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Hyper-cross-linked resins with controllable pore structure

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Abstract

Hyper-cross-linked resins were synthesized by post cross-linking precursor resins prepared by suspension polymerization of vinylbenzyl chloride (VBC), divinylbenzene (DVB) and styrene (St) in the presence of inert porogens. The research results showed that porogen type had significant influences on the surface area, the average diameter and the total pore volume of the final products. The highest specific surface area was achieved with the resins prepared with mixture of toluene and hexane as inner porogens. Moreover, clear bimodal pore size curves were observed with the hyper-cross-linked resins prepared with mixture of hexane and toluene, or sole hexane as porogens. It was therefore indicated that hyper-cross-linked resins with different pore structure could be controllably prepared via varying porogen type.

Keywords: Polymers; Porosity

1. Introduction

Hyper-cross-linked polystyrene resins are microporous, and low density materials. However, their porosity has little in common with the porosity of traditional macroporous styrene-divinylbenzene (St-DVB) sorbents, activated carbons, silica gels, etc. The hyper-cross-linked resins have considerably high specific surface area, relatively small pore size, unprecedented sorption capacity with polar and non-polar organic compounds, and an easy regeneration process [1]. Up to now, these materials have been successfully applied in many fields, such as adsorbents [2–5], as ion-exchange resins [6], and packing materials for liquid chromatography [7]. Recently, these resins were even tried to be used as the matrix for reversible hydrogen storage [8,9].

Davankov and Tsyurupa [10,11] have systematically investigated the preparation techniques, pore structure, various properties and applications of hyper-cross-linked polystyrene resins. They introduced numerous rigid bridges into linear polystyrene or St-DVB copolymers by using various bifunctional compounds as cross-linking agents, such as monochlorodimethyl ether, *p*-xylylene dichloride, and so on. Recently, Sherrington and co-workers [12,13] prepared Davankov-type resins via incorporating the third monomer of vinylbenzyl chloride (VBC) into polymer chains. The chloromethyl substituents in precursor resins were used to perform post cross-linking reaction in the presence of Friedel–Craft catalyst. However, it is still a difficult issue to prepare hyper-cross-linked resins with controllable pore structure via a simple and effective technique [14]. We think that porogen type has significant influence on the pore structure of precursor resins, thus, when hyper-cross-linked resins were prepared from porous chloromethylated precursors using Sherrington's technique, it will have an effect on the pore structure of hyper-cross-linked resins. Hence, the present work attempts to investigate the role of porogen and its effect on the pore structure of hyper-cross-linked resins.

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2. Experimental

Porous precursor resins (*R1* ~ 3) were prepared by conventional free radical suspension polymerization. Typically the aqueous phase consisted of distilled water (130 cm^3), PVA (0.975 g) and NaCl (4.29 g). The corresponding organic phase (the total volume, 13 cm^3) comprised DVB (2.60 g), St (1.04 g), VBC (9.98 g), and AIBN (0.164 g) together with toluene and/or *n*-hexane as the inert porogens. The two phases were mixed and heated to 75 °C for 8 h. The precursor beads were collected, washed with water and acetone in a Soxhlet, and finally dried in vacuum oven at 60 °C.

The precursor beads (3.0 g) were swollen in 40 cm^3 of 1,2-dichloroethane for 2 h. The mixtures were cooled to 4 °C in an ice bath, before another 40 cm^3 DCE containing Friedel–Crafts catalyst (0.8 g $FeCl_3$) were added. Then, the mixtures were heated to 80 °C for 8 h. The products (***HCLR1*** ~ 3) were washed with methanol, a mixture of ethanol and HCl (0.5 mol/L), and finally deionized water. The resulting products were dried in vacuum oven at 50 °C.

The surface area, average pore diameter, total pore volume and pore size distribution of hyper-cross-linked resins were evaluated using Nitrogen sorption technique (micromeritics ASIC-2). The solvent uptakes of hyper-cross-linked resins with toluene and methanol were determined gravimetrically (g/g) by the dry polymer being weighed first and then the swollen one. Average size and surface morphology of beads were determined by a scanning electron microscope (SEM, HITACHI, S4800). Elemental microanalytical data for each resin were obtained from a Perkin-Elmer Series II2400 elemental microanalyzer.

