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Synthesis of monodisperse porous poly(divinylbenzene) microspheres by distillation–precipitation polymerization

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Abstract

Highly crosslinked monodisperse porous poly(divinylbenzene) (PDVB) microspheres were prepared by distillation–precipitation polymerization in acetonitrile containing up to 25 vol% of toluene as porogen with 2,2′-azobisisobutyronitrile (AIBN) as initiator in the absence of any stabilizer or surfactant. The porous polymer microspheres were formed through a precipitation manner during the distillation of the solvent from the reaction system. Monodisperse porous polymer particles with spherical shape and smooth surface were synthesized with diameters in the range of 1.86 and 3.06 μm, total porosity of up to 0.30 cm^3/g and specific surface area as high as 762 m^2/g. The growth procedure of porous PDVB microsphere was characterized by SEM technique for morphological observation and isotherm nitrogen adsorption for the determination of the special surface area and porosity. The resultant porous polymer microspheres had a novel structure with the gradual increasing of pore volume during distillation of the solvent out of the reaction system.

Keywords: Distillation–precipitation polymerization; Divinylbenzene; Porous microspheres

1. Introduction

Highly crosslinked porous polymer microspheres are attractive for many applications, including as adsorbents, the stationary phase for chromatography, supports for exchange, membrane materials, and carriers for catalysts as well as biologically active substances [1–8]. These porous materials have good mechanical strength and excellent chemical stability with a wide variety of diameters and pore sizes, in which mass transfer is considerably enhanced by convective flow through the pores [9].

The porous structure is typically developed during the polymerization of both mono- and polyvinyl monomers in the presence of a porogen, in which thermodynamically poor solvent (precipitant) and thermodynamically good soluble polymers can be used as porogen. The type of porogen used has a critical influence on the porous properties of the resultant polymer materials. Polymer beads with mesoporous and specific area of up to 100 m^2/g were obtained in the presence of a precipitant as a porogen [5] and porous materials with microporous contributed to the specific surface area as high as several hundreds m^2/g by using good solvents as porogen [9,10]. On the other hand, very large pores even in the micrometer range are formed with linear polymers as porogens leading to the small surface areas, typically less than 10 m^2/g [11–13].

During the last two decades, porous polymer microspheres have been prepared by microsuspension polymerization [14–16], which cannot be used widely for the chromatographic methods due to a broad particle size distribution and a tedious process of size classification after the preparation. The modified suspension process including Vanderhoff's multi-step seeded polymerization [17] and Ugelstad's activated swelling and polymerization method [18] has been utilized for the preparation of macroporous monodisperse polymer beads. However, these techniques involve the tedious and complicate procedures for the synthesis of the template particles and

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polymer porogen [12,13], which made it difficult to control the pore size and size distribution, the chemical composition and nature of the polymer porogen, the content of the polymer porogen, and the crosslinking content for the polymerization. The porous polymer microsphere surfaces are free of any residues and have a homogeneous porosity, which is afforded by precipitation polymerization of divinylbenzene (DVB) in acetonitrile containing toluene as porogen [6].

Recently, we developed the distillation–precipitation polymerization as a novel technique to afford monodisperse poly(divinylbenzene) (PDVB) [19] and polymer microsphere with various functional groups [20–23]. The resultant polymer microspheres had clean and surfactant free surfaces as the polymerizations occurred in the absence of any surfactant or steric stabilizer. However, the functional polymer microspheres in our previous work were highly crosslinked without any porosity. In the present work, we tried to extend this technique to afford mono- and narrowdisperse porous polymer microspheres. Considering the difference in boiling points between toluene (108 °C) and acetonitrile (82 °C), the toluene fraction remained in the reaction medium would increase gradually with the distillation of solvent, which would induce higher porosity and specific surface area in the outer layer of the resultant microspheres. Therefore, the porous PDVB microspheres with a gradual increase of specific area and porosity would be afforded by this method, which might have more potential applications for chromatographic separation.

2. Experimental

2.1. Materials

Divinylbenzene (DVB80, 80% divinylbenzene isomers) was supplied as technical grade by Shengli Chemical Technical Factory, Shandong, China, which was washed with 5% aqueous sodium hydroxide and water and then dried over anhydrous magnesium sulfate prior to use. 2,2′-Azobisisobutyronitrile (AIBN, 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. Toluene (Tianjin Chemical Reagents II Co.) was dried over calcium hydride overnight, refluxed with sodium powder and then distilled before utilization. All the other reagents were of analytical grade and utilized as received without further purification.

2.2. Preparation of monodisperse porous poly(divinylbenzene) microspheres

A typical procedure for the distillation–precipitation polymerization: AIBN (0.036 g, 0.022 mmol, 2 wt% relative to the monomer) and DVB (2 mL, 1.8 g, 2.5 vol% corresponding to the reaction medium) were dissolved in 72 mL of acetonitrile and 8 mL of toluene mixture in a dried 100-mL of two-necked flask, attached with a fractionating column, Libieg 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. The initially homogeneous reaction mixture became milky white after boiling for 15 min. The reaction was ended after 40-mL of co-solvent was distilled from the reaction system within 1.5 h. After the polymerization, the resulting porous PDVB microspheres were separated by vacuum filtration over a G-5 sintered glass filter and washed successively three times with THF, acetone and ether. The resulting porous polymer microspheres were dried at 50 °C in a vacuum oven till constant weight.

