

Preparation and Characterization of Crosslinked Polymer Beads with Tunable Pore Morphology

Qingquan Liu, Yanlu Li, Shaohua Shen, Qiuguo Xiao, Lijuan Chen, Bo Liao, Baoli Ou, Yue Ding

Institute of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China

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ABSTRACT: Crosslinked polymer beads with tunable pore morphology were prepared by suspension polymerization of styrene (St) and divinylbenzene (DVB) with polypropylene in combination with toluene as co-porogens. The effect of DVB content on the pore morphology was investigated by changing DVB amount in monomer mixture. The results indicated that the specific surface area, the total pore area, and the total pore volume increased with increasing DVB content of polymer beads. Moreover, high-DVB concentration was favorable to produce more micropores and mesopores. At a given DVB concentration, the volume ratio of co-porogen/DVB has

significant impact on the pore morphology in crosslinked polymer beads. As the co-porogen amount was increased, the specific surface area, the total pore area, and the total pore volume were dramatically increased, furthermore, the pore size distribution derived from Hg intrusion shifted toward macropore. Overall, the present article provided a novel route to prepare crosslinked polymer beads with tunable pore morphology. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 654–659, 2011

Key words: crosslinking; macroporous polymers; polystyrene

INTRODUCTION

Macroporous polymer beads were efficient materials for many industrial separation or purification processes, and had extensive applications such as ion-exchange resins, adsorbents, column-packing materials for high performance liquid chromatography, catalyst support, and templates for nanoparticle growth.^{1–3} Therefore, the formation conditions of macroporous structure in polymer beads have been the subject of both applied and fundamental research for many years. Generally, crosslinked polymer beads with different pore morphology are required for different separation or purification processes. As a consequence, the preparation of crosslinked polymer beads with tunable pore morphology was an important issue and received many attentions.^{4,5}

Seed-swelling polymerization was extensively used for the preparation of macroporous polymer beads with linear polystyrene and organic solvent as co-porogens. For example, linear polystyrene in combination with toluene (TOL), or hexane, or heptane

was used as co-porogens to prepare macroporous St-DVB copolymer beads, and pore size distribution shifted toward larger pores as molecular weight of linear polystyrene porogen was increased.^{6,7} Similar results were obtained by Frechet and coworkers, who used linear polystyrene or styrene (St)-methyl methacrylate copolymers and dibutyl phthalate as co-porogen to synthesize macroporous St-DVB beads.^{8–10} Seed-swelling polymerization could obtain almost monodisperse macroporous beads and improve the average pore size of the final products, but the surface area was a bit limited ($<100 \text{ m}^2/\text{g}$).^{11–13} This problem can be solved by traditional suspension polymerization. For example, the elegant work by Macintyre and Sherrington¹⁴ using poly(propylene glycol) or poly(dimethylsiloxane) oligomers and TOL as co-porogens provided a simple route for preparing PDVB resins via suspension polymerization, the surface area of macroporous beads could achieve $800 \text{ m}^2/\text{g}$. Our previous works also indicated that linear polypropylene (PP) in combination with TOL could be used as co-porogens to prepare polydivinylbenzene (PDVB) beads with high-specific surface area and total pore volume.¹⁵ In that publication, we just used divinylbenzene (DVB) as the sole monomer for the preparation of macroporous beads. However, it is well known that the crosslinking density of macroporous beads and co-porogen amount has significant effects on the pore morphology of polymer beads. Therefore, in the present article, we attempt to change DVB

Correspondence to: Q. Liu (qqliu@hnust.edu.cn).

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concentration in monomer mixture or co-porogen amount when solutions of 6.0 wt % PP in TOL were used as co-porogens to prepare crosslinked polymer beads with tunable pore morphology.

EXPERIMENTAL

Materials

DVB (mixtures of isomers, 80% grade, Sigma-Aldrich Chemie) and styrene (St, Sinopharm Chemical Reagent, Shanghai, China) were extracted with 5 % (w/w) hydroxyl sodium solution to remove inhibitor, respectively, and then were washed with deionized water until neutralization. After dried by anhydrous magnesium sulfate, the monomers were distilled under vacuum and stored in the refrigerator, respectively. PP was prepared in our lab. 2,2'-Azo-bis-isobutyronitrile (AIBN) was purchased from Linfeng Chem, China. It was recrystallized from methanol and used as the initiator. Poly(vinyl alcohol) (PVA, 88% hydrolyzed, average M.W. 88,000), and TOL were purchased from the Aldrich Chemical and used without further purification.