3. Results and discussions

In the present work, three porous precursor resins were prepared with the mole ratios of comonomers St: DVB: VBC = 1:2:7 in the presence of toluene and/or *n*-hexane as inert porogens. Note that toluene is a thermo-dynamically good solvent for linear polystyrene, and *n*-hexane is a typical precipitating solvent. Here, toluene, *n*-hexane and their mixtures (50/50, v/v) were used as the inert porogens to evaluate the role of porogen and its effect on the pore structure of hyper-cross-linked resins. Typically, the chlorine contents of the precursor resins (Table 1) were a little below than the theoretical value, 18.25%. This is due to minor hydrolysis of the VBC monomer, which has been proved by Sherrington et al. [14]. The precursor resins were collected in the form of spherical beads with diameter in the range 100–500 μm, and all the beads were used in the following hyper-cross-linked reaction. Fig. 1 presents the simplified scheme of post cross-linking reaction by internal electrophilic addition. The dihydroanthracene structure is the possible one that has been proposed by Sherrtinton et al. [15], but we believe a variety of cross-linking structures will exist in the actual materials.

Table 1
Characterization data of precursor resins and their hyper-cross-linked species

Run	Porogen	BET S_a (m^2/g)	BJH D_p (nm)	BJH W_o (cm^3/g)	% Cl content	Uptake (g/g)	
						Toluene	Methanol
R1	Tol[a]	116	15.2	0.25	17.62	1.4	0.7
HCLR1	Tol	638	3.9	0.37	4.30	1.9	0.9
R2	Tol/Hex[b]	74	29.6	0.35	17.81	1.3	0.4
HCLR2	Tol/Hex	951	4.2	0.55	2.25	2.3	1.0
R3	Hex[c]	53	37.5	0.44	17.73	1.6	0.5
HCLR3	Hex	562	8.7	0.50	3.51	2.0	1.2

[a] Tol: toluene; [b] Tol/Hex: 50/50 (vol/vol); [c] Hex: *n*-hexane. S_a: surface area; W_o: total pore volume; D_p: average pore diameter.

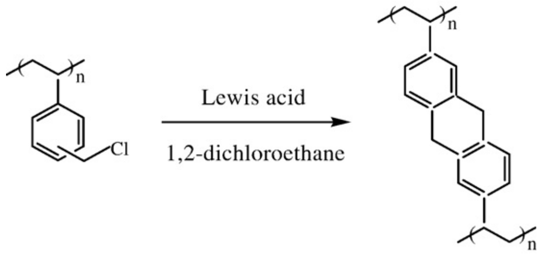

Fig. 1. Possible reaction during hyper-cross-linking precursor resins via internal electrophilic addition.

SEM images of the precursor resins and their derivatives are presented in Fig. 2. The low resolution images reveal that the diameters of the beads are in the range of 100–500 μm. Although most of products can retain their spherical shape, some agglomerations are observed in the resins prepared with hexane as inert porogens. High resolution images show different surface morphology before and after modification. After post cross-linking reaction, surface of hyper-cross-linked resins become even, moreover, porogen type seems to have no obvious effect on the surface morphology of the final products.

The surface area, pore volume, and average pore diameter of precursor and hyper-cross-linked resins calculated by standard procedures from nitrogen sorption data are shown in Table 1. These data dramatically demonstrate the generation of extensive microporosity in the resins during hyper-cross-linking reaction. The dry state surface area of precursor *R1* is 116 m^2/g, but this rises sharply to a high value 638 m^2/g (*HCLR1*) with the generation of pores with average diameter of 3.9 nm and a pore volume of 0.37 cm^3/g. Interestingly, the maximum value of surface area was achieved with resin *HCLR2* prepared with toluene and *n*-hexane as co-porogens, although the surface area of precursor *R2* (74 m^2/g) is smaller than that of resin *R1*. Hexane leads to the minimum surface area value (*HCLR3*, 562 m^2/g). It is not clear why such unexpected order of surface area arises after hyper-cross-linking reaction, but one factor may be attributed to the larger pores originally present in *R2* resin (29.6 nm), which facilitate catalyst $FeCl_3$ transporting in the beads and improve the conversion of the chloromethyl groups. This deduction is further proved by the chlorine contents of the final beads, in which *HCLR2* has the lowest chlorine content (2.25%).

As expected, after modification, the average diameter declined and the pore volume increased due to generation of numerous micropores in the resins. Notably, the decrease in average diameter from 29.6 nm of *R2* to the lowest value of 4.2 nm for *HCLR2* by almost 7-fold indicates that the cross-linking degree reaches a higher value than that of *HCLR1* and *HCLR3*, and this also supports the above deduction. The similar results can also be observed with the total pore volume of resins before and after modification. The responses of the resins to solvents, toluene and methanol, are investigated by the solvent uptake data in Table 1. In comparison with the precursor resins, the uptake data of hyper-cross-linked resins increase for thermodynamically good solvent, toluene, and the thermodynamically poor solvent, methanol, also show a measurable rise. The unusual sorption of thermodynamically incompatible solvents by these hydrophobic polystyrene-based resins is the character of Davankov-type morphology [11].