

Preparation of Poly(divinylbenzene) Microspheres with Controllable Pore Structure Using Poly(propylene)/Toluene as Coporogen

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ABSTRACT: Poly(divinylbenzene) (poly(DVB)) microspheres with controllable pore structure were synthesized by suspension polymerization in the presence of toluene and low-molecular weight poly(propylene) (PP) as coporogen. The weight fraction of PP in toluene varied from 0 to 20 wt %, and the feed ratio of coporogen and DVB was kept at 1/1 (vol/vol). Effects of PP weight fraction in coporogen on the specific surface area, the average pore size, the pore size distribution and the total pore volume of final microspheres were examined. As expected, poly(DVB) microspheres prepared with toluene as sole porogen had a high specific surface area (558 m²/g). Using mixtures of toluene and PP as coporogen, it was found

that the specific surface area shifted higher values when low levels of PP (2.0–6.0 wt %) in toluene were used as coporogen. However, further increase of PP weight fraction in toluene resulted in progressive decline of the specific surface area. Hg intrusion/extrusion curves and N₂ sorption isotherms implied caged pore structure with some small entrances. Furthermore, most of pore connectivity limitations may be eliminated when the weight fraction of PP in toluene exceeded 10.0 wt %. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2997–3004, 2009

Key words: macroporous polymers; poly(propylene) (PP)

INTRODUCTION

Porous styrene-divinylbenzene (St-DVB) microspheres have been the hot research area for many years because of a wide range of applications such as ion-exchange resins, adsorbates, column-packing materials for various chromatographies, polymer supported catalysts, and pharmaceutical products.^{1–3} Porous microspheres with different specific surface area, pore size, and porosity are required for various applications. Consequently, controllable preparation of polystyrene microspheres with different pore structure was a very important issue and received many attentions.^{4,5}

Up to now, a variety of organic solvents or their mixtures have been used as porogen or coporogen to prepare porous St-DVB microspheres. In addition, linear polymer was also widely applied to synthesize porous polymer microspheres by Vanderhoff's multistep seeded polymerization⁶ and Ugelstad's activated swelling and polymerization techniques.⁷ For example, Cheng et al.⁸ used polystyrene and

toluene, or hexane, or heptane as coporogen to prepare porous St-DVB microspheres. They found that average pore size increased and pore size distribution shifted toward larger pores as molecular weight of PS porogen was increased, and curve shape of pore size distribution strongly depended on molecular weight distribution indexes of PS porogen. Wang et al.⁹ found similar results when they used styrene-methyl methacrylate copolymer and dibutyl phthalate as coporogen to synthesize St-DVB microspheres. Seed swelling polymerization with polystyrene and solvent as coporogen could increase the average pore size, but the specific surface area of products was a bit limited. Poinescu and Vlad¹⁰ used poly(vinyl acetate) with different molecular weight and C₁₀–C₁₁ aliphatic alcohols as coporogen to prepare St-DVB microspheres. They found that low-molecular weight PVAc produced a broader pore size distribution than high-molecular weight PVAc. Recently, the elegant work by Macintyre and Sherrington¹¹ using poly(propylene glycol) oligomers or poly(dimethylsiloxane) oligomers and toluene as coporogens provided another methodology for preparatipn of poly(divinylbenzene) (poly(DVB)) resins, and thdy evoked the possibility of double phase separation. However, it is still a difficult issue

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to prepare St-DVB microspheres with controllable pore structure via a simple and effective technique.

Undoubtedly, linear polymer plays crucial role in controllable preparation of porous St-DVB microspheres. Although use of PP porogen has not been reported so far, but we felt poly(propylene) (PP) were a good porogen candidate to prepare porous poly(DVB) microspheres. First, PP can be effectively dispersed within monomer phase due to its nonpolar character, which can result in homogeneous pore structure in products. Second, similar solubility parameter to polystyrene and softer chains can enhance interaction between linear PP and poly(DVB) aggregates during polymerization, and this may be increase the specific surface area and improve pore connectivity more efficient than polar polymeric porogen. Finally, PP is a low-cost and commercially available material. Therefore, in the present work, low-molecular weight PP in combination with toluene were used as coporogen to prepare porous poly(DVB) microspheres. Effect of PP weight fraction in toluene on the average pore size, the specific surface area, the total pore volume and the pore size distribution was investigated.