Suspension polymerization

Crosslinked polymer beads were prepared by free radical suspension polymerization in three-necked glass reactor. Aqueous solution (60 cm³) containing 0.3 g PVA (0.5 wt %) and 1.98 g NaCl (3.3 wt %) was charged into the glass reactor, and then was heated to 50°C under argon atmosphere. At the stirring speed of 300 rpm, mixture solution containing AIBN (0.033 g), monomers (3.0 cm³) and co-porogens (solutions of 6.0 wt % PP in TOL) was added into the reactor. The reaction 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. The beads were extracted with TOL for 24 h in a Soxhlet to remove PP porogen 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 total pore area, average pore size, and porosity of crosslinked polymer beads. The beads were spread onto electric glue, which was spread on a metallic base. Dried samples were coated with a thin layer of gold in vacuum before scanning electron microscope (SEM) analysis. Surface morphologies of PDVB beads were determined by a SEM (JSM-6380LV).

RESULTS AND DISCUSSION

Preparation of crosslinked polymer beads

In this article, crosslinked polymer beads were prepared by tradition suspension polymerization of DVB or/and St with linear PP in combination with TOL as co-porogens. PP used in this article has a low-number average molecular weight (3157), but a relatively high-polydispersity index (4.25). Our previous work indicated that solutions of 6.0 wt % PP in TOL can generate the highest pore area, indicative of excellent pore connectivity.¹⁵ Therefore, in this article, solutions of 6.0 wt % PP in TOL were still used as co-porogens to prepare crosslinked polymer beads, at the same time, DVB/St volume ratios (W01–W04) or co-porogen amounts (W05–W06) were changed to investigate the effects of DVB contents or co-porogen amounts on the pore morphology of polymer beads. The optical microscopy images of crosslinked polymer beads were given in Figure 1. Obviously, all of products kept in good spherical shape, and the diameters of the beads were about 50–500 μm.

Effect of DVB content on the pore morphology

Characterization data of crosslinked polymer beads were measured by N₂ sorption and Hg intrusion techniques, respectively, and the data were summarized and presented in Table I. It should be noted that N₂ sorption technique neglected the largest pores, and Hg intrusion was difficult to probe the smallest pores (< 3 nm). Therefore, it is unsuitable to compare the data derived from two different techniques.

As can be seen in Table I, the specific surface area of crosslinked polymer beads strongly depended on DVB content in monomer mixture. From bead W01 to W04, the values dramatically declined with decreasing DVB/St volume ratio. This result was agreement with those obtained by Moustafa et al.¹⁶ and Galia et al.¹⁰ Because the specific surface area was mainly originated from the surface of the nuclei (Figure 2), which were the smallest composition units of crosslinked polymer beads. Thus, the factors decreasing the size of the nuclei or increasing their stiffness could increase the specific surface area. At high-DVB concentration, the nuclei were highly intramolecularly crosslinked. Therefore, high-DVB concentration not only effectively declined the size

