: D2, the second aliquot; D6, the sixth aliquot.

Doublet and secondary initiated nucleation particles were observed occasionally, in particular after AIBN initiator and DVB were successively introduced two times to the reaction system. This may be due to higher initiator and monomer concentration of DVB80 monomer and soluble oligomer with successive addition of AIBN and monomer for several aliquots. A mixture of 0.184 g (1.12 mmol) of AIBN initiator and 5.0 mL DVB (35.3 mmol) in 200 mL of acetonitrile and a mixture of only 0.184 g (1.12 mmol) of AIBN in 200 mL of acetonitrile were alternatively introduced to the reaction system. There were many residual DVB80 monomers in the reaction system after each addition of the new DVB80 with only polymerization for one time. The successive addition of the reagents in such turn prevented the reaction system from bumping during the distillation−precipitation polymerization.

The size and size distribution of the particles are listed in Table 5 by the multi-semibatch mode distillation−precipitation polymerization. The particle sizes increased significantly from 1.99 $\mu$m (D1) to 3.41 $\mu$m (D6) by successively introducing AIBN initiator and the designed amount of DVB80 monomer in acetonitrile into the reaction system five times, and the conversion of the monomer increased noticeably from 31% (D1) to 76% (D6). If no new particles were formed (no secondary nucleation), the particles volume (proportional to $D^3$)

**Table 5. Size and Size Distribution of Polymeric Microspheres with a Multibatch Mode by Successive Addition of AIBN Initiator and the Designed Amount of DVB Monomer[a]**

| | feed | | microsphere | | | |
|---|---|---|---|---|---|---|
| entry | AIBN (g) | DVB (mL) | $D_n$ ($\mu$m) | $D_w$ ($\mu$m) | $U$ | yield (%) |
| D1 | 0.184 | 10.0 | 1.99 | 2.03 | 1.019 | 31 |
| D2 | 0.184 | 0.0 | 2.34 | 2.37 | 1.017 | 48 |
| D3 | 0.184 | 5.0 | 2.80 | 2.83 | 1.012 | 53 |
| D4 | 0.184 | 0.0 | 2.96 | 3.08 | 1.037 | 68 |
| D5 | 0.184 | 5.0 | 3.25 | 3.30 | 1.016 | 67 |
| D6 | 0.184 | 0.0 | 3.41 | 3.50 | 1.028 | 76 |

[a] Reaction conditions: the polymerization finished until distillation of 200 mL of acetonitrile from the reaction system for each aliquot, and the total of initial acetonitrile was 400 mL in the reaction system. AIBN = 2,2′-azo(bis(2-methylpropinitrile); DVB = divinylbenzene.

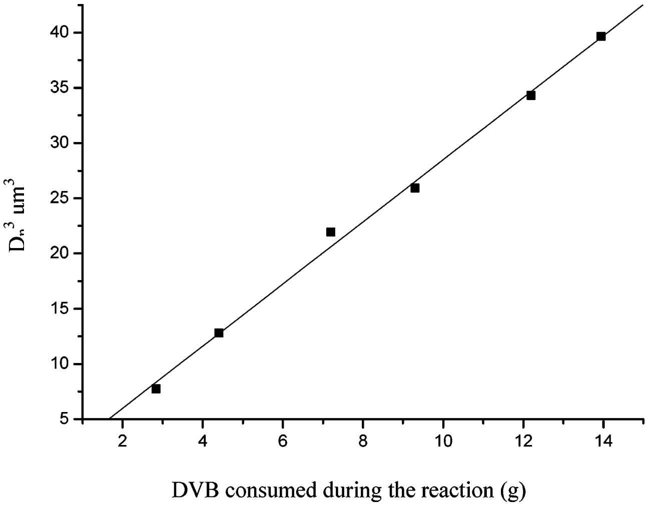

**Figure 5.** Effect of the amount of DVB conversed in multibatch mode on the final particle volume.

should increase linearly with the amount of DVB monomer consumed during the reaction. We found that our reaction system followed this prediction as shown in Figure 5. Furthermore, all the resulting microspheres held a narrow size distribution with the polydispersity index around 1.02. Therefore, the monodisperse microspheres with different diameters can be easily controlled by the multi-semibatch mode distillation−precipitation polymerization.

A key requirement to form monodisperse microspheres by precipitation was that one of the monomers must be a cross-linker. The mechanism of the polymer particle growth by successive addition of the mixture of AIBN and the designed amount of DVB monomer was much similar as the synthesis of the core−shell structure polymer by a two-stage precipitation polymerization.[23] During the distillation−precipitation polymerization, the transient swellable gel layer on the particle surface continuously dissolved and collapsed even while nearly formed oligomer radicals were captured from the solution by the residual vinyl groups on the particle surface. The microspheres grew larger and larger in diameter in a uniform fashion without coagulation due to the comparative low concentration of monomer in the reaction system even after successive addition of AIBN initiator and the designed amount of DVB80 monomer for six aliquots. Accordingly, the particle surface at any instance during the polymerization should be a solvent-swollen, partially cross-linked gel layer. Such surface gel layer sterically stabilized the particles and prevented coagulation, which would otherwise lead to a broad size distribution.

## Conclusion

Highly cross-linked poly(divinylbenzene) microspheres with narrow or monodisperse were synthesized from commercial available DVB80 by distillation−precipitation polymerization in the absence of any stabilizer with AIBN as initiator in acetonitrile as a novel polymerization technique. The SEM characterization showed that the resulting microspheres had spherical shapes and a smooth surface. The narrow or monodisperse polymer microspheres with the size in the range of 1.10 and 3.41 $\mu$m were prepared by varying the reaction conditions, such as initiator concentration, DVB concentration, cross-linking degree, and successive addition of AIBN initiator and DVB monomer. The monodisperse polymeric microspheres with different diameters can be easily controlled by the multi-semibatch mode distillation−precipitation polymerization without formation of the new particles. Furthermore, the conversion was improved from 31% for the first aliquot to 76% for the sixth aliquot. The study on the scope of this technique, including extension to other monomers, control of the functional groups at the particle surface, and preparation of core−shell microspheres, is in progress.

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