EXPERIMENTAL SECTION

Materials

Divinylbenzene (DVB, mixtures of isomers, 80% grade, Sigma-Aldrich Chemie) was extracted with 5% (wt/wt) hydroxyl sodium solution to remove inhibitor, and then was washed with deionized water until neutralization. After dried by anhydrous magnesium sulfate, it was distilled under vacuum and stored in the refrigerator. PP ($M_n = 3157$, $M_w = 13,417$, PDI = 4.25) was used as received. 2,2'-Azobis-isobutyronitrile (AIBN) was purchased from Linfeng Chem Co. Ltd, China. It was recrystallized from methanol and used as the initiator. Poly(vinyl alcohol) (PVA, degree of polymerization: 1700–1800) and toluene were also from Sinopharm Chemical Reagent Co. Ltd and used without further purification.

Suspension polymerization

Porous poly(DVB) microspheres were prepared by conventional suspension polymerization in a three-neck glass reactor. One hundred twenty milliliters of 1.0 wt % PVA containing 3.96 g NaCl (3.3 wt %) were charged into the glass reactor, and then the solution were heated to 80°C under argon atmosphere. At the stirring speed of 300 rpm, mixture of 0.033 g AIBN, 3.0 mL DVB and 3.0 mL porogen (toluene or PP in toluene) was added into the reactor. The polymerization was carried out at 80°C for 6 h. After polymerization, the products were washed

twice with hot water, three times with methanol, and vacuum filtered to remove the stabilizer, PVA. Poly(DVB) microspheres were extracted with toluene for 24 h in a Soxhlet to remove PP and residual monomers, and then were washed twice with acetone, three times with methanol to ensure complete removal of impurities. Finally, the products were dried in a vacuum oven at 50°C for at least 12 h.

Characterization

Nitrogen sorption porosimetry was performed on a micromeritics ASIC-2 instrument. The experiments were carried out at the temperature of liquid nitrogen (77.3 K). The samples were first heated in a tube under vacuum at 70°C for 12 h to remove adsorbed materials from the surface. The relevant porosity parameters were obtained using the standard software. Also, an Autopore IV 9500 instrument was used to determine the pore area, average pore size, and porosity of poly(DVB) microspheres.

Surface morphologies of poly(DVB) microspheres were determined by a scanning electron microscope (SEM, HITACHI, S4800).

Solvent uptake measurements of poly(DVB) microspheres were carried out in excess toluene, methanol and tetrahydrofuran at room temperature for 2 h to allow a swollen equilibrium. After the excess solvent was removed by centrifugation, the swollen poly(DVB) microspheres were weighed. The uptake data were given as gram of solvent per gram of dry sample.

RESULTS AND DISCUSSIONS

Preparation of poly(DVB) microspheres

PP, which is explored as porogen, has a low number average molecular weight (3157), but a relatively high polydispersity index (4.25). This fact indicates that there are some PP molecules with considerably high molecular weight. Therefore, high viscosity occurred when PP was used at high weight fraction in toluene (>20.0 wt %). But in the range of 0–20.0 wt %, monomer (DVB) and coporogen (PP in toluene) could form a quite homogeneous and transparent solution, which suggests a very good dispersion of PP in monomer droplets. The yields of poly(DVB) microspheres are given in Table I, and some loss of products may be due to repetitive washing process. In addition, weights of poly(DVB) microspheres before and after extraction with toluene suggest that little PP are retained in poly(DVB) microspheres. Fourier transform infrared spectrum of porous poly(DVB) microspheres was presented in Figure 1. Peaks at 3100 cm^{-1} , 2900 cm^{-1} , and 1600 cm^{-1}

TABLE I
Porosity and Solvent Uptake Data of Poly(DVB) Microspheres

Code	PP in toluene (wt %) ^a	Yield of poly(DVB) (%)	Surface area ^b (m ² /g)	Pore area ^c (m ² /g)	Average pore size /nm		Porosity (%)		Solvent uptake (g/g) ^e		
					N ₂ BET	Hg intrusion	N ₂ BET ^d	Hg intrusion	MeOH	THF	TOL
C1	0	86	558	51.3	2.8	51.2	40	52	1.5	1.7	2.0
C2	2	90	640	85.6	3.5	31.7	56	55	1.2	1.4	1.4
C3	4	91	579	84.9	3.8	33.1	55	55	1.3	1.3	1.5
C4	6	91	620	101.5	4.1	26.8	64	55	1.5	1.7	1.7
C5	8	89	542	74.9	3.5	39.8	48	56	1.2	0.4	2.8
C6	10	86	500	45.3	2.6	82.1	32	62	1.7	1.8	2.3
C7	20	82	224	42.1	3.2	111.6	18	68	1.2	1.4	2.3

^a Balance is toluene, and DVB/porogen = 1/1, vol/vol.

^b Measured by measured by N₂ BET.

^c Measured by measured by Hg intrusion.