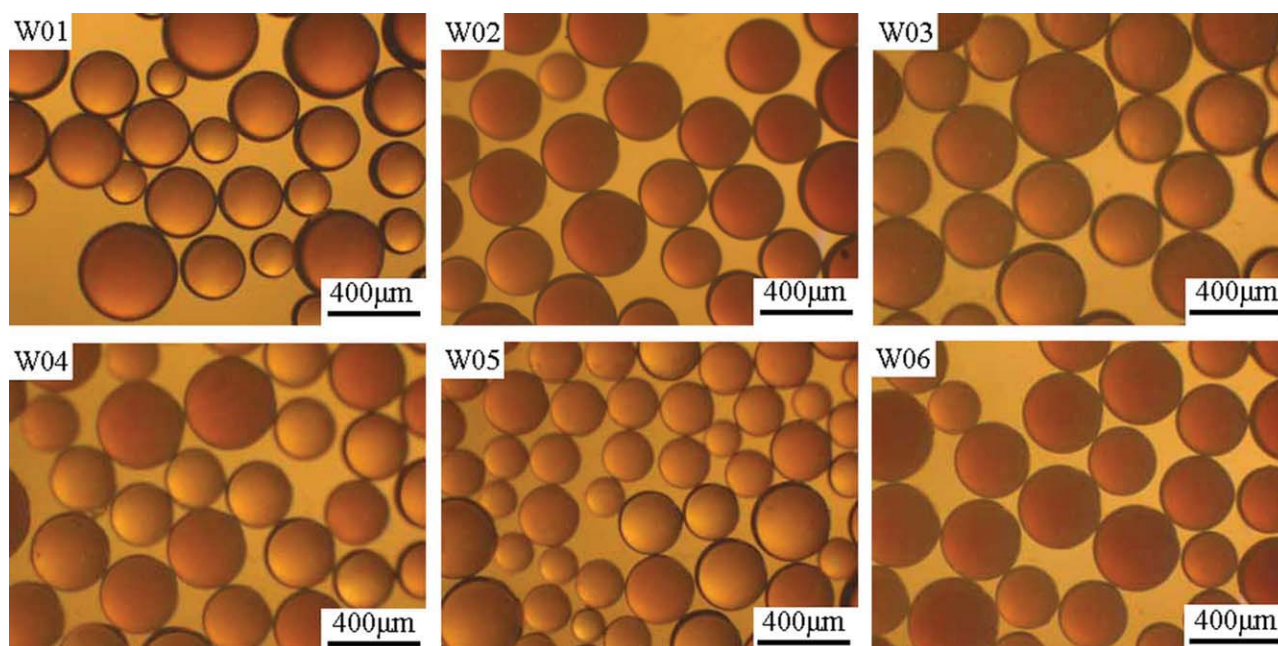


Figure 1 Optical microscope images of crosslinked polymer beads (W01–W06) prepared by suspension polymerization with 6.0 wt % PP in toluene as co-porogens. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the nuclei but also created rigid nuclei, which increased the number of micropores and decreased the pore diameter.⁵ Although the average pore diameters calculated from N₂ sorption technique had some scatters, the values (Table I) originated from the latter technique further demonstrated this fact. From another point of view, as DVB/St volume ratios increased, the contribution of micropores to the specific surface area increased, and on the contrary, the contribution of mesopores and macropores to the specific surface area declined.

Our previous works indicated that co-porogen of 6.0 wt % PP in TOL could generate the highest total pore area. We proposed that double phase separa-

tion induced by PP and TOL could be responsible for the excellent pore connectivity.¹⁵ Obviously, the total pore areas of crosslinked polymer beads increased with DVB content, which revealed that high-crosslinking density was also helpful to form excellent pore connectivity in crosslinked polymer beads. We thought that smaller nuclei induced by high-DVB content could also explain the increased pore area. In industrial application of adsorption or purification process, crosslinked polymer beads with excellent pore connectivity were required to improve adsorption or purification efficiency. Therefore, this article provided a simple methodology to prepare polymer beads with tunable pore connectivity.

TABLE I
Characterization Data of Crosslinked Polymer Beads

Run	DVB (mL)	St (mL)	CP ^a (mL)	SSA ^b (m ² /g)	TPA ^c (m ² /g)	APD ^d (nm)		TPV ^e (cm ³ /g)		Porosity (%)	
						N ₂ Sorp	Hg Intr	N ₂ Sorp	Hg Intr	3–50 nm	50–4000 nm
W01	3.0	0	3.0	608	130	3.9	16.5	0.64	0.58	11.6	12.1
W02	2.25	0.75	3.0	479	119	2.9	17.5	0.35	0.52	11.0	8.9
W03	1.5	1.5	3.0	314	108	2.8	24.6	0.22	0.68	10.7	13.5
W04	0.75	2.25	3.0	91	23	6.8	37.3	0.16	0.29	5.2	7.9
W05	3.0	0	2.0	106	37	2.8	11.8	0.18	0.31	7.1	5.0
W01	3.0	0	3.0	608	130	3.9	16.5	0.64	0.58	11.6	12.1
W06	3.0	0	4.0	652	159	4.7	22.7	0.77	0.90	13.1	13.6

^a CP: co-porogen (solution of 6.0 wt % PP in TOL).

^b SSA: specific surface area.

^c TPA: total pore volume.

^d APD: average pore diameter.

^e TPV: total pore volume.

