

Hierarchical Porous Polymer Beads Prepared by Polymerization-induced Phase Separation and Emulsion-template in a Microfluidic Device

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Abstract Porous polymer beads (PPBs) containing hierarchical bimodal pore structure with gigapores and meso-macropores were prepared by polymerization-induced phase separation (PIPS) and emulsion-template technique in a glass capillary microfluidic device (GCMD). Fabrication procedure involved the preparation of water-in-oil emulsion by emulsifying aqueous solution into the monomer solution that contains porogen. The emulsion was added into the GCMD to fabricate the (water-in-oil)-in-water double emulsion droplets. The flow rate of the carrier continuous phase strongly influenced the formation mechanism and size of droplets. Formation mechanism transformed from dripping to jetting and size of droplets decreased from 550 μm to 250 μm with the increase in flow rate of the carrier continuous phase. The prepared droplets were initiated for polymerization by on-line UV-irradiation to form PPBs. The meso-macropores in these beads were generated by PIPS because of the presence of porogen and gigapores obtained from the emulsion-template. The pore morphology and pore size distribution of the PPBs were investigated extensively by scanning electron microscopy and mercury intrusion porosimetry (MIP). New pore morphology was formed at the edge of the beads different from traditional theory because of different osmolarities between the water phase of the emulsion and the carrier continuous phase. The morphology and proportion of bimodal pore structure can be tuned by changing the kind and amount of porogen.

Keywords: Porous polymer beads; Hierarchical; Polymerization-induced phase separation; Emulsion-template; Microfluidic device.

INTRODUCTION

Porous polymers beads (PPBs) are defined as spherical polymer particles consisting of numerous tortuous interconnected pores; PPBs are widely used for ion-exchange resins^[1], catalysts^[2, 3], adsorbents^[4], chromatographic media^[5, 6] and blood plasma detoxification^[7]. In these applications, the molecules that transport into and out of PPBs pores are controlled by diffusion effect. This mechanism makes pore size becomes one of the most important parameters for PPBs. Generally, PPBs can be classified as microporous (less than 2 nm), mesoporous (2–50 nm), macroporous (50–200 nm), and gigaporous beads (more than 200 nm) in terms of pore size^[8]. Microporous, mesoporous, and macroporous beads with relatively small pore size and large surface area are highly suitable for small molecule separations because small entities, such as gases or ions, move relatively easily in small pores. By contrast, gigaporous beads with micrometer-scale pore size and low surface area are beneficial for large molecule separation, such as protein, polysaccharides, or synthetic polymers, because their diffusion coefficients are considerably smaller than those of small molecules. The gigapores can enhance mass transport for large molecules that pass into and out of the porous structure. For these reasons, microporous,

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mesoporous, and macroporous beads are commonly used as supported catalysts and gas chromatography packing. On the contrary, gigaporous beads are applied on nucleic acids and polymer separation^[6, 9, 10].

One of the most traditional and effective method of producing PPBs is polymerization-induced phase separation (PIPS)^[11–13]. It is a process that applies free-radical copolymerization of monomer with multifunctional cross-linking agent in the presence of an inert porogen. The porogen is miscible with the monomer mixture; however this substance cannot dissolve formed polymer. The newly formed polymer molecules precipitate from the system and result in phase separation when the polymerization reaction is initiated. The porogen does not react during the polymerization process but remains within the newly formed polymer network. PPBs are actually formed by porogen removal after polymerization. Microporous, mesoporous, or macroporous PPBs with small pore size and large surface area can be prepared using this method^[11–13]. However, preparing gigaporous PPBs through PIPS process is difficult.

Emulsion-template is a flexible and controllable technique for gigaporous material fabrication, this method is commonly achieved by polymerizing continuous phase in a water-in-oil or oil-in-water emulsion with different internal phase volumes^[14–16]. Internal phase volume shows dominant influence on gigaporous materials structure. The materials usually present close-cell porous structure when the internal phase volume is less than 74 vol%. An interconnected open-cell porous structure can be obtained when a greater than 74 vol% internal phase volume is applied. Large pore size and interconnected open-cell porous structure are beneficial for mass transport of large molecules. However, large pore size and interconnected open-cell porous structure can lead to low surface areas and weak mechanical properties, such as brittleness and chalkiness.