^d Assuming density poly(DVB) = 1 g cm⁻³.

^e MeOH = Methanol, THF = Tetrahydrofuran, TOL = Toluene.

correspond to stretching vibration of methylene, methine, and benzene, respectively.

Effect of coporogen on the specific surface area and the total pore area

In the present work, Brunauer et al. (BET)¹² method was used to calculate the specific surface area of poly(DVB) microspheres prepared with different level PP in toluene as coporogen. The specific surface area data, together with the total pore area derived from Hg intrusion are presented in Table I.

Although there are some scatters in the data, the specific surface area undergo a rise, and a subsequent fall as the level of PP used is increased. The maximum value is achieved with 2.0 wt % PP (C2), which suggests that adding low level of PP in tolu-

ene as coporogen will increase the specific surface area. The total pore area derived from Hg intrusion also undergo the same trend as the specific surface area, but the maximum value is achieved with 6.0 wt % PP (C4). However, it is well known that linear polymer porogen induces an earlier phase separation and results in formation of macropore structure (Fig. 2). Therefore, the increased specific surface area and the total pore area may be due to the improved pore connectivity, which was proposed by Macintyre and Sherrington.¹¹ There were some closed or inaccessible micropores when poly(DVB) microspheres were produced with toluene as sole porogen. However, low molecular weight of PP changed the pore structure of poly(DVB) microspheres via formation of some porous channels between micropores. Thus, the closed micropores became accessible or available, namely, PP improved the connectivity of previously existing small pores, presumably via macropore network formed at early stage (Fig. 2). This argument seems to be further confirmed by the following fact: although macropore number of C4 increased due to earlier phase separation induced by PP, the total pore area of sample C4 was almost two times as that of C1.

Effect of coporogen on the average pore size and pore size distribution

The average pore sizes derived from N₂ sorption and Hg intrusion measurement are shown in Table I, respectively. As expected, the data calculated from Hg intrusion are apparently larger than that derived from N₂ sorption, because it is questionable for Hg intrusion to probe the smallest pores, and the largest pores are neglected by N₂ sorption technique.⁵ Therefore, an attempt to compare data measured by

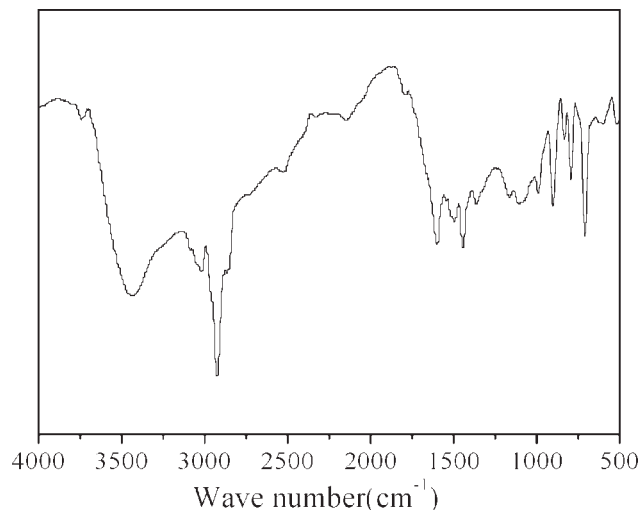


Figure 1 FTIR spectrum of porous poly(DVB) microspheres.