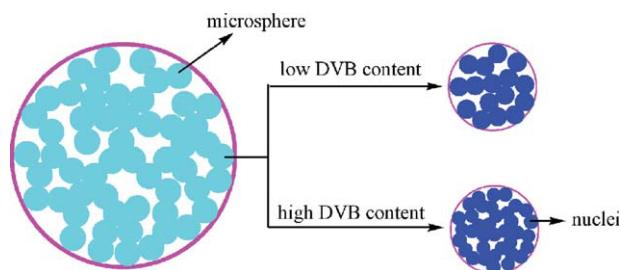


Figure 2 Schematic model of various agglomerates in crosslinked polymer beads. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The total pore volumes of crosslinked polymer beads (W01–W04) derived from N₂ sorption were proportional to DVB content. The work by Sheu et al.¹⁷ indicated that high-DVB concentration increased elasticity-contraction stresses inside the polymer beads. This kind of stress resulted in com-

plete phase separation and particles with high-crosslinking density. Therefore, the total pore volume could be improved by increasing the crosslinking density of polymer beads. The similar results were also obtained by Okay⁵ and Galia et al.¹⁰ However, the total pore volumes originated from Hg intrusion technique revealed little scatter such as bead W03 exhibiting the highest value (0.68 cm³/g). This may be due to the fact that mesopores and macropores constituted the major porosity of bead W03, which could be effectively measured by Hg intrusion technique. This viewpoint seems to be further verified by the porosity in the macropore region, in which bead W03 displayed the largest porosity (13.5%) in this region. In addition, porosity in mesopore region exhibited the same changing trend as that of the total pore volume.

Pore size distribution curves of bead W01 and W04 derived from N₂ sorption and Hg intrusion