The procedures for the other distillation–precipitation polymerizations were much similar to that for the typical one by changing the volume ratio of toluene as porogen and acetonitrile (ranging from 0 to 40 vol%) with total volume of co-solvent maintaining at 80 mL, while the monomer loading and AIBN initiator were kept at 2.5 vol% of the whole reaction medium and 2 wt% corresponding to the monomer, respectively. The initially homogeneous reaction turned milky white after boiling for 10–50 min, which became longer with increasing the fraction of toluene in the co-solvent. The treatment for these particles was the same as the typical one.

2.3. Growth procedure of the porous polymer microspheres

The growth procedures for the porous polymer microspheres were traced by SEM observation for the morphology and BET characterization with nitrogen adsorption for pore size, porosity and specific surface area of the resultant porous PDVB microspheres. The reaction was conducted in a 1000-mL of two-necked flask through the polymerization of 20 mL of DVB (18.4 g, 141 mmol, 2.5 vol% corresponding to the reaction medium) with 680 mL of acetonitrile and 120 mL of toluene as co-solvent in the presence of 0.37 g (0.22 mmol, 2 wt% corresponding to the monomer) of AIBN as initiator. The heating process was much similar to the typical one. During the course of polymerization, the reaction system was sampled for 20-mL each at various time intervals indicating with the volume of the co-solvent distilled from the reaction medium, and the polymerization for the sampled mixture was stopped immediately by quenching the reaction mixture with hydroquinone in ice-water. The component of the solvent distilled out of the reaction system was determined by refractive method with an Abber-62 refractometer. Then the concentration of the toluene remained in the reaction system is calculated according to the following formula:

$$C_{\mathrm{T}} = \frac{120 - V_1 \times 10\%}{800 - V_1} \times 100\%$$

where C_{T} is the concentration of toluene remained in the reaction medium, V_1 is the volume of the solvent distilled out of the reaction system, and the concentration of toluene in the distilled solvent is kept around 10 vol% during the polymerization.

The porous polymer microspheres for SEM and BET characterization were separated by either filtration over a G-5 sintered glass filter for micrometer-size particles or ultracentrifugation for nanospheres and washed successively three times each with THF, acetone and ether. The resultant polymer microspheres were dried at 50 °C in vacuum oven till constant weight.

2.4. Particle characterization

The surface morphology, particle size and size distribution were determined by scanning electron microscopy (SEM) using a Scanning Electron Microscope (Philips-XL-30). All of the size data reflect the averages about 100 particles each, which were calculated according to the following formula:

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

where U is the polydispersity index, D_{n} is the number-average diameter, D_{w} is the weight-average diameter, N is the total number of the measured particles, D_i is the diameter of the determined microsphere.

The pore volume, pore-size distribution and specific surface area of the final porous particles were measured with a Quantachrome Autosorb-1 automated gas adsorption system using nitrogen at 77 K as adsorbate. The polymer microspheres were dried under vacuum oven at 100 °C overnight prior to BET measurement.

Fourier transform infrared analysis was performed on a Bio-Rad FTS 135 FT-IR spectrometer to determine the surface structure of porous polymer microspheres. All samples were mixed and whetted with spectroscopy grade potassium bromide prior to place in the sample cell, and all the diffuse reflectance spectra were scanned over the range of 400–4000 cm^{-1}.

3. Results and discussion

The previous research results indicate that acetonitrile meets the solvency conditions requiring for the monodisperse particle formation [6,19–23]: that is, it dissolves the monomer but precipitates the resultant polymer. Acetonitrile is a nonsolvent for PDVB as indicated by comparison of their solubility parameters for PDVB, 24.6 $\mathrm{MPa}^{1/2}$ for $\mathrm{CH_3CN}$ *vs* 18.6 $\mathrm{MPa}^{1/2}$, respectively [24]. Furthermore, the boiling point of acetonitrile at 82 °C provides a suitable temperature for the polymerization with AIBN as initiator, in which AIBN decomposes into radical for efficient initiation of the polymerization. With toluene as a porogen, phase separation occurs late and results in the polymer network with small pores during the suspension polymerization [10,11] and precipitation polymerization [6]. In the present work, the incorporation of pores into PDVB network by the distillation–precipitation polymerization technique with 5–30 vol% of toluene as a co-solvent with acteonitrile for reaction medium was investigated in detail in the absence of any additive or surfactant.

3.1. The effect of toluene content in the reaction medium on the structure of porous PDVB microspheres

The low monomer loading (less than 7.5 vol% of the reaction medium) for the distillation–precipitation polymerization with suitable amount of AIBN initiator is essential to afford monodisperse PDVB microspheres without any coagulation [19]. Here, all of the polymerizations were carried out containing 2.5 vol% of PDVB monomer (relative to the reaction medium) with 2 wt% of AIBN initiator (corresponding to the monomer), in which the porous PDVB microspheres were formed simultaneously through a precipitation polymerization manner during the distillation of the co-solvent out of the reaction system.