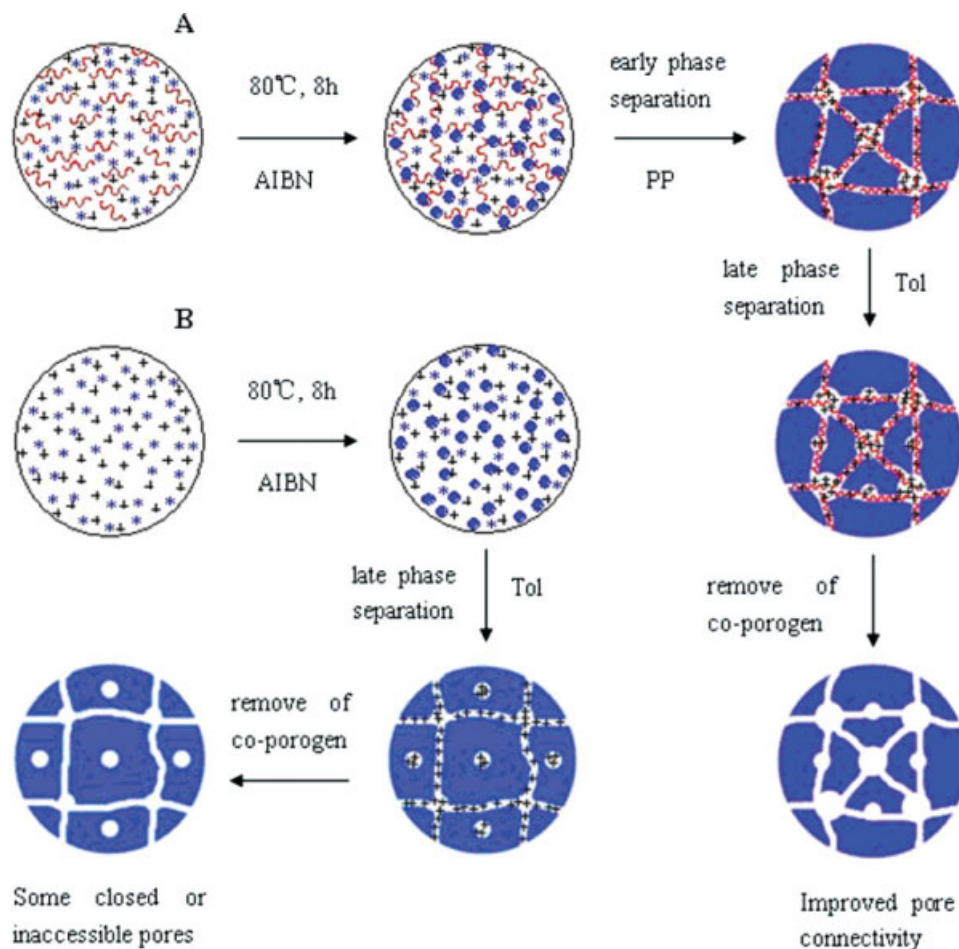


Figure 2 Schematic model of pore formation in poly(DVB) microspheres and improved pore connectivity via using PP and toluene as coporogen. A, using mixture of toluene and PP as coporogen; B, using toluene as sole porogen. *, divinylbenzene; +, toluene; ●, propylene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the two techniques would be not appropriate. Although there are some scatters in the data derived from Hg intrusion measurement, the average pore sizes increase on raising the weight fraction of PP in toluene. This is due to the fact that macropore number increased with increasing the PP weight fraction.

The pore size distribution curves can present entire information about pore structure. Some representative curves derived from N_2 sorption and Hg intrusion are given in Figure 3. Figure 3(A) show the pore size distribution curves of sample C1 prepared with toluene only as porogen. The curve derived from N_2 adsorption exhibits almost all of pores locating in the micro and mesopore region, whereas the Hg intrusion-derived curve suggests large numbers of mesopores, but a little micropores and macropores. In the case of sample C3 produced with 4.0 wt % PP in toluene as coporogen, the main changes in contrast to sample C1 [Fig. 3(B)] are some macropores displayed in the N_2 adsorption-derived curve and more mesopores exhibited in the Hg intrusion

derived curve. The increase of mesopore explained higher specific surface area of sample C3 in comparison with C1. The similar changes are observed in sample C5 [Fig. 3(C)] prepared with 8.0 wt % PP as coporogen, but the peak of C5 in mesopore region shifts to larger value. Here, linear PP has the similar solubility parameter with toluene and poly(DVB), as a consequence, it seems plausible that with low-level PP in toluene, coporogen act together to induce an earlier phase separation in contrast to toluene. This fact results in large numbers of mesopores in sample C3 and C5. As for sample C7, the two curves [Fig. 3(D)] suggest little pores in the mesopore region. The curve from N_2 adsorption shows a significant fraction of micropores, whereas the plot from Hg intrusion reveals large numbers of macropores. Moreover, the latter suggests large numbers of pores with diameter $>1 \mu\text{m}$, which may be correspond to the interstices between poly(DVB) microspheres. This can be understood by double phase separation evoked by Macintyre and Sherrington,¹¹ when they

