Asian Journal of Chemistry; Vol. 25, No. 5 (2013), 2755-2757

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13779

Synthesis of A Novel Hyper-Crosslinked Resin with 1,4-*Bis*(chloromethoxyl)butane

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(*Received*: 23 March 2012; *Accepted*: 21 November 2012) AJC-12447

A kind of novel hypercrosslinked resin has been synthesized with 1,4-*bis*(chloromethoxyl)butane and naphthalene. The micromorphology of the resin was characterized with Brunauer-Emmett-Teller (BET), in addition, IR spectra and elemental analysis of the resin was also characterized. The results indicated that, the novel adsorption resin have a high specific surface area of 509.02 m^2/g and abundant micropore structure with average pore diameter 1.134 nm.

Key Words: Hypercrosslinked resin, Naphthalene, 1,4-*Bis*(chloromethoxyl)butane.

INTRODUCTION

Hypercrosslinked polymers represent a class of predominantly microporous polymeric materials that have been widely applied for water pollution control[1-3], analytical purposes[4,5] and catalyzer carrier[6,7], as well as in gas storage[8,9]. Hypercrosslinked polystyrene is efficient material with extremely high crosslinking degree and large specific surface area. These performances provide potential applications as various sorbents and ion exchangers. Moreover, it was also used to store gases such as hydrogen and methane, purification of wastewater, separate natural products[9-11]. The pore structure, the formation conditions and various applications of hypercrosslinked polystyrene have been hot research for many years[12,13]. Traditionally, hypercrosslinked polymers were generally synthesised includes two steps: firstly, precursors such as St-DVB copolymers or linear polystyrene were produced by traditional suspension polymerization. Secondly, precursors was swelled in 1,2-dichloroethane or nitrobenzene, then, catalyst and crosslinking agents such as *p*-xylylenedichloride (XDC), 1,4-*bis*-chloromethyldiphenyl (CMDP), chloromethyl methyl ether (CME) and dimethyl formamide (DMF) were added into reaction system to form numerous rigid bridges between the aromatic rings *via* the Friedel-Crafts reaction.

However, the above methodologies contain its flaws and lack. That is the higher production cost and fussy synthetic. processes. So, search for new methods to preparate hypercross linked resins turned out to be highly important and necessary. Chloromethyl methyl ether (CME) was often used to synyhesize hypercrosslinked resins or used as chloromethylation reagent for its lower price. But, as a noxious and carcinogenic chemical reagent, chloromethyl methyl ether will be displaced sooner or later, so, develop innocuous chloromethylation reagent was very urgent.

As a kind of new chloromethylation reagent, 1,4-*bis*-chloromethyldiphenyl has many virtues such as innocuous and high boiling point[14]. In this paper, a kind of hypercrosslinked resin was facilely prepared use 1,4-*bis*-chloromethyldiphenyl and naphthalene *via* chloromethylation and succedent Friedel-Crafts alkylation polymerization. The structure and micromorphology of the novel resin were preliminarily characterized.

EXPERIMENTAL

Synthesis of 1,4-*bis*(chloromethoxyl)butane: As a chloromethylation reagent 1,4-*bis*(chloromethoxy)butane (BCMB) was self-synthesized[15] and the main procedures are as follows: phosphorus trichloride was added dropwise into a mixed solution of 1,4-butanediol and formaldehyde and controlled the reaction temperature in a range of 10-25 ºC with a ice-water bath. After the reaction was finished, separated the oil layer with a separating funnel and dried with anhydrous magnesium.

