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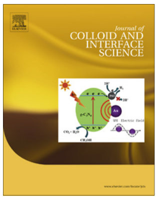

A novel polar-modified post-cross-linked resin: Effect of the porogens on the structure and adsorption performance

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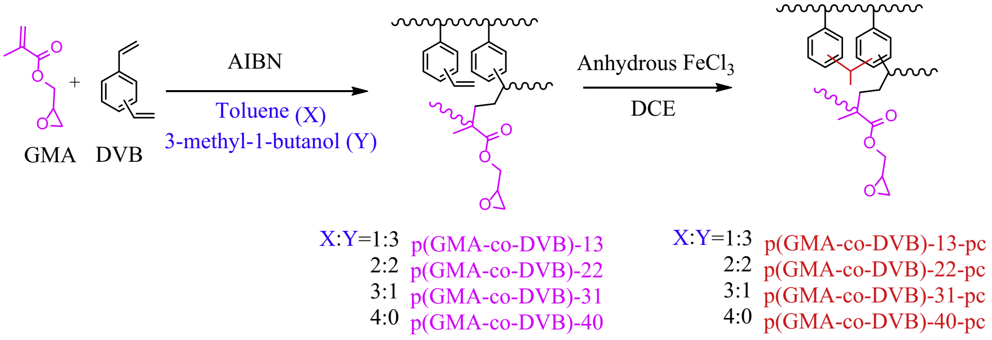
GRAPHICAL ABSTRACT

The porogens used in the polymerization play important roles in the pore structure and adsorption performance for the polar-modified post-cross-linked resins.



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ABSTRACT

The porogens used in the polymerization play important roles in the structure and adsorption performance for the polar-modified post-cross-linked resins. A series of novel polar-modified post-cross-linked resins were prepared using different mass percentage of toluene and 3-methyl-1-butanol as the mixed porogens. The results indicated that the resins using a higher mass percentage of toluene in the mixed porogens possessed a higher content of pendent vinyl groups, the greater Brunauer–Emmett–Teller (BET) surface area and *t*-plot micropore surface area. What's more, the Friedel–Crafts alkylation reaction induced a higher increment of the BET surface area and *t*-plot micropore surface area before and after the post-cross-linking. The resin p(GMA-co-DVB)-22-pc using 50% (w/w) of toluene and 50% (w/w) of 3-methyl-1-butanol in the mixed porogens held the largest equilibrium capacity to phenol among the four considered resins. The equilibrium data was well characterized by the Freundlich model and the isosteric enthalpy decreased dramatically with increasing of the fractional loading. The resin using a lower mass percentage of toluene in the mixed porogens required less time to reach equilibrium because of its less micropores and the minor diffusion resistance in the pores. p(GMA-co-DVB)-22-pc exhibited a dynamic saturated capacity of 55.4 mg/mL wet resin at an initial concentration of 1250 mg/L and a flow rate of 1.4 mL/min, and it could be completely regenerated by 0.001 mol/L of sodium hydroxide (w/v) and 80% of ethanol (v/v).

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1. Introduction

In recent years, porous materials are extensively used in various fields including energy [1–3], adsorption [4,5], separation [6], medicine [7] and catalysis [8], and hence have attracted increasing attentions. Hyper-cross-linked polymer (HCP) [9,10] possesses high Brunauer–Emmett–Teller (BET) surface area, well-defined porosity and tunable surface chemistry, and is recognized as one of the most efficient porous materials for capture of gases [11] and organic vapors [12], recovery of aromatic compounds [13,14] and removal of toxic trace metals [15]. It has also gained considerable interests as the adsorbing materials for high-performance liquid chromatography (HPLC), size-exclusion chromatography and solid-phase extraction [16,17].

Veverka and Jeřábek [18] reported that macroporous low cross-linked chloromethylated polystyrene was one of the most excellent precursors for synthesis of HCP, and the synthesized HCP contains the original macropores as well as the new micropores generated during the post-cross-linking process [19], which facilitate the transportation of the adsorbates and offer a much enhanced adsorption performance. However, the synthetic procedure for the corresponding HCP is frequently confronted with some problems, and the most serious one is utilizing the recognized carcinogen chloromethyl methylether (CMME) as the post-cross-linking reagent. As a result, more and more researchers have been exploiting new methods for design and synthesis of novel HCP without using CMME, including the modification of polystyrene by the Friedel–Crafts acylation reaction, the UV irradiation of benzoylated polystyrene and the self-assembly of the polymeric nanospheres [20]. Particularly, Macintyre et al. [21] and Bratkowska et al. [22] used vinylbenzyl chloride (VBC) as the polymeric monomer containing benzyl chloride to prepare another HCP, and they found that the obtained HCP also exhibited extremely high BET surface area and excellent adsorption performance. In the year of 1988, Ando et al. [23] firstly proposed another post-cross-linking method for fabrication of the post-cross-linked resin by consuming the residual pendent vinyl groups of the highly cross-linking polystyrene without adding external cross-linking reagent. A considerable number of pendent vinyl groups are located in the dense cores for the highly cross-linking polystyrene [24], and they can be further cross-linked with the neighboring aromatic rings by the Friedel–Crafts alkylation reaction, leading to an increased BET surface area and preferable pore structure [25,26].