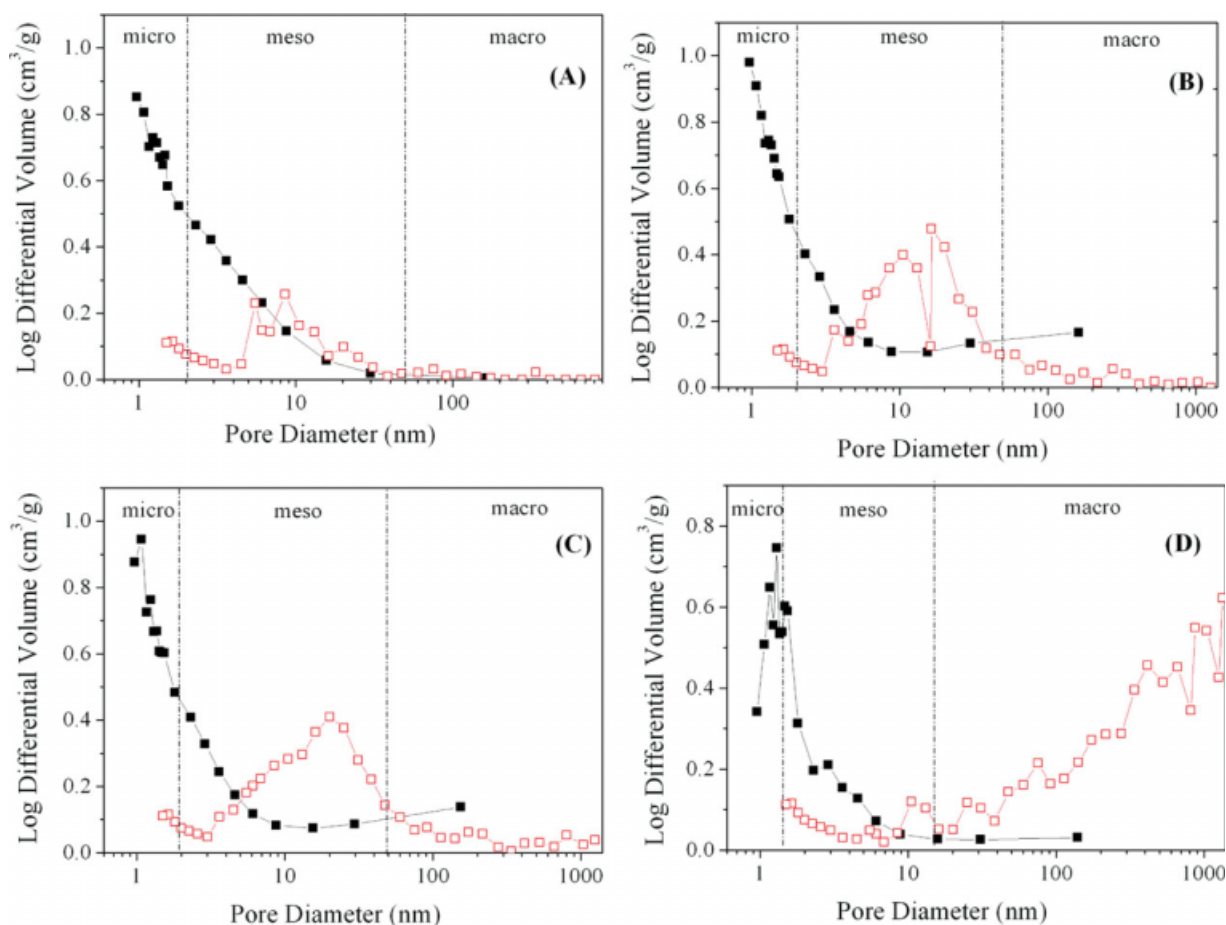


Figure 3 Pore size distribution curves derived from N₂ adsorption (■) and Hg intrusion (□) for poly(DVB) microspheres. (A) toluene as sole porogen, (B) 4 wt % PP in toluene, (C) 8 wt % PP in toluene, (D) 20 wt % PP in toluene. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

used a solvent porogen (toluene) in combination with an oligomer porogen (polyether or polysiloxane) to prepare poly(DVB) microspheres. Here, with high level PP in toluene, nonpolar PP and toluene may act independently to result a double phase separation. PP induces an early phase separation and obtains macroporous structure, whereas toluene leads to phase separation much later and yield microporous structure [Fig. 2(A)]. As a result, sample C7 has a clearly bimodal distribution of pore size as shown in Figure 3(D). Moreover, C7 also retains a high specific surface area, 224 m²/g.

Effect of coporogen on the porosity

Porosity can be determined by several methods, such as calculation from true and apparent densities, Hg intrusion and N₂ sorption techniques. Here, N₂ sorption data are used to calculate BJH pore volume and then a percent porosity, and the data from Hg intrusion are used to obtain a percent porosity. Swollen measurement can also character porosity by

measuring mass of solvent absorbed by poly(DVB) microspheres. These data are summarized and presented in Table I.