Hierarchical porous polymer materials contain multi-level pores, from micropores to gigapores, in a 3D continuous mode. These polymer materials have recently received a great deal of attention because they provide both accessible diffusion pathways and high surface area for separation and catalyst carrier applications^[17–19]. Improved mass transport is achieved by gigapores in hierarchical porous structure, and high surface area is provided by micro-macropores in hierarchical porous structure. Hierarchical porous materials in previous studies have been generally prepared in monolith form^[18, 19]. However, particulate materials are preferred in some fields because these materials can be easily packed into existing reactors, columns, or fixed beds. Wang *et al.* have recently fabricated polymeric microspheres with hierarchical porous structure using the traditional double Pickering emulsion template technique. Unfortunately, the beads in their work exhibited a broad size distribution^[20].

A new method of synthesizing hierarchical PPBs by PIPS and emulsion-template technique in a glass capillary microfluidic device (GCMD) is presented in this study. The (water-in-oil)-in-water double emulsion droplets were fabricated and initiated polymerization by an on-line UV-irradiation to generate the PPBs. In these beads, the meso-macropores are formed by PIPS, the gigapores are obtained from the emulsion-template, and the uniform size of beads is achieved by the microfluidic technique. Combining the conventional PIPS, emulsion-template and microfluidic techniques produces PPBs with hierarchical bimodal porous structure, relatively high surface area and uniform size.

EXPERIMENTAL

Materials

Monomer glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA) were purchased from TCI and Alfa Aesar Company, respectively. These substances were passed through an alumina column before their application for complete removal of inhibitors. Photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was obtained from Alfa Aesar Company. Surfactant Pluronic® L121 (PEO-PPO-PEO copolymer, M_n 4400, PL121) was supplied by BASF Corporation. Stabilizer polyvinyl alcohol (PVA-205, 86.5%–89% hydrolyzed) was supplied by Kuraray Company. Dibutyl phthalate (DBP), dioctyl phthalate (DOP) and anhydrous CaCl_2 were purchased from local suppliers and were used directly.

Fabrication of GCMD

GCMD with co-flowing geometry was fabricated by aligning three capillaries on glass slides as first outlined by Utada *et al.*^[21] An injecting capillary (0.76 mm in outer diameter and 0.58 mm in inner diameter) was tapered to desired diameters (100 μm to 200 μm) and was assembled in an outer cylindrical glass capillary (1.0 mm in inner diameter). A collecting capillary (0.76 mm in outer diameter and 0.58 mm in inner diameter) was assembled in the outer glass capillary from the other blocked side. The three capillaries were carefully arranged in concentric manner and subsequently fixed with commercial fast-curing epoxy glue. Polytetrafluoroethylene tubing was used to connect GCMD inlets and syringes. Flow rates were controlled by syringe pumps (Longer, LSP01-1A) during droplets generation, and the process inside the device was observed using an inverted microscope equipped with a camera.

Preparation of Water-in-oil Emulsion

Oil phase that comprises GMA, EGDMA (40% *V/V* of GMA), PL121 (15% *W/V* of oil phase), DMPA (2% *W/V* of monomer) and various amounts of porogen (DOP, DBP) (Table 1) was added to a 50 mL three-neck round-bottomed flask. The flask was fitted with a D-shaped paddle driven by an overhead stirrer. Moreover, the flask was entirely covered with a piece of aluminum foil to avoid light penetration. The oil phase was stirred at 400 r/min for 5 min. The same volume fractions of aqueous 2% *W/V* CaCl_2 solution (water phase) were subsequently added dropwise into the oil phase under constant stirring. After aqueous phase addition, stirring was continued for another 5 min to produce homogeneous white water-in-oil emulsion.

Preparation of PPBs

Freshly prepared water-in-oil emulsion was injected into the above mentioned GCMD through the injecting capillary. Aqueous 2% *W/V* PVA solution served as the carrier continuous phase was injected into the interstices between the outer capillary and the injecting capillary. Flow rates were controlled using programmable syringe pumps at 100 $\mu\text{L/h}$ to 500 $\mu\text{L/h}$ and at 1000 $\mu\text{L/h}$ to 10000 $\mu\text{L/h}$ for the emulsion and carrier continuous phase, respectively. Droplets were formed at the tip of injecting capillary and flowed through the collecting capillary exposed to UV light (produced by two 6W UV lamps). Droplets were irradiated for at least 2 min to transform into solid PPBs. PPBs were thoroughly washed with acetone and methanol thrice and dried under vacuum at room temperature overnight.