A series of experiments were initially designed to investigate the effect of the toluene content in the reaction medium on the structure of the resulting porous PDVB microspheres. An important standard for the choice of a suitable toluene concentration in the reaction medium is that it can lead to the porous domains in the final polymer network during the polymerization, while the resultant polymer microspheres were narrow- or monodisperse. The SEM images of the prepared porous PDVB particles with different toluene contents in the reaction system are illustrated in Fig. 1.

The precipitated microspheres from neat acetonitrile (Fig. 1, T1) and in the presence of toluene co-solvent less than 20 vol% (Fig. 1 T2–T4) had spherical shapes with smooth surfaces. In contrast, a few of second-initiated particles were noticeable from 25 vol% of toluene in the reaction medium, including several instances where two or more particles coalesced together during their growth. Only macrogel and soluble polymer were afforded with 30 and 40 vol% of toluene in the reaction medium.

The reaction conditions, the size, size distribution, the average pore diameter, pore volume and specific surface area of the final porous PDVB microspheres are summarized in Table 1 with different toluene contents in the co-solvent varying from 0 to 40 vol%.

The average diameter of the resulting porous particles varied in the range of 2.17 and 2.55 μm with toluene content increasing from 5 to 25 vol% in the reaction medium. The size of the final PDVB particles increased considerably from 1.99 μm in neat acetonitrile to around 2.20 μm in the presence of toluene as co-solvent for the polymerization. The porous polymer particles had monosize distribution with polydispersity index (U) around 1.02 with toluene in the range of 0–20 vol% in the co-solvent. The maximum particle size with diameter of 2.55 μm and narrow dispersity of 1.048 was obtained from around 25 vol% of toluene in the co-solvent. This was much similar to the phenomena occurring in the precipitation polymerization of DVB with toluene as a porogen [6]. In the presence of 30 vol% toluene in the co-solvent, the whole reaction mixture was macrogelled. Only soluble polymer was afforded from polymerizations in 40 vol% of toluene in the reaction medium without formation of any precipitate. This was somewhat different from the results reported in the literature, in which soluble polymer was