Synthesis of the hypercrosslinked resin[16]: The synthesis of the resin was carried out typically as follows: naphthalene 1.0483 g (8 mmol), 1,4-*bis*(chloromethoxy)butane 2.2655 g (12 mmol) and $ZnCl_2$ (1.5423 g) were dissolved with nitrobenzene in a 50 mL flask equipped with the reflux condenser and anhydrous $CaCl_2$ tube. Then the system was stirred, heated and kept reaction tempreture at 50 ºC for 5 h. After the chloromethylation reaction was completed, another catalyst

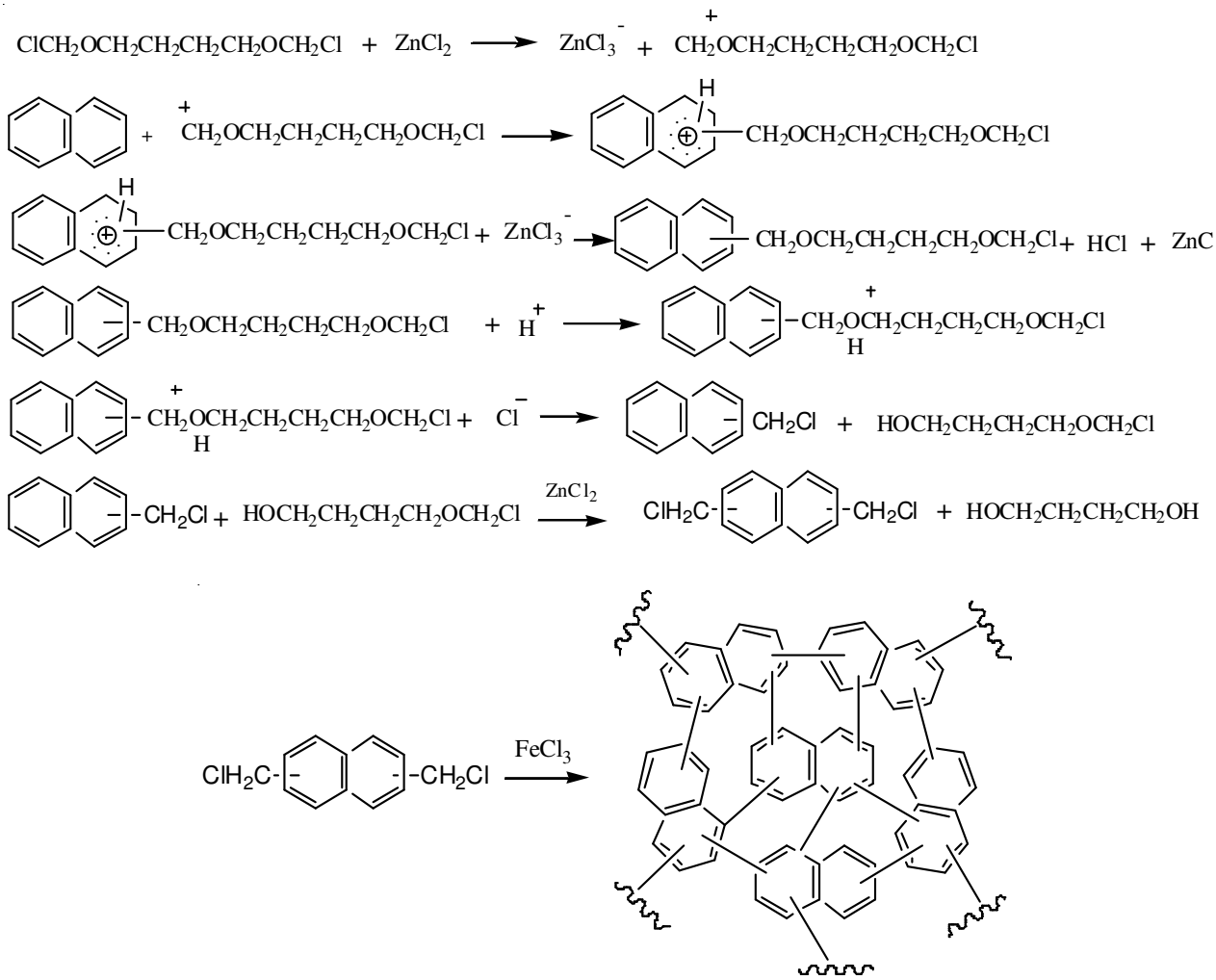

Fig. 1. Synthesis process of the hypercrosslinked resin

$FeCl_3$ (0.2260 g) was added to above system and the temperature was changed to 70 ºC for another 16 h. After the polymerization was finished, the obtained resin was collected and successively washed with aq. H_2SO_4 and water, extracted with acetone in a Soxhlet, finally dried in vacuum oven at 80 ºC. The hypercrosslinked resin (2.0028 g) was obtained (theory 1.3843 g), finally, the FT-IR transmission spectra and 1the elemental analysis of the resin was characterized, the synthesis process of the resin was described in Fig. 1.