Characterization

The morphologies of the PPBs were investigated using a Philips XL 30 FEG scanning electron microscope (SEM). PPBs were randomly selected and sectioned with a razor blade to show the internal structure of the beads. The samples were sputter coated with gold film before the SEM imaging. Nitrogen adsorption was performed on a Quantachrome NOVA system. The samples were degassed at 100 $^{\circ}\text{C}$ overnight under vacuum before collecting the data, which were then analyzed using the Brunauer-Emmett-Teller (BET) method. Mercury intrusion porosimetry (MIP) analysis was performed using a Micromeritics Autopore IV 9500 instrument. The samples were degassed under vacuum at room temperature before intrusion. The intrusion and extrusion mercury contact angles of 130° and surface tension of 0.485 N/m were used. The pressure ranged from 3.45 kPa to 228 MPa. The measurements involved in this study were conducted based on the set-time equilibration mode. Penetrometers with a stem volume of 1.1310 mL were used.

RESULTS AND DISCUSSION

(Water-in-oil)-in-water double emulsion droplets are fabricated in GCMD as illustrated in Fig. 1. The water-in-oil emulsion, prepared by emulsifying the water solution (water phase) in monomer solution (oil phase), is added into the injecting capillary of the GCMD using syringe pumps. An aqueous 2 wt% PVA solution, which serves as carrier continuous phase to prevent droplet coalescence, is inserted into the GCMD interstices using syringe pumps. The (water-in-oil)-in-water double emulsion droplets are formed at the orifice of the tapered injecting capillary. This process resulted from two competing forces, namely, the surface tension force of the emulsion

holding the droplets to the tip and the drag force of the carrier continuous phase pulling the droplets downstream^[22]. The droplets are formed by dripping or jetting mechanism according to the flow rate of the carrier continuous phase. The surface tension of the emulsion phase is dominant at low flow rate, in which the droplets are formed by dripping (Fig. 2a). The drag forces of the outer phase are dominant at high flow rate, in which the droplets are formed by jetting (Fig. 2b). The transition from dripping to jetting is similar to the process of slowly increasing the flow rate of the water from a kitchen faucet. The diameter of the droplets decreases from 550 μm to 250 μm , whereas the frequency increases from 90 droplets/min to 800 droplets/min when the flow rate of the carrier continuous phase is increased from 1 mL/h to 10 mL/h (Fig. 2).

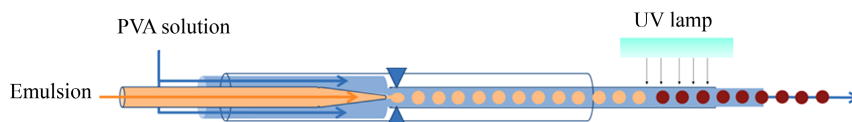


Fig. 1 Schematic of PPBs preparation in a GCMD

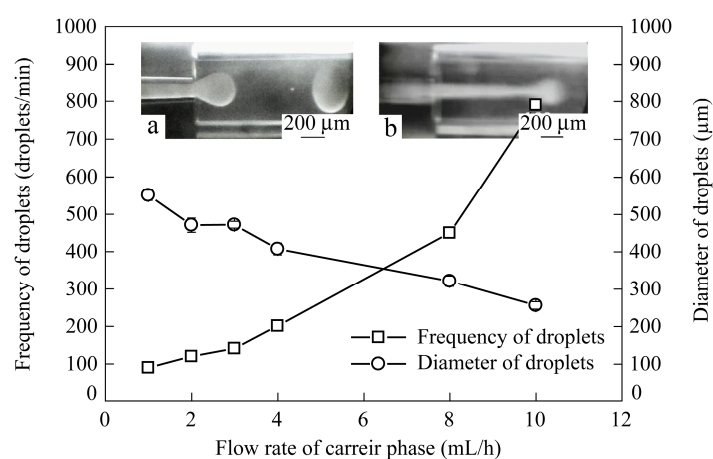


Fig. 2 Effects of the carrier continuous phase flow rate on the frequency and diameter of droplets: (a) formation of droplets by dripping and (b) formation of droplets by jetting

The droplets flow in the collecting capillary and are exposed to UV light for at least 2 min. The droplets containing the photoinitiator and monomer are initiated for polymerization and are finally converted into solid porous beads. Figure 3(a) shows the uniform PPBs with an average size of 410 μm , prepared at 0.3 mL/h of emulsion phase and at 4 mL/h of carrier continuous phase. The porous surface morphology with micrometer scale pores is presented in Fig. 3(b).