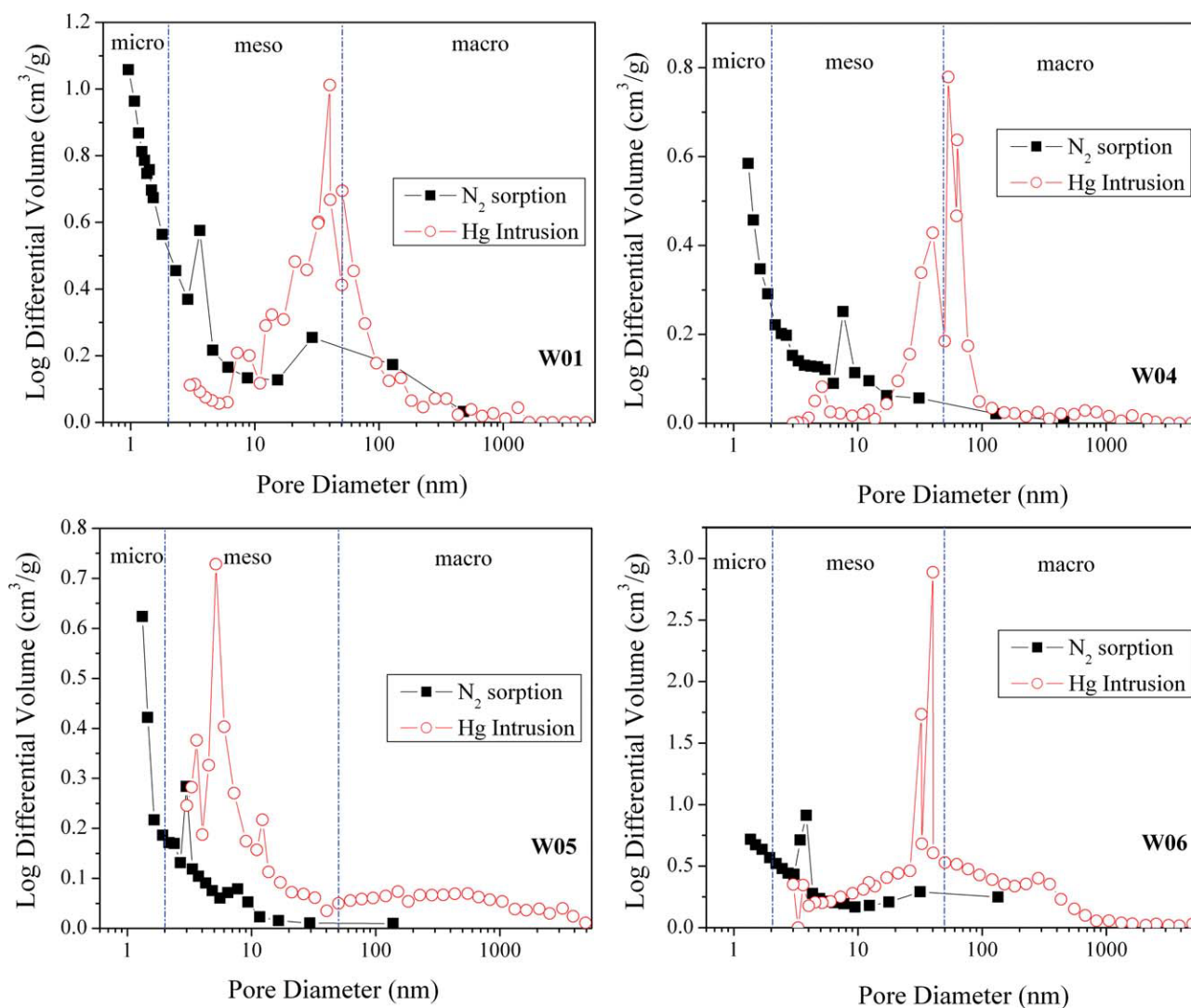


Figure 3 Pore size distribution curves of crosslinked polymer beads prepared by suspension polymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

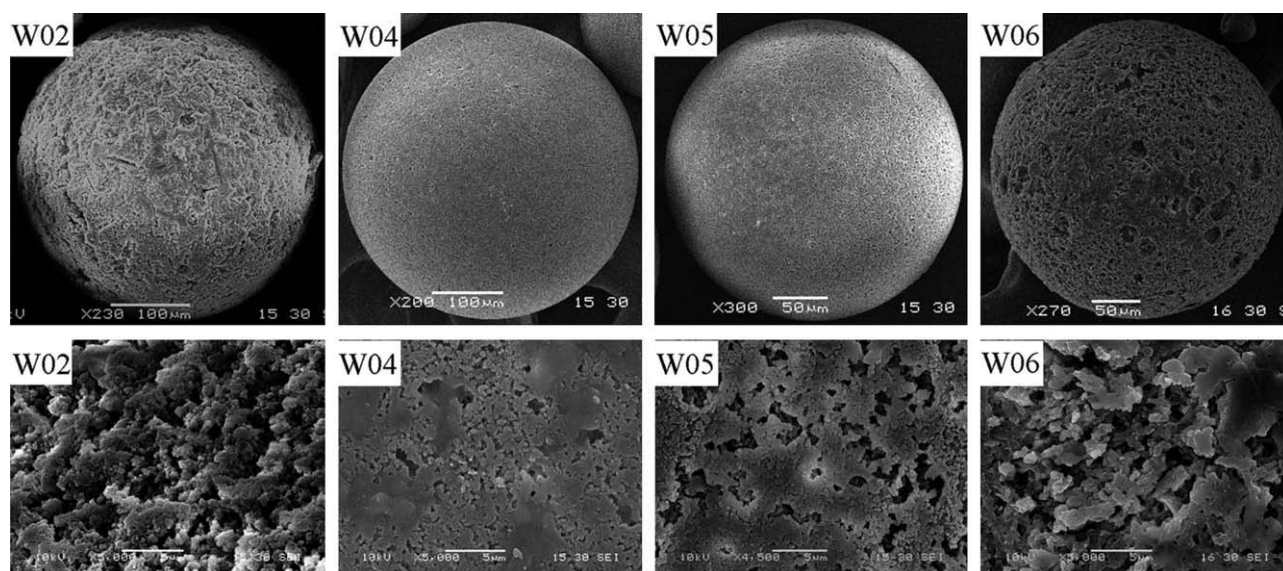


Figure 4 SEM images of crosslinked polymer beads prepared by suspension polymerization.

techniques were presented in Figure 3. At high-DVB content (W01), the plot calculated from the former technique displayed a large population of micropores and mesopores extending to the lower fraction of macropores. The curve derived from the latter technique suggested a mass of mesopores and lower part of macropore region but entirely failed to probe the micropore region. In the case of bead W04 prepared with low-DVB concentration, the pore number declined due to decreased crosslinking density, which accounted for the lower specific surface area and total pore volume. The major change in the plots originated from the latter technique was the peak shifted toward macropore region.