The data derived from N₂ sorption first raise, and then fall progressively. However, the porosity data from Hg intrusion reveal a continuous increase as the level of PP used is increased. The last three groups of porosity data (C5, C6, and C7) derived from the two techniques exhibit great discrepancy because N₂ sorption method can not effectively probe the pore volume of the largest pores. Remarkably, porosity data of all samples derived from Hg intrusion are larger than 50%, a relatively high value. This fact indicates that nonpolar PP not only build high porosity but also provide poly(DVB) microspheres with great resistance to collapse during washing and drying. Interestingly, the porosity data of C2 and C3 derived from the N₂ sorption and Hg intrusion show a very good agreement. The most possible explanation for this agreement is that there are a significant mesopore population in sample C2 and C3, which can be effectively determined by the

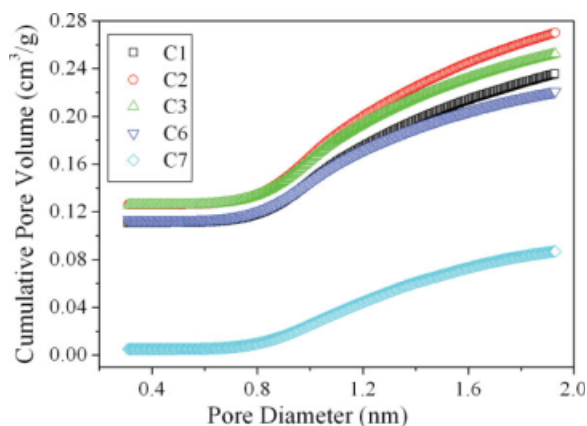


Figure 4 Cumulative pore volume in the range of micropores (<2 nm) for C1, C2, C3, C6, and C7 calculated by the Horvath–Kawazoe method (carbon-slit pore model). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

two techniques. This result is in accord with that derived from pore size distribution curves.

In addition, to clarify the change of pore structure with varying the composition of coporogen, the cumulative pore volume in the range of micropore (<2 nm) for sample C1, C2, C3, C6, and C7 are present in Figure 4. The cumulative pore volume of samples C2 and C3 are larger than that of C1, and the values (C6 and C7) shifted progressively below that of C1 as the PP weight fraction in toluene is increased. This suggests that more small channels with diameter of <2 nm are formed between the previous existing pores when low-level PP in toluene is used as coporogen. Moreover, this fact further probes the aforementioned deduction that low-level PP can improve the pore connectivity.

Two typical nonsolvating solvents for styrene-based polymer, methanol and tetrahydrofuran, and a solvating solvent, toluene, are used to determine the solvent uptake data of poly(DVB) microspheres. Nonsolvating solvent is expected to fill pores inside the poly(DVB) microspheres, while solvating solvent is able to both filling pores and swelling poly(DVB) matrix. As seen in Table I, almost all of uptake data are >1.0 g/g, a relatively high value, which further prove PP modified poly(DVB) microspheres with great pore volume. Moreover, for each poly(DVB), higher toluene uptake data in contrast to that of methanol and tetrahydrofuran reveal that the process of filling pore and swelling the polymer matrix do occur during swollen by toluene.

Effect of coporogen on pore structure

Hg intrusion/extrusion curves and N₂ adsorption/desorption isotherms of C1, C2, C4, C6, and C7 are

presented in Figure 5. The curves or isotherms of sample C1 are given in each picture.

The main discrepancy between the Hg curves and the N₂ isotherms is the mercury, which is injected into the pores of microspheres, cannot be entirely ejected when the pressure is decreased, whereas the absorbed N₂ in microspheres almost completely desorbs when the relative pressure P/P_0 is progressively declined. These facts indicate caged pore structure with some small entrances, mercury cannot squeeze through them when the pressure is not high enough. However, once mercury is intruded into the cages as the pressure is increased, the mercury resided in cages is difficult to be ejected again when the pressure is declined.

As the PP level is increased, the Hg intrusion/extrusion curves [Fig. 5(E,G)] shift well above that of C1 at the relative pressure $P/P_0 > 10$ pisa, indicative of increased pore volume. This is in agreement with the porosity data in Table I. Moreover, the cumulative intrusion of particle C1, C2, and C4 retain a relatively steady value in the pressure range of 10–2000 pisa, and then the values further raise on increasing the pressure. This increase of cumulative intrusion suggests higher pressure is required to force mercury into pores, indicative of micropores or mesopores. However, the same trend can not be observed in the intrusion arms of C6 and C7, in which the cumulative intrusion values increase progressively with increasing the pressure. The plausible explanation is that most of pore connectivity limitations are eliminated when PP level used is >10 wt %.