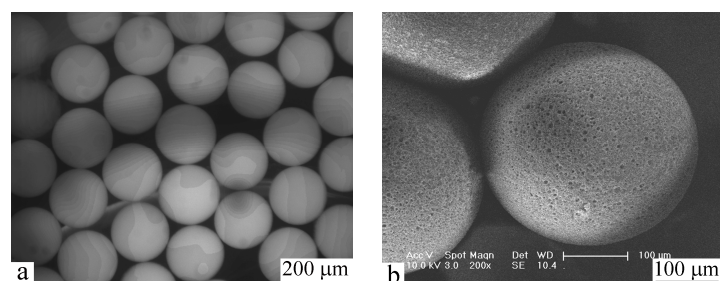


Fig. 3 (a) Optical microscopy image and (b) SEM image of PPBs

Figure 4 shows the pore morphology and pore size distribution of PPBs1 without porogen added into the oil phase (Table 1). The pores at the interior of the beads (Fig. 4a) are separated by an intact wall and exhibit a

closed-cell structure. This condition corresponds to the general theory. The water phase at 50 vol% in this study is less than 74 vol%. Thus, the water droplets cannot contact each other and a closed-cell structure is formed. By contrast, the cells are interconnected with throats and display an open-cell structure at the edge of the beads (Fig. 4b). The pore structure from the close-cell to open-cell can be clearly observed in Fig. 4(c). The open-cell structure appears at approximately 20 μm depth, which is significantly different from the traditional emulsion-template theory. This phenomenon may be caused by the different osmolarities of the CaCl_2 solution in the water phase of emulsion and the PVA solution of the carrier continuous phase. The osmolarities of the PVA and CaCl_2 solution are 9 mOsm/L and 414 mOsm/L, respectively. The water molecules in the PVA solution inevitably penetrate into the CaCl_2 solution after the droplets are formed. Subsequently, the ratio of the water phase at the edge of the droplets increases above 74%. Therefore, the pore structure normally observed in high internal phase emulsion is displayed on the edge of the beads. Water molecules cannot penetrate into the interior of the droplets before the latter are transformed into solid beads. Hence, closed-cells are formed inside the PPBs.

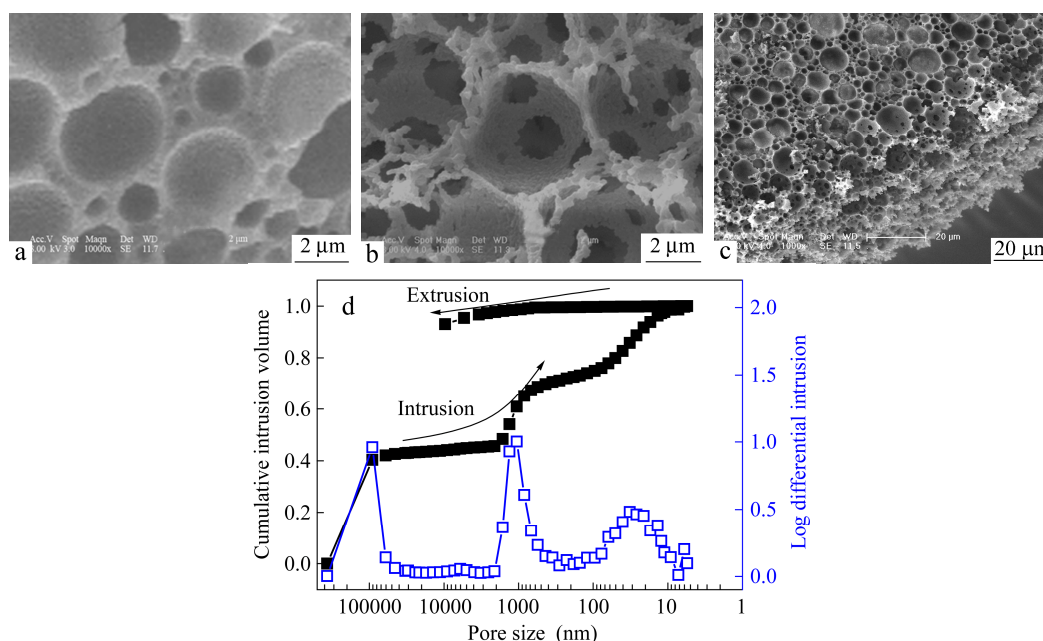


Fig. 4 (a) Surface SEM image of PPBs 1; (b) Cross-sectional SEM image of PPBs 1; (c) Edge of the cross-sectional SEM image of PPBs 1 and (d) Pore size distribution of PPBs 1 determined by the MIP (The total cumulative intrusion volume and peak heights have been normalized for easier comparison.)