In addition, DVB content also had a dramatic impact on the surface morphology of crosslinked polymer beads. SEM images of some beads (W02 and W04) were presented in Figure 4. At high-DVB concentration (W02), there were massive small tracks on the bead surface. Complete phase separation induced by high-crosslinking density may be responsible for the loose structure of bead W02. Although bead W04 prepared with low-DVB content displayed a relatively smoother surface in the low-magnified SEM image, the high-magnified image revealed a large clear macropore population even at the bead surface.

Overall, the pore size distribution plots and the SEM images of bead W01 and W04 were well consistent with the characterization data in Table I.

Effect of co-porogen amount on the pore morphology

Effects of co-porogen amounts on the pore morphology were investigated by changing the volume ratios

of co-porogens to DVB. As can be seen in Table I, as amounts of the co-porogens (solution of 6.0 wt % PP in TOL) increased (W05–W06), the specific surface areas, the total pore areas, the average pore diameters, and the total pore volumes of crosslinked polymer beads progressively declined. The similar results have been reported in our previous work, in which 1-chlorodecane was used as porogen to produce macroporous PDVB beads.¹⁸ Okay et al.^{19–21} also obtained the similar results via preparing St-DVB copolymer beads with TOL/cyclohexanol as a co-porogen. It has been demonstrated by the swelling measurement and inverse gas chromatography that St-DVB copolymer beads prepared with a large amount of porogen have a looser structure than those obtained with less amount of porogen.²²

According to the syneresis model proposed by Dusek, if a linear polymer was used as porogen, phase separation may occur in the reaction system before the gel point.²³ Therefore, PP used maybe induce a phase separation before the gel point, which led to generate a dispersion of discontinuous polymer phase in the continuous monomer (DVB) and porogen (TOL) phase. Subsequent polymerization resulted in the separated particles agglomerated into larger clusters, which are called microspheres (Figure 2). Continuing the reactions increased the number of microspheres in the reaction system, and, finally, the polymer phase also became continuous. Thus, the reaction system involved two continuous phases. After removing the co-porogens from the gel, macroporous polymer beads were generated. It was seen that, in the presence of linear polymers as porogens, the incompatibility between the polymer segments and porogens was responsible for the porosity formation. Furthermore, porosity formation

was due to the dilution of the co-porogens. Higher concentration the co-porogens induced crosslinked polymer beads with more loose structure. Therefore, amount of co-porogens could also be another way to tune the pore morphology of crosslinked polymer beads.

The pore size distribution curves for bead W05 prepared with low co-porogen amount were shown in Figure 3. Obviously, the curve calculated from N₂ sorption displayed a large population of pores in the micropore region. Hg intrusion derived data suggested a low fraction of macropore. Interestingly, two plots derived from different techniques exhibited excellent agreement in the mesopore region. In the case of bead W06 prepared with high co-porogen amount, the curve calculated from N₂ sorption displayed a significant micropore and mesopore population as well as a certain amount of macropores. This change may be account for the increase in the specific surface area of bead W06 in relative to W05. Another major variation for bead W06 was that the peak of the distribution curve originated from Hg intrusion shifted from ~ 4 to ~ 40 nm; however, the agreement between the two plots was less good here.

Co-porogen amount also had an obvious impact on the surface morphology of crosslinked polymer beads (Figure 4). Bead W05 displayed a relatively smooth surface in comparison with W06. The latter exhibited a looser surface morphology, and numerous pores could be observed on the surface of bead W06. In a word, these SEM images were in good agreement with the porosity data and the pore size distribution curves derived from two techniques.

CONCLUSIONS

Crosslinked polymer beads with tunable pore morphology were successfully prepared via traditional suspension polymerization with solution of 6.0 wt % PP in TOL as co-porogens. Research results showed that DVB content and co-porogen amount had a dramatic effect on the pore morphology of crosslinked polymer beads. Crosslinked polymer beads with high porosity could be obtained with high-DVB concentration or with high co-porogen amount. Furthermore, high-DVB content was favorable to

generate more micropores and mesopores for polymer beads. Crosslinked polymer beads with looser structure could be produced by high co-porogen amount at a given monomer concentration. Overall, the pore morphology could be tuned by DVB content or co-porogen amount when solutions of 6.0 wt % in TOL were used as co-porogens. Therefore, it is clear that this article provided a feasible technique to prepare crosslinked polymer beads with tunable pore morphology.

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