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The influence of different porogens with halogen substituents on the pore structure of polydivinylbenzene beads

Qingquan Liu*, Yinxiang Duan, Zhihua Zhou, Juan Wang, Mingyu Wang, Shaohua Shen

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

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ABSTRACT

Polydivinylbenzene (PDVB) beads with high surface area and porosity were prepared via suspension polymerization in the presence of solvents with halogen substituents as porogens. The porogens employed in the present work were *p*-dichlorobenzene, chlorobenzene, bromobenzene, benzyl chloride, and tetrachloroethane. The porogens were used in a 1/1 volume ratio with divinylbenzene (DVB). As predicted from previous knowledge of porogen with halogen substituents possessing strong capacity to construct porosity, the surface area of PDVB beads prepared with the above porogens reached 647.1–744.6 $m^2\,g^{-1}$, which mainly depended on the difference of solubility parameter of the porogens and PDVB networks. The smaller the difference, the larger the surface area of PDVB beads was. Overall, research results of the present study indicated that in comparison with other types of porogen, solvent with halogen substituent could generate larger surface area and construct higher porosity in PDVB beads.

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1. Introduction

Over the past several decades, a considerable amount of work on porous polymer has been carried out because porous polymer materials have a wide range of applications such as ion-exchange resins, adsorbents, column-packing materials for high performance liquid chromatography, catalyst support and templates for nanoparticle growth [1–3]. Polymer beads with large surface area and high porosity have attracted widespread interest owing to its potential applications such as specific sorbents [4]. Up to now, much effort has been made to improve the surface area and the porosity of polymer microspheres [5–7]. For example, Macintyre and Sherrington [5] prepared polydivinylbenzene (PDVB) resins with surface area of 815 $m^2\,g^{-1}$ and porosity of 44% using poly(propylene glycol) oligomers, or poly(dimethylsiloxane) oligomers and toluene as co-porogens. Beldie and coworkers [6] have found that cyclohexanol was one of the most efficient porogens for building up the highest porosity even at the low level of divinylbenzene. Li and Stöver [7] have used mixtures of acetonitrile with toluene to precipitate PDVB beads with 4–7 μm in diameter, 0.52 $ml\,g^{-1}$ in total pore volume and 800 $m^2\,g^{-1}$ in surface area.

It is well known that porogen type is one of the key factors for the generation of large surface area and high porosity. Therefore, it is essential to develop novel porogens for preparing PDVB beads with large surface area and high porosity. Errele [8–11] systematically investigated the swelling behavior of poly(styrene-divinylbenzene) (PSDVB) in various solvents, and found that halogen substituent in solvent could increase the compatibility of solvent with PSDVB. We have reported the unexpected behavior of 1-chlorodecane as a novel porogen in the preparation of high-porosity PDVB beads [12,13]. In the present study, in order to research the effect of different solvents with halogen substituents on the pore structure of PDVB beads, some solvents with halogen substituents like *p*-dichlorobenzene, chlorobenzene, bromobenzene, benzyl chloride, and tetrachloroethane are employed as porogens to prepare PDVB beads.

2. Experimental

2.1. Materials

Divinylbenzene (mixtures of isomers, ≥80%, Sigma–Aldrich Chemie, USA) was extracted with 5% ($w\,w^{-1}$) 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. 2,2′-azo-bis-isobutyronitrile (AIBN) was purchased from Linfeng Chem Co. Ltd, China. It was re-crystallized from methanol and used as the initiator. Poly(vinyl alcohol) (PVA, 88% hydrolyzed, average M.W. 88,000) was purchased from the Aldrich Chemical Co and used without further purification. Chlorobenzene (CB), *p*-dichlorobenzene (*p*-DCB), bromobenzene (BB), benzyl chloride (BC) and tetrachloroethane (TCE) (Sinopharm Chemical Reagent Co. Ltd, china) were used as received.

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* Corresponding author. Fax: +86 731 5829 0045.
E-mail address: qqliu@hnust.edu.cn (Q. Liu).

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2.2. Suspension polymerization

Porous PDVB beads are prepared by suspension polymerization in three-neck glass reactor. Solution (60 cm^3) containing 0.3 g PVA (0.5 wt%) and 1.98 g NaCl (3.3 wt%) is charged into the glass reactor, and then is heated to 50 °C under argon atmosphere. At the stirring speed of 300 rpm, mixture solution containing AIBN (0.033 g), DVB (3.0 cm^3), and porogen (3.0 cm^3) is added into the reactor. The reaction is carried out at 80 °C for 6 h. After polymerization, the products are washed twice with hot water, three times with methanol, and vacuum filtered to remove the stabilizer, PVA. The beads are extracted with acetone for 24 h in a Soxhlet to remove porogen and residual monomers, and then are washed twice with acetone, three times with methanol to ensure complete removal of impurities. Finally, PDVB beads are dried in a vacuum oven at 50 °C for at least 12 h.

2.3. Characterization

Nitrogen sorption porosimetry was performed on a Micromeritics ASIC-2. 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 data were manipulated using the software supplied to yield the relevant porosity parameters. The apparent density, the average pore size and porosity are also determined by Hg intrusion porosimetry using Autopore IV 9500, and appropriate porosity parameters are generated using the packed software.