Table 1. Summary of the synthetic conditions

Samples	Oil phase volume		Water phase volume
	Monomer	Porogen	CaCl_2 Solution
PPBs 1	50%	0	50%
PPBs 2	42.5%	7.5% DBP	50%
PPBs 3	37.5%	12.5% DBP	50%
PPBs 4	32.5%	17.5% DBP	50%
PPBs 5	42.5%	7.5% DOP	50%
PPBs 6	37.5%	12.5% DOP	50%
PPBs 7	32.5%	17.5% DOP	50%

The polymer skeleton at the edge of the beads is composed of a large amount of microglobules, which is different from using traditional emulsion-template theory. Microglobules may be formed by emulsification, similar to the emulsion polymerization process. However, the exact rationale behind this mechanism still remains unclear. The pore size distribution is measured by MIP. The results are shown in Fig. 4(d) and Table 2.

The first step in the cumulative intrusion curve (*i.e.*, first peak in the differential intrusion curve) of all samples at 30 μm to 50 μm is the interspace between the PPBs. The other steps (*i.e.*, other peaks in differential intrusion curve) are the internal pore of the beads. PPBs 1 shows a hierarchical bimodal pore structure with gigapores and meso-macropores in the differential intrusion curve. The peak of 1055 nm is the window size between the cells at the edge of the beads because mercury enters the pore at a pressure determined by the entrance size. The peak at 26 nm represents the size of interspace between the microglobules of the beads because of the same reason. The relative pore volume of the meso-macropores is 49% estimated by cumulative intrusion curve. However, this value is not the true volume fraction of meso-macropores, but the volume fraction of cells interconnected by meso-macropores. The surface area is 15.9 m^2/g from BET treatment of N_2 adsorption data.

Table 2. Summary of the pore structure of the PPBs

Samples	Relative pore volume ^a		Peak ^b		Pore volume of extrusion mercury ^c (%)	Surface area ^d (m^2/g)
	Gigapores 200 nm–2 μm (%)	Meso-macropores < 200 nm (%)	Gigapores (nm)	Meso-macropores (nm)		
PPBs 1	51	49	1055	26	7.0	15.9
PPBs 2	26	74	1052	32	5.7	32.5
PPBs 3	26	74	1058	66	9.6	40.7
PPBs 4	21	79	832	63	15.7	50.2
PPBs 5	80	20	1052&284	—	11.0	18.9
PPBs 6	96	4	554	—	14.0	18.3
PPBs 7	100	0	1052	—	40.4	11.0

^a Estimated by cumulative intrusion volume curve; ^b Estimated by differential intrusion volume curve;

^c Estimated by extrusion volume curve; ^d From BET treatment of N_2 adsorption data

To improve the pore volume of meso-macropores and the surface area of beads, DBP is added as porogen to the oil phase of the emulsion, generating PPBs 2 to PPBs 4 (Table 1). Figure 5 shows that more microglobules are formed, both at the interior and at the edge of the beads. The size of the microglobules increases with increasing DBP. The microglobules are formed by both the emulsification process and PIPS. The solubility parameter of DBP is 19.0 $\text{MPa}^{1/2[23]}$, similar to that of the poly(GMA-*co*-EGDMA) at 24 $\text{MPa}^{1/2[23]}$. Therefore, DBP can readily swell the formed poly(GMA-*co*-EGDMA) network. The cross-linked network becomes incapable of absorbing more DBP when more monomer is transformed into the polymer. In this event, phase separation occurs and microglobules are formed. Meso-macropores are formed between the microglobules by removing DBP. This mechanism is called ν -induced syneresis^[11, 13], where ν is crosslink density of the network. The pore size distribution is shown in Fig. 5 and Table 2, which display the bimodal pore distribution containing gigapores and meso-macropores. The volume fraction of cells interconnected by meso-macropores is above 70%, much larger than that of PPBs 1. The surface area increases from 32 m^2/g to 50 m^2/g when the amount of DBP is increased because more meso-macropores are formed on the polymer skeleton. The surface area of PPBs 4 is almost threefold higher compared to the previously reported monodisperse poly(HIPE) beads^[24].