To improve the surface polarity of the post-cross-linked resin, Zeng et al. [27–29] introduced polar monomers such as methyl acrylate (MA), ethylene glycol dimethacrylate (EGDMA) and vinyl pyridine (VP) in the polymerization. Ma et al. [30] used methyl methacrylate (MMA) as the polar monomer and prepared another polar-modified post-cross-linked resin. Specifically, the content of the pendent vinyl groups of the precursors as well as the increment of the BET surface area before and after the post-cross-linking is proven exactly dependent on the dosage of the polar monomer in the polymerization, and the pendent vinyl groups of the precursors cannot be detected as the polar monomer is up to 40% (mol/mol) [28]. Recently, we further improved the surface polarity of the post-cross-linked resin by introduction of certain specific amino/amide groups on the surface [31], and there appears an obvious improvement of the adsorption performance for the amino/amide-modified post-cross-linked resin.

The physicochemical character as well as the dosage of the porogens used in the polymerization plays an important role in the structure for the precursors as well as the post-cross-linked resins. Zhou et al. [32] found that the increment of the BET surface area before and after the post-cross-linking was much greater using a lower percentage of *n*-heptane in the mixed porogens, and the dosage of the porogens also greatly influenced the pore structure of the synthesized resins. Aleksieva et al. [33] reported that the content of the pendent vinyl groups of the precursors using 1,2-dichlorethane (DCE) as the porogen was a little higher than those using gasoline as the porogen. Moreover, the bimodal pore characteristic (macopores and micropores) was apparent for the precursors using gasoline as the porogen, and the Friedel–Crafts alkylation reaction influenced more significantly the big pores than the small ones. While only monomodal pores (mesopores) presented for the precursors using DCE as the porogen, and the pore volume remained essentially unchanged after the Friedel–Crafts alkylation reaction. Hao et al. [34] indicated that the post-cross-linked resin using toluene as the porogen held a much higher BET surface area than that using *n*-heptane as the porogen. However, to the best of our knowledge, no papers have reported the effect of the porogens on the adsorption performance of the post-cross-linked resins until now.

We propose that the porogens should also have great effects on the structure of the polar-modified post-cross-linked resin and its adsorption performance, and hence optimization of the porogens in the polymerization would be of significance for synthesis of efficient polar-modified post-cross-linked resin. To the best of our knowledge, there is no paper focusing on this topic. For this purpose, in the present study, glycidyl methacrylate (GMA) and divinylbenzene (DVB) were adopted as the polar monomer and the cross-linking reagent, toluene and 3-methyl-1-butanol were applied as the porogens, and a series of starting copolymers were prepared using different mass percentage of toluene and 3-methyl-1-butanol as the mixed porogens. The Friedel–Crafts alkylation reaction was then carried out for the starting copolymers and the polar-modified post-cross-linked resins with different pore structure were synthesized accordingly. The adsorption performance of the synthesized polar-modified post-cross-linked resins was comparatively evaluated using phenol as the adsorbate.

2. Materials and methods

2.1. Materials

GMA and DVB (purity: 80%) were purchased from Gray West Chengdu Chemical Co. Ltd., they were washed by 5% of sodium hydroxide (w/v) and followed by de-ionized water, and then dried by magnesium sulfate before use. The initiator 2,2-azobisisobutyronitrile (AIBN) was recrystallized by methanol. Toluene, 3-methyl-1-butanol, DCE, ferric (III) chloride and phenol were obtained from Yongda Chemical Co., and they were all analytical reagents and used without further purification.

2.2. Preparation of the starting copolymers

As shown in Scheme 1, the starting copolymers were prepared by a typical suspension polymerization. Briefly, the organic phase composed of GMA (1 g), DVB (19 g), AIBN (0.2 g), 3-methyl-1-butanol and toluene was added to the aqueous phase (200 mL) containing polyvinyl alcohol (PVA, 1 wt% in relation to water). GMA was the polar monomer, DVB was the cross-linking reagent and the cross-linking degree of the starting copolymers was set to be 95% (w/w). Toluene and 3-methyl-1-butanol were adopted as the porogens, the total mass of them was 40 g and the mass ratio between toluene and 3-methyl-1-butanol was defined as 1:3, 2:2, 3:1 and 4:0 (w/w), respectively. The reaction mixture was copolymerized at 358 K for 12 h and the starting copolymers labeled as p(GMA-co-DVB)-*XY* (*X* denotes the mass ratio of toluene, while *Y* represents that of 3-methyl-1-butanol) were collected, washed and extracted by petroleum ether in Soxhlet apparatus for 12 h and then dried under vacuum at 333 K for 8 h. The sieved starting