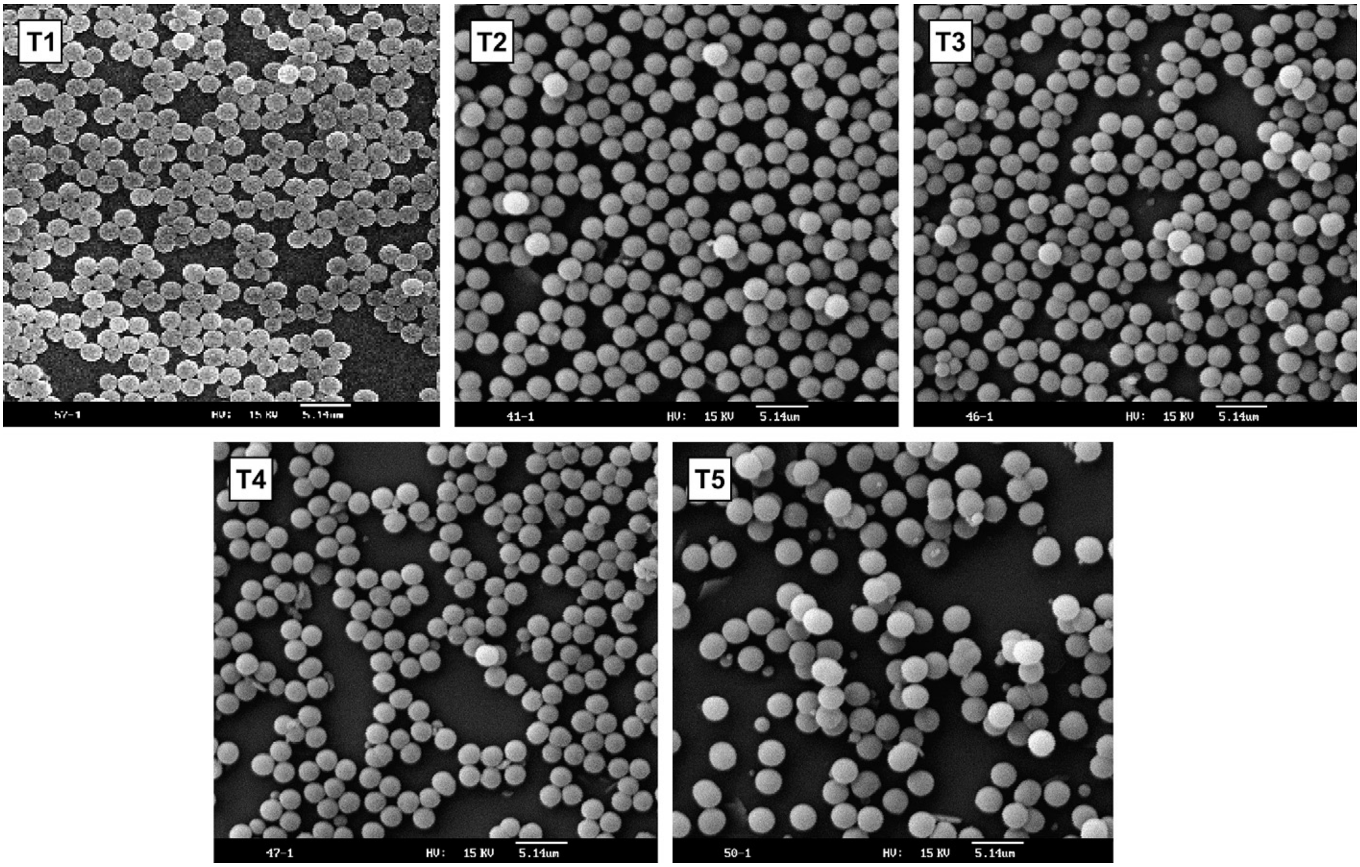


Fig. 1. SEM micrographs of porous PDVB microspheres obtained in the presence of various amounts of toluene indicated as volume ratio in the reaction medium: (T1) 0; (T2) 5 vol%; (T3) 10 vol%; (T4) 15 vol%; (T5) 25 vol%.

only formed in neat toluene for suspension polymerization [25] and precipitation polymerization [6]. The formation of macrogel and soluble polymer in the presence of high toluene content may be due to the increasing solvency of the reaction medium in such cases, which was proven further by the higher molecular weight of the resulting soluble polymer as reported for the precipitation polymerization [6].

The porosity of the precipitated polymer particles with different toluene fractions in the reaction medium was measured by nitrogen adsorption with Quantuchrome Autosorb-1 as illustrated in Table 1, as the BET method was a suitable choice for small pores [26]. Fig. 2 shows typical N_2 gas adsorption–desorption isotherm for three samples (Samples T5, V7, and V8). The isotherm adsorption displays the typical type IV curve, which is usually attributed to the predominance of mesopores. There are also practically no micropores present. The results demonstrated that both the total pore volume and specific surface area of the microspheres significantly increased with enhancing the toluene fraction in the co-solvent. The particles obtained from the presence of less 5 vol% toluene in the reaction medium behaved negligible porosity (only 0.007 cm^3/g) and a small surface area of 11.7 m^2/g (Entry T1, Table 1).

Table 1
The reaction condition, the size, size distribution, the pore size, porosity and specific surface area of porous PDVB microspheres from different toluene fractions as in volume ratio in the reaction medium[a]

Entry	Toluene (vol%)	Porous microsphere					
		D_n (μm)	D_w (μm)	U	Langmuir surface area (m^2)	Porosity (cm^3/g)	Average pore diameter (Å)
T1	0	1.99	2.03	1.019			
T2	5	2.39	2.40	1.003	12	0.007	36.0
T3	10	2.18	2.25	1.032	413	0.166	21.6
T4	15	2.17	2.21	1.017	654	0.254	20.8
T5	25	2.55	2.68	1.048	762	0.298	21.1
T6	30	Macrogel					
T7	40	Soluble polymer					

[a] The polymerization performed with total DVB loading of 2.5 vol% relative to the reaction medium and 2 wt% of AIBN initiator corresponding to DVB monomer.