DOP can also be used as porogen preparing PPBs 5 to PPBs 7 (Table 1) as shown in Fig. 6. The size of the microglobules, which increases with increasing DOP, is larger than that of the DBP with the same ratio. This phenomenon is caused by the different solubility parameter values of the DOP and the final polymer. The solubility parameter of DOP is 16.2 $\text{MPa}^{1/2[23]}$, which is substantially lower than that of poly(GMA-*co*-EGDMA). DOP is miscible with the monomer; however, DOP cannot swell or dissolve the growing polymer chains. At the beginning of polymerization, the polymer chains precipitate to form microglobules and DOP is squeezed out of the microglobules because of phase separation. This mechanism is called χ -induced syneresis^[11, 13], where χ is the polymer-porogen interaction parameter. Through this mechanism, the microglobules are larger than those formed with DBP. The interspace between the microglobules is 284 nm when 15 vol% DOP is used. This measurement is much larger than that of the DBP. The interspace between the microglobules is comparable to

the size of throats between the cells when more DOP is used. Hence, only one peak is identified on the differential intrusion curve (Fig. 6 and Table 2).

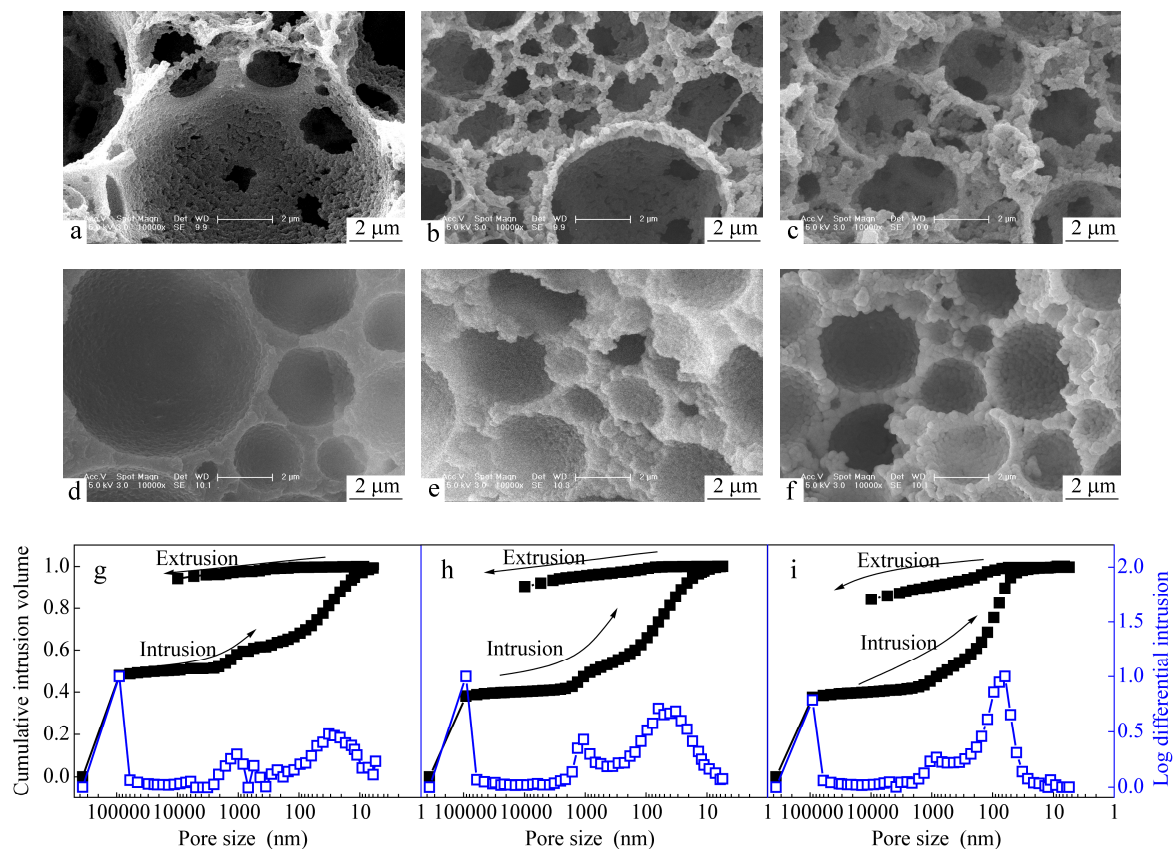
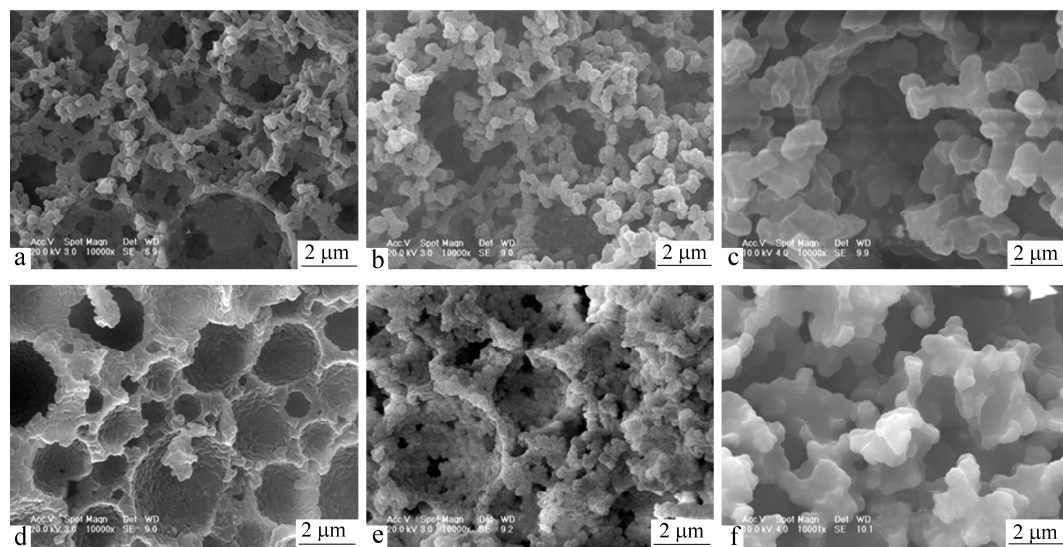