As seen in Figure 5, N₂ desorption branch of the isotherms for sample C1 shows an abrupt fall at $P/P_0 = 0.5$, indicative of delayed capillary evaporation and caged pores with a window size smaller than 5 nm. The isotherms of C2 [Fig. 5(B)] locate above that of C1, suggesting higher specific surface area. However, there is an enlarged hysteresis loop at $P/P_0 > 0.5$, which reveals that the larger pores derived from coporogen are also subject to connectivity limitations at low-level PP. The C4 isotherms are partly overlapped with that of C1 at $P/P_0 > 0.4$ [Fig. 5(D)], the contractive hysteresis loop indicates the improved connectivity limitations as the PP level used is increased. The C6 isotherms [Fig. 5(F)] have entirely moved down to that of C1, and this trend continues with the C7 isotherms. Interestingly, the relatively small hysteresis loop of C6 and C7 suggests the formed pore structure with a good connectivity, this is in agreement with the results derived from the Hg intrusion/extrusion curves.

Note that good pore interconnection in poly(DVB) microspheres is achieved when PP weight fraction in toluene is larger than 10 wt %, suggesting that linear PP is more efficient porogen to prepare

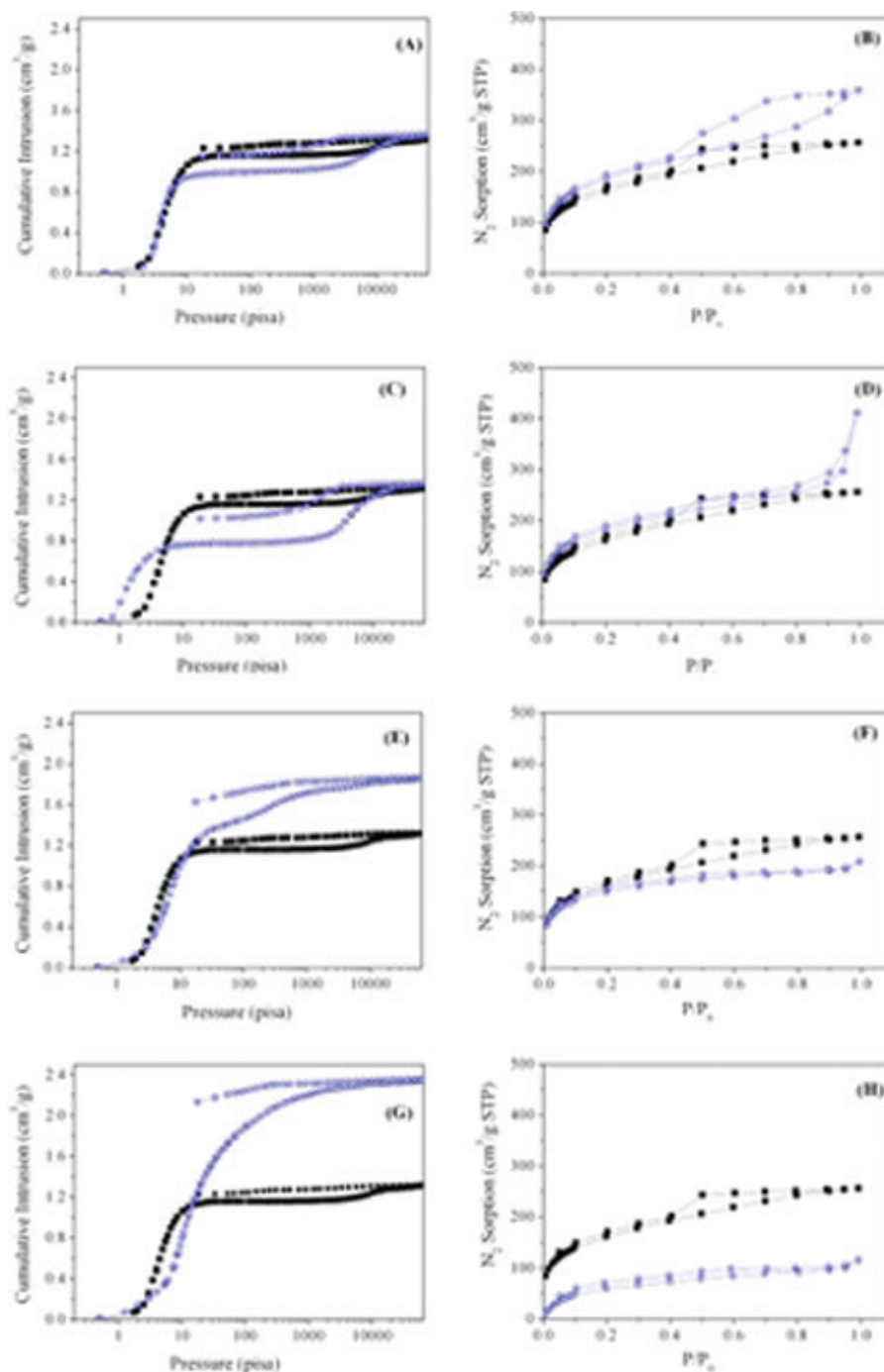


Figure 5 Hg intrusion/extrusion curves (A, C, E, and G) and N₂ adsorption/desorption isotherms (B, D, F, and H) of poly(DVB) microspheres. ■ toluene porogen 100%, □ PP coprogen (A) and (B) 2 wt %; (C) and (D) 6 wt %; (E) and (F) 10 wt %; (G) and (H) 20 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

poly(DVB) with good pore connectivity due to its compatibility with toluene and polymer.