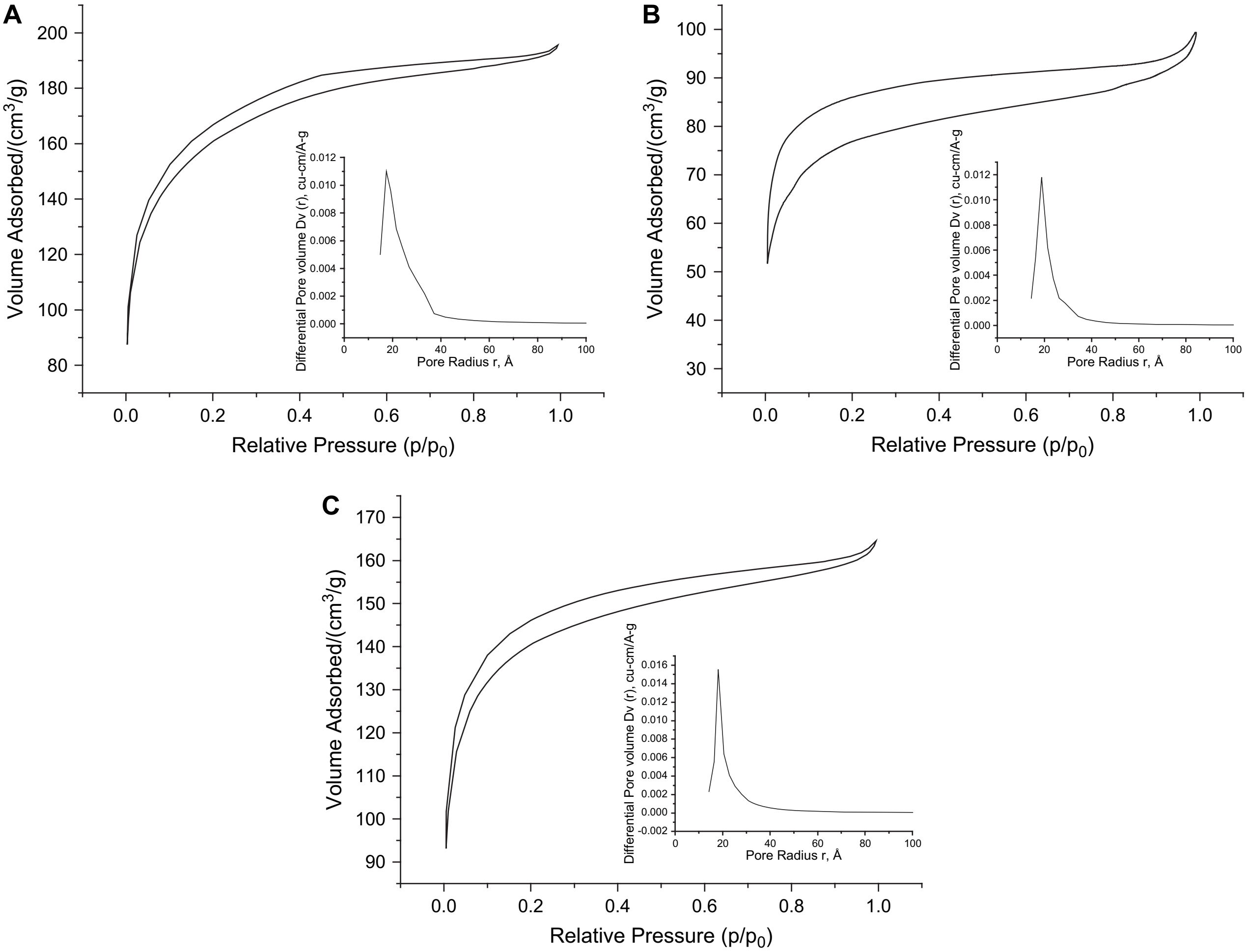


Fig. 2. BET measurement. Nitrogen absorption–desorption isotherms and pore-size distribution plots (inset) for porous microspheres: (A) Sample T5; (B) Sample V7; (C) Sample V8.

The surface area and the total pore volume of the final porous polymer particles were significantly enlarged with the addition of more toluene as porogen in the co-solvent. The porous microspheres prepared from toluene of 25 vol% in the co-solvent had the largest pore volume (0.298 cm^3/g) with the highest surface area of up to 762 m^2/g (Entry T5, Table 1). The overall pore size was kept around 20 Å in average, which was independent of the toluene volume fraction in the reaction medium. A narrow peak in the range of 15–30 Å pore radii corresponding to about 20 vol% of the total pore volume was afforded by precipitation polymerization [6] and the suspension polymerization resulting in porous particles with a much broader distribution of pore sizes in the presence of toluene as porogen [9,10].

The solubility parameters of the solvent played a key role in disseminating the successful formation of a stable spherical shape in dispersion polymerization [26] as well as precipitation polymerization [27]. The solubility parameters of acetonitrile, toluene and PDVB are 24.6, 18.6 and ca. 17.5 $MPa^{1/2}$, respectively [24]. It can be said that acetonitrile is a precipitate and toluene is a good solvent for PDVB chains. The solubility parameters of the co-solvent mixture from acetonitrile and toluene should be in the range of 17.5–24.6 $MPa^{1/2}$, which depends on the fraction of toluene in the co-solvent. When the toluene fraction in the co-solvent feed was increased from 0 to 25 vol%, the solubility parameter of the reaction system became closer to that of PDVB. In such cases, the oligomers of DVB can be dissolved well in the solvent to decrease the number of nuclei, which delayed the formation of polymer microspheres and tended to enlarge the particle size. Furthermore, the toluene feed in the reaction medium swelled the nuclei, expanded the polymer network and filled the pores of the resulting polymer network during the polymerization, which led to the formation of small pores as observed by BET technique. The larger is the fraction of toluene in the co-solvent feed in the polymerization medium, the later the phase separation or precipitation of polymer microspheres occurred, which was indicated by the occurrence of the milky-white mixture with longer time during the distillation–precipitation polymerization. When the toluene fraction was increased further higher than 40 vol%, the resultant polymer network cannot precipitate from the reaction system, which led to the formation of soluble hyper-branched polymer as in Entry T6, Table 1.

3.2. The growth procedure of porous PDVB microspheres

Distillation–precipitation polymerization started with a homogeneous organic solution containing the crosslinkable comonomer DVB, AIBN initiator, and co-solvent of toluene and acetonitrile. The first stage involved the formation of lightly crosslinked oligomer radicals by aggregation of soluble oligomers to form swollen microgels, which subsequently desolvate to be termed as nuclei for the further growth of polymer microspheres. Distillation–precipitation polymerization with DVB loading of 1.0–7.5 vol% gave narrow- or monodisperse polymer microspheres without overlapping but growing individually by capturing the subsequently formed oligomers and monomer from the reaction medium [19]. The results indicated that the phase separation occurred early for distillation–precipitation polymerization of DVB in a non-solvent, acetonitrile, to result in non-porous polymer microspheres dispersed within the continuous acetonitrile liquid phase, which was much different from that of suspension polymerization by creating large interstitial pores in non-solvent medium [10,11].