The microspheres were spread onto electric glue, which was spread on a metallic base. Dried samples were coated with a thin layer of gold in vacuum. Then, scanning electron microscope (SEM, JSM-6380LV) was used to analysis surface morphology of PDVB microspheres.

3. Results and discussion

3.1. Preparation of porous PDVB beads

In present paper, five samples of PDVB beads (PM1–PM5) are prepared with different porogen with halogen groups like *p*-dichlorobenzene (*p*-DCB), chlorobenzene (CB), bromobenzene (BB), benzyl chloride (BC) and tetrachloroethane (TCE), to investigate the effect of halogen groups in porogens on the pore structure of PDVB beads. During the preparation of porous PDVB beads, the initial volume ratio of DVB to porogen is set to be 1/1. The SEM images of PDVB beads are shown in Fig. 1. Obviously, the beads are found to be 50–400 μm, and display a smooth surface texture. SEM images of PM1–PM5 (Fig. 1A–E) show no obvious difference at the resolution of the SEM used. However, the internal morphology of PM3 prepared with bromobenzene as porogen reveals visibly porosity (Fig. 1F).

3.2. The N_2 sorption isotherms and Hg intrusion curves

The pore structure of porous PDVB beads is determined by N_2 sorption and Hg intrusion, and the N_2 adsorption/desorption isotherms and Hg intrusion/extrusion curves of PM1–PM3 are presented in Fig. 2. The absorbed N_2 in PDVB beads almost completely desorbs when the relative pressure $PP^{-1}{}_0$ is progressively declined, whereas the mercury cannot be entirely ejected even at low pressure. The fact indicates caged pore structure with some small entrances, and mercury cannot squeeze through them when the pressure is not high enough. However, once mercury is intruded into the cages at a relatively high pressure, the mercury resided in cages is difficult to be ejected again with deceasing pressure.

As can be seen in Fig. 2, the isotherms of PM1 locate above that of PM3 and PM2, indicative of higher surface area. The desorption branches of the isotherms for PDVB beads show an abrupt fall at $PP^{-1}{}_0 = 0.5–0.7$, indicative of delayed capillary evaporation and caged pores. In addition, there is a hysteresis loop at $PP^{-1}{}_0 > 0.5$. Our previous [14] work indicated that pore connectivity limitations could be responsible for the hysteresis loop. The cumulative intrusion of PDVB beads retains a relatively steady value in the pressure range of 10–2000 psia, and then the value abruptly increase with the pressure. This increase of cumulative intrusion suggests higher pressure is required to force mercury into pores, indicative of micro- or mesopores.

The characterization data derived from N_2 sorption and Hg intrusion are summarized and given in Table 1. It should be noted that it is questionable for Hg intrusion to probe the smallest pores, and the largest pores are neglected by N_2 sorption technique [15]. Therefore, it is unsuitable to compare the data calculated from different technique.

3.3. The surface area

The pore structure of macroporous PDVB beads is profoundly influenced by the nature of the porogen. Generally, in the presence of a thermodynamically compatible solvent as porogen, phase separation occurs at a much later stage since the porogen has good compatibility with PDVB networks. During the process of gel formation, the microgel particles retain their individuality, and this fact results in materials with small pore diameter and high surface area. Conversely, phase separation occurs before the gel point, a much earlier stage, when a thermodynamically incompatible solvent is used as porogen. The microgel particles fuse and agglomerate into larger clusters because of poor compatibility with PDVB networks, and this leads to formation of large pore size and low surface area [15].

Our previous work indicated that 1-chlorodecane displayed unexpected behavior in building high porosity in PDVB beads due to the excellent compatibility of chloro group with phenyl rings in the copolymers [12,13]. Here, in spite of halogen group in porogen, examination of PM1–PM5 clearly demonstrated that the porogen influenced the surface area, which increased on changing from benzyl chloride (PM4, 647.1 $m^2 g^{-1}$) to tetrachloroethane (PM5, 744.6 $m^2 g^{-1}$). The compatibility between porogen and polymer could be expressed by their solubility parameters (δ), which were defined as the square root of the cohesive energy density and presented in Table 1. The difference of the values with that of polymer could reveal the extent of interaction between the porogen and polymer; the smaller the difference, the greater the interaction and consequently, the better was that solvating the polymer chains. The Hildebrand solubility parameter approach can be expressed quantitatively according to the following equations:

$$\frac{\Delta H_m}{V} = (\delta_1 - \delta_2)^2 \varphi_1 \varphi_2$$

$$\Delta G_m = \Delta H_m - T\,\Delta S_m$$

where ΔH_m, ΔG_m and ΔS_m are the enthalpy, free energy and entropy of mixing, respectively; V is the molar volume of the solvent; δ and φ are the solubility parameter and volume fractions of the porogen (1) and the polymer (2), respectively. Consequently, when δ_1 and δ_2 are similar, ΔH_m is small and ΔG_m is negative.

The solubility parameters (δ_2) of poly(styrene-divinylbenzene) (PSDVB) quoted in the literature is 9.2 $(cal\,cm^{-3})^{0.5}$. In comparison with δ_1 of various porogen given in Table 1, no evidence indicated that there is an obvious correlation between δ difference ($\delta_1 - \delta_2$) and surface area of PDVB beads (as shown in Fig. 3). The elegant works by Errele [8–11] indicated that cohesive energy

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