Scanning electron microscope of poly(DVB) microspheres

The surface morphologies of poly(DVB) microspheres were observed by scanning electron micros-

copy (SEM), and some representative micrographs (C1, C4, and C7) were shown in Figure 6. Graphs of particle C1 [Fig. 6(A)] exhibit a rather uniform surface texture, but lots of rumples and a little small pores can be observed with the high resolution micrograph. However, graphs of particle C4 [Fig. 6(B)] shows a definitive macropore structure. The pores in the size range of 10 to >100 nanometers can

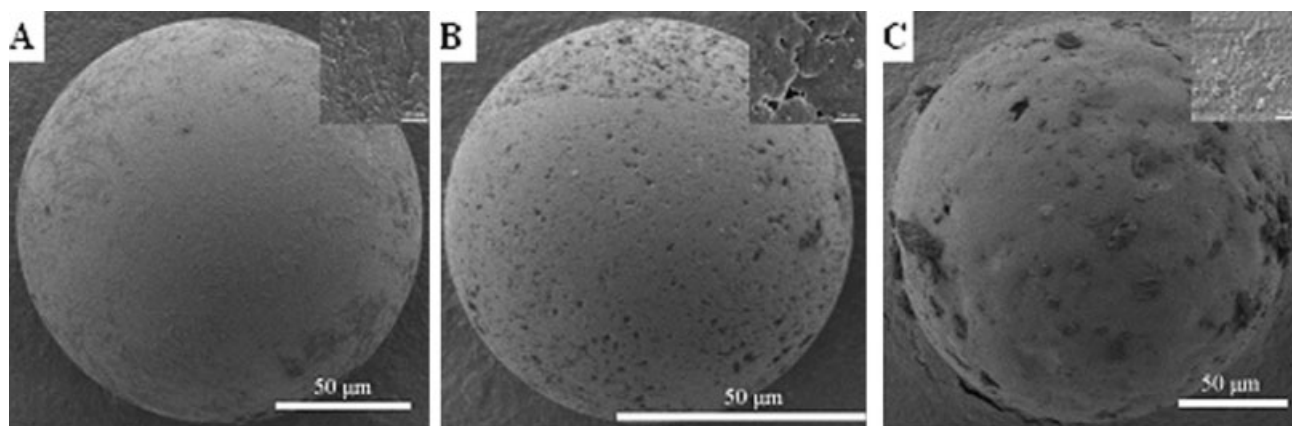


Figure 6 Scanning electron micrographs of poly(DVB) microspheres prepared using (A) toluene only as porogen, (B) 6 wt % PP in toluene as coporogen, and (C) 20 wt % PP in toluene as coporogen.

be clearly observed in Figure 6(B). Undoubtedly, increased macropores of C4 in contrast with C1 are derived from early phase separation of poly(DVB), which is induced by PP. Finally, particle C7 [Fig. 6(C)] reveal a relatively rough, and contaminated surface with lots of fragments associated with it. Overall, SEM images agree well with the porosity data in Table I.

CONCLUSIONS

Poly(DVB) microspheres with controllable pore structure were prepared via suspension polymerization using low-molecular weight of PP and toluene as coporogen. Effects of PP weight fraction in toluene on the specific surface area, the average pore size, the pore size distribution, and the pore volume were investigated. The results showed that low PP level yielded higher specific surface area in contrast to toluene as sole porogen, which was attributed to improved pore connectivity. With low PP level in toluene as coporogen, phase separation occurred earlier than sole toluene because PP and toluene acted together, and this resulted in large population of mesopores. Although with high PP level in toluene, a bimodal pore size distribution originated from double phase separation induced by high viscosity. Furthermore, PP is a more efficient porogen to prepare poly(DVB) microspheres with good pore inter-

connection due to its similar solubility parameters with polystyrene.

Overall, using PP and toluene as coporogen provides a routine for preparation of poly(DVB) microspheres with controllable pore structure. It would be expected that PP with lower molecular weight and lower polydispersity index is explored to prepare poly(DVB) microspheres, because the weight fraction of PP can be further increased without causing viscosity problems during suspension polymerization.

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