Replacing some of the acetonitrile with toluene improved the solvency of the reaction medium for the polymerization of DVB, which can be confirmed by the later occurrence of the phase separation as a milky white during the polymerization. In this way, some good solvent of toluene was trapped inside the crosslinking polymer network to result in the small pores. Such growth manner for porous polymer microspheres is not likely to create large pores. The porosity analysis from BET (Table 1 and Fig. 2) proved the absence of pores having radii larger than 30 Å.

To investigate the growth procedure of porous microspheres, a study of the resulting particle morphology over the distillated acetonitrile volume was conducted. Monitoring of the morphologies, the porosity and specific surface area was expected to provide key insight into the particle growth mechanism. As a sample, the growth processes of porous PDVB microspheres from toluene/acetonitrile (15/85, V/V) co-solvent were traced with SEM observation for morphological study as shown in Fig. 3.

In the present work, only soluble branched polymers were obtained at distillation of 50 mL of solvent out of the reaction system in the presence of 15 vol% toluene in the reaction system. Then the initially homogeneous reaction turned milky white after distilling of 100 mL acetonitrile out of the reaction system. Irregular polymer particles were afforded, which may be due to the formation of many nanospheres with small size and the presence of too many oligomers in the system at this stage. Such structures are believed to serve as nucleation sites for future growth of polymer microspheres and collapse to aggregate to each other during the centrifugation for separation from the reaction medium. This was much similar to the result during the precipitation polymerization reported by Stöver et al. [31]. As the reaction continued, the polymer particles having spherical shapes with smooth surfaces were observed when 150 mL acetonitrile was distilled from the reaction system. These results confirmed that, at this stage of the reaction, the monodisperse polymer porous microspheres can be formed and grown larger via the capture of the oligmers or monomers from the system by the surface residual double bonds, which was much similar to the case in precipitation polymerization [30].

The sampled time interval indicating as the volume of solvent distilled from the reaction system, the component of the co-solvent in the reaction medium, the size, size distribution, the average pore diameter and porosity of the porous microspheres at different reaction times are summarized in Table 2.

The toluene fraction remained in the reaction medium was increased gradually from 15 vol% at the initial stage of the polymerization to 20 vol% at the end of the polymerization (after distilling 400 mL of solvent out of the reaction system), which was due to the much higher boiling point of toluene (108 °C) than that of acetonitrile (82 °C). The results demonstrated that the size of the polymer microspheres grew significantly from 1.86 μm at the beginning of the reaction (after distilling off 150 mL of solvent from the reaction system) to 3.06 μm of the final microspheres (after distilling off 400 mL solvent from the reaction system), while the polydispersity index (U) remained monodisperse at around 1.020 in the absence of second-initiated particles. In other words, no new particles were formed during the further polymerization to grow the particle size after the formation of nuclei. All the microspheres enlarged stably and simultaneously with the amount of DVB consumed through the capture of the oligomers from the reaction system during the polymerization.

It was confirmed that PDVB particles prepared by precipitation polymerization contained more residual double bonds than those by suspension polymerization due to the poor solvent medium and the much lower monomer concentration in the former case [28,29]. In the present work, there were still a few residual vinyl groups on the surface of the porous PDVB microspheres proven by FT-IR spectra (not shown here in detail) with a peak at 1630 $\mathrm{cm^{-1}}$ corresponding to the stretching vibration of the C=C bonds, although the solvency of the reaction medium was improved greatly with more and more toluene content in the reaction medium during the polymerization.

The results in Table 2 and Fig. 2 indicated that the pore volume of the porous microspheres was developed gradually with distilling more and more solvent out of the reaction system, while the average diameter of the pores was maintained at 20 Å independent of the reaction time. The specific surface area of the porous microsphere was increased significantly from 25.3 $\mathrm{m^2/g}$ (after distilling 250 mL of solvent from the reaction system) to 647 $\mathrm{m^2/g}$ at the end of the polymerization (after distilling 400 mL of solvent out of the reaction system). These results demonstrated that the mesopores distributed in-homogeneously inside the PDVB microspheres. In other words, the porous PDVB microspheres had the gradual increase of porosity structure with the pores mainly on the outer layer and with highly crosslinked inner core having high density, which may also be due to the gradual development of the reaction medium with more and more good solvent during the distillation–precipitation polymerization.