Fig. 5 Surface SEM images of (a) PPBs 2, (b) PPBs 3, (c) PPBs 4; Cross-sectional SEM images of (d) PPBs 2, (e) PPBs 3, (f) PPBs 4; Pore size distribution of (g) PPBs 2, (h) PPBs 3, (i) PPBs 4



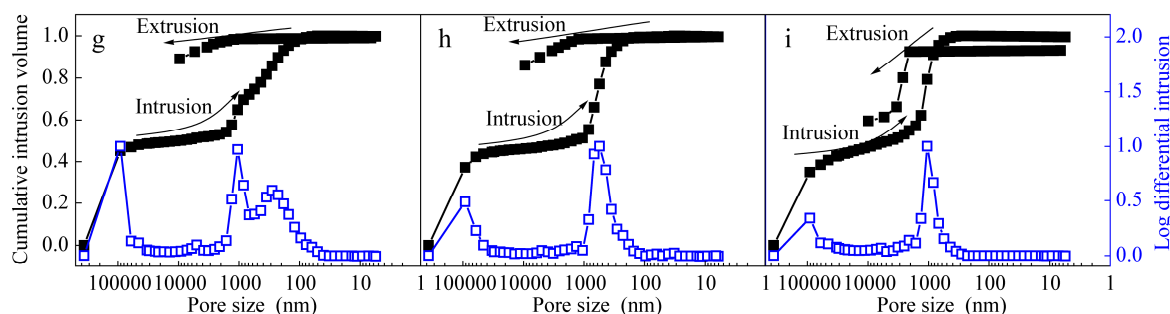


Fig. 6 Surface SEM images of (a) PPBs 5, (b) PPBs 6, (c) PPBs 7; Cross-sectional SEM images of (d) PPBs 5, (e) PPBs 6, (f) PPBs 7; Pore size distribution of (g) PPBs 5, (h) PPBs 6, (i) PPBs 7

The hysteresis between intrusion (increasing pressure) and extrusion (decreasing pressure) is evidently observed in all samples. This phenomenon can be explained by the ink bottle theory proposed by Wardlaw *et al.*^[25]. The throat size is smaller than the cavity size in PPBs. So, mercury will enter the cavity at a pressure determined by the throat size and not the actual cavity size. A large amount of mercury will be trapped inside the sample during the extrusion process. More mercury remains in the cavity with the increasing ratio of pore size to throat size. The size of throats increases with increasing porogen as mentioned above, so the ratio of pore size to throat size decreases and less mercury retention. This tendency is observed in PPBs with both DOP and DBP as the porogen.