The specific surface area of the resin was obtained with the Brunauer-Emmett-Teller (BET) method, elemental analyses was determined with elemental analyzer, FT-IR transmission spectra was taken with spectrometer using KBr pellets.

RESULTS AND DISCUSSION

In present study, a novel hypercrosslinked resin was firstly synthesized with naphthalene and 1,4-*bis*(chloromethoxyl)-butane. The specific surface, average pore diameter and pore size distribution curve were gived in Fig. 2 and Table-1, respectively.

TABLE-1
PORE CHARACTERIZATION OF THE RESIN

BET S_a (m^2/g)	BJH V_p (cm^3/g)	BJH D_p (nm)
509.02	0.07	1.134

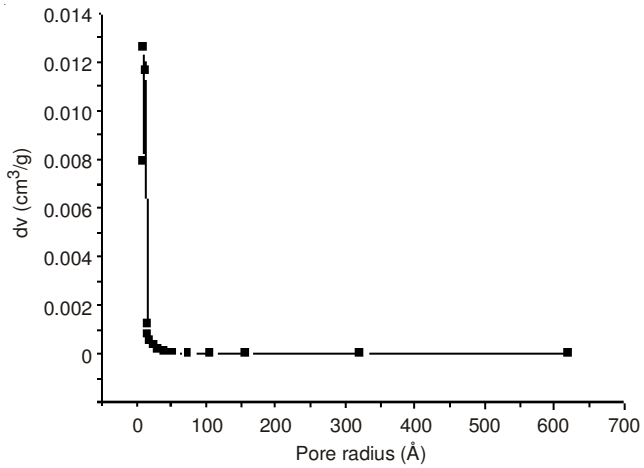

Fig. 2. Pore size distribution curve of the resin

The specific surface area of the resin was 501.04 m^2/g (Table-1) and average pore diameter was 1.128 nm. Obviously, the novel adsorptive polymer has the typical structural characteristics of porous adsorption resin, absorption peak of naphthalene on IR spectra is 546.8 and 1360.4 cm^{-1} and IR adsorption at 1074 and 1159 cm^{-1} proved that, the ether bonds exists on the novel hypercrosslinked resin (Fig. 3).

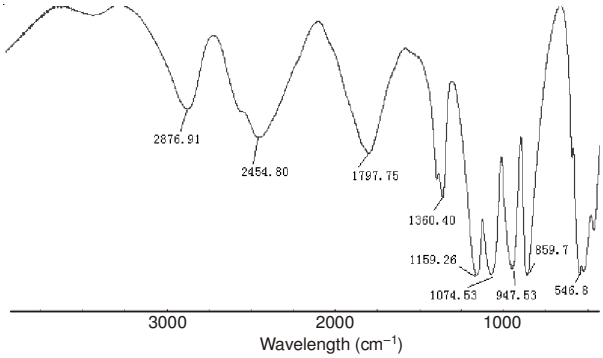

Fig. 3. IR spectrum of the resin

The elemental analysis data showed that the total content of C (73.36 %) and H (5 %) of the resin (total C and H = 78.38 %) was lower than the theoretic deta(theory: C and H = 100 %), all of these analysis results proved that the postcrosslinking reaction was inadequate,the further inverstigation is in progress.

Conclusion

1,4-*Bis*(chloromethoxyl)butane was first used to synthesis hypercrosslinked resin by a facile one-pot methord based on the Friedel-Crafts reaction. The resin had high surface area (501.04 m^2/g) and this study extend the synthetic methods of hypercrosslinked resins.

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