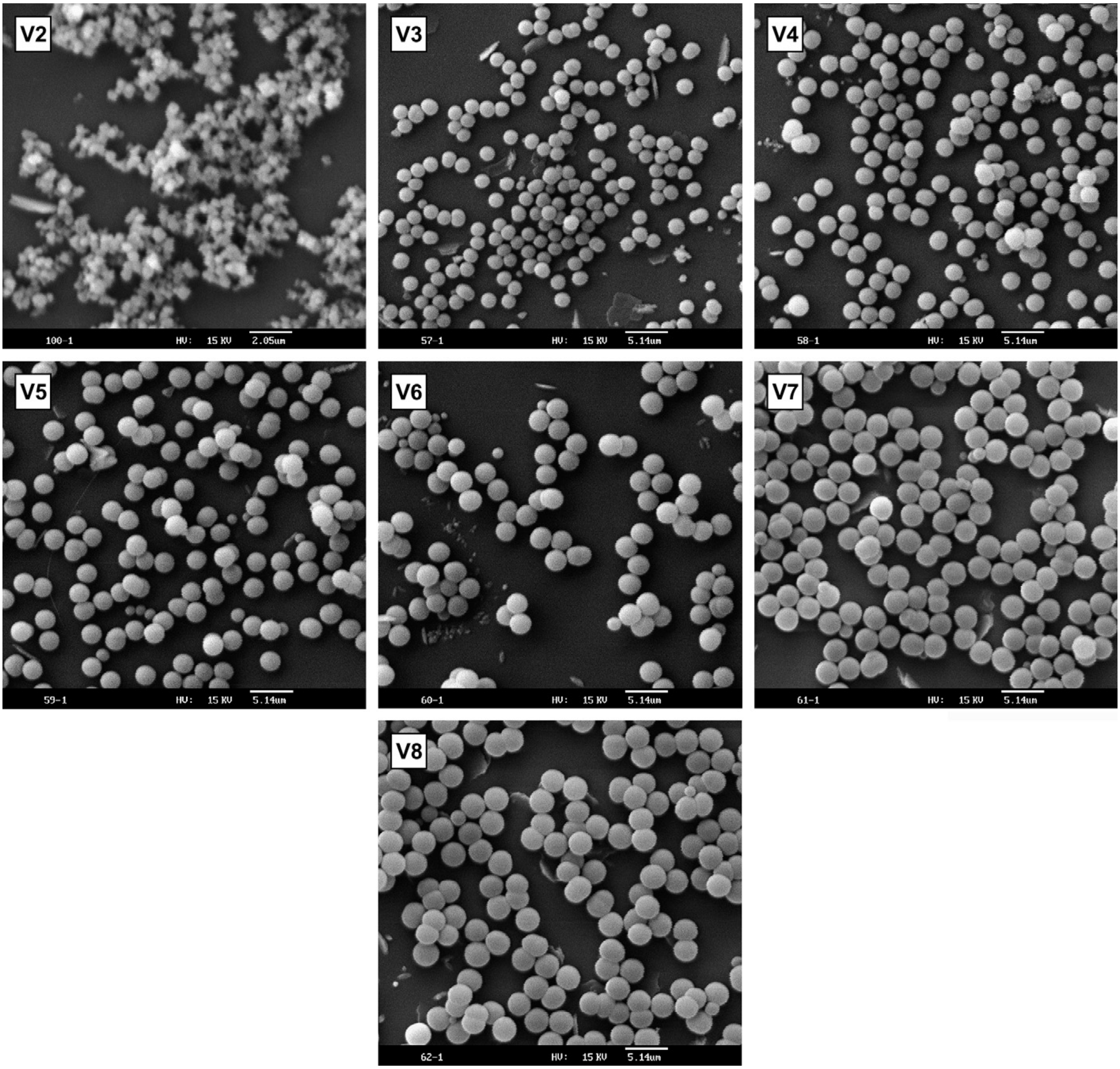
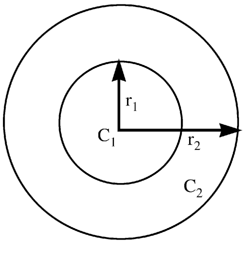


Fig. 3. SEM micrographs of porous PDVB microspheres sampled at different reaction media indicated as the volume of the solvent distilled from the reaction system: (V2) 100 mL; (V3) 150 mL; (V4) 200 mL; (V5) 250 mL; (V6) 300 mL; (V7) 350 mL; (V8) 400 mL. The toluene fraction in volume ratio is referred as the amount of toluene remaining.

The pore volume in the newly formed outer layer of the porous PDVB microspheres during the present distillation–precipitation polymerization can be calculated according to the following formula:



$$4/3 \times \pi r_1^3 = M_1/\rho + C_1 \times M_1 \tag{1}$$

$$4/3 \times \pi r_2^3 = M_2/\rho + C_2 \times M_2 \tag{2}$$

$$4/3 \times \pi\left(r_2^3 - r_1^3\right) = (M_2 - M_1)/\rho + C_{12} \times (M_2 - M_1) \tag{3}$$

$$C_{12} = \frac{4/3 \times \pi\left(r_2^3 - r_1^3\right)}{M_2 - M_1} - \frac{1}{\rho} \tag{4}$$

The sketch map indicated that the porous PDVB microspheres' radii increased from r_1 to r_2 when the solvent volume distilled out of the reaction system was increased from V_1 to V_2 during

Table 2
The component of the solvent in the reaction medium, the size, size distribution, the pore size, porosity and specific surface area of porous PDVB microspheres sampled at different polymerization time intervals[a]