CONCLUSIONS

A strategy of preparing hierarchical bimodal pore structure PPBs with gigapores and meso-macropores is developed using PIPS and emulsion-template technique in GCMD. The synthetic approach for these hierarchical structures involves the preparation of (water-in-oil)-in-water droplets, followed by an on-line initiated polymerization to form PPBs. This procedure leads to the formation of uniform-sized beads with gigapores from emulsion-template and meso-macropores from PIPS. By easily changing the flow rate of the carrier continuous phase, the size and frequency of the PPBs can be tuned from 550 μm to 250 μm and from 90 droplets/min to 800 droplets/min, respectively. The kinds and amount of porogen influence the pore size distribution of meso-macropores and gigapores significantly. Only gigapores are formed because the interspace between the microglobules is comparable to the size of throats between the cells when 25 vol% to 35 vol% DOP is used. Hierarchical bimodal pore structure is formed with volume fraction of cells interconnected by meso-macropores at 79% and surface area of 50 m^2/g , which is almost threefold higher compared to the previously reported monodisperse poly(HIPE) beads, when 35 vol% DBP is used. These PPBs will become promising material for separation and catalyst carrier fields.

REFERENCES

- 1 Smigol, V., Svec, F. and Frechet, J. M., *Anal. Chem.*, 1994, 66(23): 4308
- 2 Zhang, Y. and Riduan, S.N., *Chem. Soc. Rev.*, 2012, 41(6): 2083
- 3 Smigol, V., Svec, F. and Frechet, J.M., *Macromolecules*, 1993, 26(21): 5615
- 4 Grzegorzczuk, D.S. and Carta, G., *Chem. Eng. Sci.*, 1996, 51(5): 807
- 5 Galia, M., Svec, F. and Frechet, J.M., *J. Polym. Sci. Part A: Polym. Chem.*, 1994, 32(11): 2169
- 6 Christensen, B.E., Myhr, M.H., Aune, O., Hagen, S., Berge, A. and Ugelstad, J., *Carbohydr. Polym.*, 1996, 29(3): 217
- 7 Malik, D., Webb, C., Holdich, R., Ramsden, J.J., Warwick, G., Roche, I., Williams, D., Trochimczuk, A., Dale, J. and Hoenich, N., *Sep. Purif. Technol.*, 2009, 66(3): 578
- 8 Li, Y., Gao, F., Wei, W., Qu, J.B., Ma, G.H. and Zhou, W.Q., *J. Mol. Catal. B: Enzym.*, 2010, 66(1): 182

- 9 Sýkora, D., Svec, F. and Fréchet, J.M., *J. Chromatogr. A*, 1999, 852(1): 297
- 10 Petro, M., Svec, F., Gitsov, I. and Fréchet, J.M., *Anal. Chem.*, 1996, 68(2): 315
- 11 Dubinsky, S., Petukhova, A., Gourevich, I. and Kumacheva, E., *Chem. Commun.*, 2010, 46(15): 2578
- 12 Svec, F. and Frechet, J.M., *Science*, 1996, 273(5272): 205
- 13 Okay, O., *Prog. Polym. Sci.*, 2000, 25(6): 711
- 14 Menner, A., Haibach, K., Powell, R. and Bismarck, A., *Polymer*, 2006, 47(22): 7628
- 15 Wu, R., Menner, A. and Bismarck, A., *J. Polym. Sci. Part A: Polym. Chem.*, 2010, 48(9): 1979
- 16 Cameron, N. and Sherrington, D., in "Biopolymers Liquid Crystalline Polymers Phase Emulsion", Springer, 1996, p. 163
- 17 Parlett, C.M., Wilson, K. and Lee, A.F., *Chem. Soc. Rev.*, 2013, 42(9): 3876
- 18 Sai, H., Tan, K.W., Hur, K., Asenath-Smith, E., Hovden, R., Jiang, Y., Riccio, M., Muller, D.A., Elser, V. and Estroff, L.A., *Science*, 2013, 341(6145): 530
- 19 Schofield, W., Bain, C. and Badyal, J., *Chem. Mater.*, 2012, 24(9): 1645
- 20 Ning, Y., Yang, Y., Wang, C., Ngai, T. and Tong, Z., *Chem. Commun.*, 2013, 49(78): 8761
- 21 Utada, A.S., Lorenceau, E., Link, D.R., Kaplan, P.D., Stone, H.A. and Weitz, D.A., *Science*, 2005, 308(5721): 537
- 22 Utada, A.S., Fernandez-Nieves, A., Stone, H.A. and Weitz, D.A., *Phys. Rev. Lett.*, 2007, 99(9): 094502
- 23 Dubinsky, S., Park, J.I., Gourevich, I., Chan, C., Deetz, M. and Kumacheva, E., *Macromolecules*, 2009, 42(6): 1990
- 24 Gokmen, M.T., Van Camp, W., Colver, P.J., Bon, S.A.F. and Du Prez, F.E., *Macromolecules*, 2009, 42(23): 9289
- 25 Giesche, H., *Part. Part. Syst. Char.*, 2006, 23(1): 9