Entry	Solvent volume[b] (mL)	Toluene[c] (vol%)	Microspheres						
			D_n (μm)	D_w (μm)	U	Langmuir surface area (m^2/g)	Porosity (cm^3/g)	Average pore diameter (Å)	Pore volume of layer (cm^3/g)
V1	50	15.3	Soluble polymer						
V2	100	15.7	Irregular particles						
V3	150	16.2	1.86	1.92	1.031				
V4	200	16.7	2.19	2.22	1.014				
V5	250	17.3	2.32	2.37	1.02	25.3	0.0036	18.8	
V6	300	18.0	2.52	2.60	1.029	145.4	0.059	21.6	0.322
V7	350	18.9	2.76	2.81	1.023	359.1	0.147	21.3	0.571
V8	400	20.0	3.06	3.11	1.017	647.2	0.250	20.3	0.671

[a] The polymerization performed with the initial 15 vol% of toluene in the reaction medium.

[b] The solvent volume referred as solvent distilled out from the reaction system at the sampled time interval.

[c] The toluene fraction in volume ratio referred as the amount of toluene remaining.

the distillation–precipitation polymerization. Here, M_1 and M_2 are the weights of the microspheres with different radii r_1 and r_2, respectively. For calculation, the density (ρ) was the amorphous polystyrene as 1.065 g/cm^3 [24]. C_1 and C_2 (g/cm^3) are the porosities of the microspheres with different radii r_1 and r_2, respectively. C_{12} is the porosity of the layer between r_1 and r_2. The whole volume of the porous PDVB microspheres can be divided as two parts: framework volume of PDVB (M/ρ) and the pore volume ($M \times C$). In such a way, the porosity of the newly formed outer layer in porous PDVB microspheres was obtained at various reaction times as summarized in Table 2.

When 300 mL solvent was distilled from the reaction system, the porosity of the resultant microspheres was only 0.059 cm^3/g. When the volume of the solvent distilled out of the reaction system was increased from 300 to 350 mL, the porosity of the newly formed layer at this stage was 0.571 cm^3/g with the diameter of microspheres increasing from 2.52 to 2.76 μm. Furthermore, the porosity of the newly formed outer layer was significantly increased to 0.671 cm^3/g with the diameter of microspheres increasing from 2.76 to 3.06 μm, while the volume of the solvent distilled off the reaction system was increased from 350 to 400 mL. These results demonstrated that the resultant porous microspheres had gradual increase of porosity structure in the present work by one-step distillation–precipitation polymerization, which had a dense core and a shell layer with much higher porosity. The resultant microspheres with a highly crosslinked inner core and a more porous shell may be due to the following reasons: (i) divinyl monomers are often more reactive than their monovinyl counterparts and, therefore, are incorporated into the structure at an earlier stage of the reaction; (ii) the core is formed much earlier than the outer surface. Therefore, the residual vinyl group in the inner core has more time to result in high crosslinking, which was similar to the results in the literature [32]. Such result is much different from that of precipitation polymerization [6], in which the porosity remained homogeneous in the polymer microspheres during the whole process of polymerization.

The co-solvent of acetonitrile and toluene with suitable ratio in the reaction medium played a key role for the formation of monodisperse porous PDVB microspheres by distillation–precipitation polymerization. The PDVB oligomers can be efficiently precipitated from the reaction system and captured continuously by the residual double bonds on the surface of PDVB microspheres to collapse the outer gel layer and grow the PDVB particles during the polymerization due to the presence of poor solvent, acetonitrile, as the reaction medium. Simultaneously, the good solvent, toluene, can swell the PDVB network well and expand the collapsed network during the polymerization, which can also be trapped inside by the PDVB network during the polymerization to afford mesopores during the formation of PDVB microspheres. Furthermore, the reaction system was gently agitated via distilling off a portion of the solvent during the polymerization. This is a simple and efficient agitation form, which can enable the reaction to be performed steadily without the shearing strength and the inhomogeneities caused by the mechanical stirring and result in monodisperse microspheres. If the experiment were carried out under boiling points without any distillation, the polydispersed polymer microspheres and polymer aggregates would be obtained. These microspheres with gradual increase of porosity structure would find attractive application as stationary phase for chromatography, compared to the bulk porous polymer particles. The study on the synthesis of porous polymer microspheres with different functional groups and the application of such porous PDVB particles as stationary phase for GPC is now in progress.

4. Conclusion

Highly crosslinked monodisperse PDVB microspheres in the micrometer-size range with nanopores, large specific surface areas and high porosity, were prepared by distillation–precipitation polymerization with the mixture of poor solvent, acetonitrile, and good solvent, toluene, as the reaction medium. The porous PDVB microspheres had gradual increase of porosity structure with pores mainly on the outer layer and highly crosslinked inner core having high density with clean and smooth surfaces. The co-solvent of acetonitrile and toluene played a key role for the formation of monodisperse porous PDVB microspheres. The porous PDVB microspheres with total porosity of 0.30 cm^3/g and high specific surface area of 762 m^2/g were prepared with toluene of 25 vol% in the reaction medium. These PDVB particles with clean, stabilizer-free surfaces and high porosity may have application as resin for selective separation or sorbents.

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