



Hyperbranched polymeric ionic liquid with imidazolium backbones for highly efficient removal of anionic dyes

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HIGHLIGHTS

- A novel hyperbranched polymeric ionic liquid ($hb\text{-PIm}^+\text{PF}_6^-$) was synthesized.
- The $hb\text{-PIm}^+\text{PF}_6^-$ exhibited high adsorption capacity toward anionic dyes.
- It selectively adsorbed the anionic dye from a mixture of cationic and anionic dyes.

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ABSTRACT

A hydrophobic hyperbranched polymeric ionic liquid ($hb\text{-PIL}$) with an imidazolium (Im^+)-salt backbone ($hb\text{-PIm}^+\text{PF}_6^-$) was proposed for efficient adsorption of anionic dyes. For this purpose, a hydrophilic $hb\text{-PIL}$ was first synthesized via the thiol-ene addition polymerization by the " $A_2 + B_3$ " method. Then, the anion exchange reaction of $hb\text{-PIm}^+\text{Cl}^-$ with KPF_6 afforded the target $hb\text{-PIm}^+\text{PF}_6^-$ adsorbent. $hb\text{-PIm}^+\text{PF}_6^-$ has high adsorption capacity toward anionic dyes. In contrast, it exhibits less adsorption amount toward cationic dyes. By using congo red (CR) as the model adsorbate, the adsorption mechanism of $hb\text{-PIm}^+\text{PF}_6^-$ was investigated in detail by Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray, and transmission electron microscopy analyses. The adsorption behavior of $hb\text{-PIm}^+\text{PF}_6^-$ towards CR was analyzed by two kinetic and four isotherm models. These results indicate the characteristic structure of $hb\text{-PIm}^+\text{PF}_6^-$ was responsible for its high adsorption capacity for CR. The main driving force for the CR adsorption was electrostatic attraction, carried out by the anion-exchange between CR and counter-ion PF_6^- of $hb\text{-PIm}^+\text{PF}_6^-$. The presence of the cavities formed by the branched chains provided storage sites for CR binding. In addition, the selective adsorption of $hb\text{-PIm}^+\text{PF}_6^-$ towards anionic dye could be used to purify cationic solution containing anionic dye.

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1. Introduction

The purification of industrial wastewater has become a crucial subject in the environmental field. Wastewater from textile, paper, plastic, and leather industries contain a large amount of dyes [1,2], which are of low biodegradability and are harmful to the environment [3]. For example, congo red (CR) is a typical acid dye and commonly used to give wool and silk red color with yellow fluorescence [4]. However, CR can be metabolized to benzidine, a human carcinogen [5,6]. Therefore, it is necessary to remove these dyes from the colored wastewater prior to discharge. Many techniques such as photocatalytic degradation [7], electrochemical method [8], biological treatment [9], and adsorption [10] have been used

to treat the colored water. The adsorption method is of low initial cost, flexibility, and operational simplicity [10,11]. Therefore, designing novel functional adsorbents for efficient adsorption of dyes is of significant interest [12–17].

Since numerous dyes are ionic (i.e., cationic or anionic) [1], the electrostatic attraction between an adsorbent and an adsorbate could markedly enhance the adsorption ability of the adsorbent [12–16]. For example, Gao et al. [12] synthesized carboxylic hyperbranched polyglycerol grafted $\text{Fe}_3\text{O}_4/\text{SiO}_2$ magnetic adsorbent ($\text{Fe}_3\text{O}_4/\text{SiO}_2/\text{HPG-COOH}$). The electrostatic interaction between the surface $-\text{COOH}$ groups of the adsorbent and the adsorbates caused it to exhibit a high adsorption capacity of 0.6 mmol g^{-1} (i.e., 245 mg g^{-1}) for cationic dye methyl violet, and this was more than twice of the previous magnetic adsorbents. Similarly, Zhou et al. [13] also used multicarboxylic hyperbranched polyglycerol to modify a calcined mesoporous silica SBA-15 and produced

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hybrid adsorbent SBA/HPG-COOH. The saturated adsorption capacity of SBA/HPG-COOH towards cationic dye methylene blue was 0.5 mmol g^{-1} (i.e., 187 mg g^{-1}), which was 10 times more than the amount adsorbed by nonmodified SBA-15.

Polymeric ionic liquids (PILs) [18] exhibit potential application in the adsorption of adsorbates including dyes [14–16,19–23], because of their ionic moieties, which can electrostatically attract adsorbates. For example, Yuan et al. [22] synthesized PIL poly(quaternary ammonium salt)-grafted PVBC microspheres (PVBC-g-PDMPMA⁺Br⁻), whose adsorption capacity towards phenol was 2.23 mmol g^{-1} (i.e., 210 mg g^{-1}). The ion exchange between phenol and the counter-ion Br⁻ was responsible for the adsorption. Imidazolium (Im⁺) salt-based PILs (PIms) have been used to adsorb anionic dyes, because their polymer chains bear cationic groups. The structure of the positive aromatic rings of PIms can provide strong electrostatic force as well as the weak interaction (i.e., π - π stacking [24]) for adsorbates binding. For instance, Kong et al. [16] synthesized a hydrophobic linear poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide) polymer (PIm⁺TFSI⁻), whose adsorption capacity towards acid dye methyl blue was 476 mg g^{-1} . The electrostatic attraction between PILs and adsorbates play an important role in the adsorptions. Obviously, the exposed IL moieties of PILs to the adsorbates (i.e., availability of the IL moieties of PILs for adsorbates) are prerequisite for the interaction. So far, the availability of the IL moieties was usually improved by increasing their porosity and specific surface area of PILs [14,15,23].

According to the above, if ionic liquid (IL) moieties are introduced into the backbone of a hyperbranched polymer (HBP) [25], the cavities are produced naturally around the IL groups [26]. Thus, the ionic groups on the HBP backbone were more accessible for guest molecules with counter charges, leading to the efficient adsorption of guest molecules around ionic groups by electrostatic attraction. The encapsulation of the cavities of a HBP was previously confirmed [26–28]. Therefore, a hyperbranched PIL (*hb*-PIL) may exhibit high adsorption capacity. However, to the best of our knowledge, this has not yet been explored. Herein, we report

a novel *hb*-PIL adsorbent, where IL groups are located on the HBP backbone. In this study, the *hb*-PIL with an Im⁺ backbone (*hb*-PIm⁺Cl⁻) was synthesized by the “A₂ + B₃” thiol-ene click polymerization (Scheme 1). The anion exchange of *hb*-PIm⁺Cl⁻ with KPF₆ afforded a hydrophobic adsorbent *hb*-PIm⁺PF₆⁻. The adsorption capacity and mechanism of *hb*-PIm⁺PF₆⁻ for anionic dyes were investigated in detail.

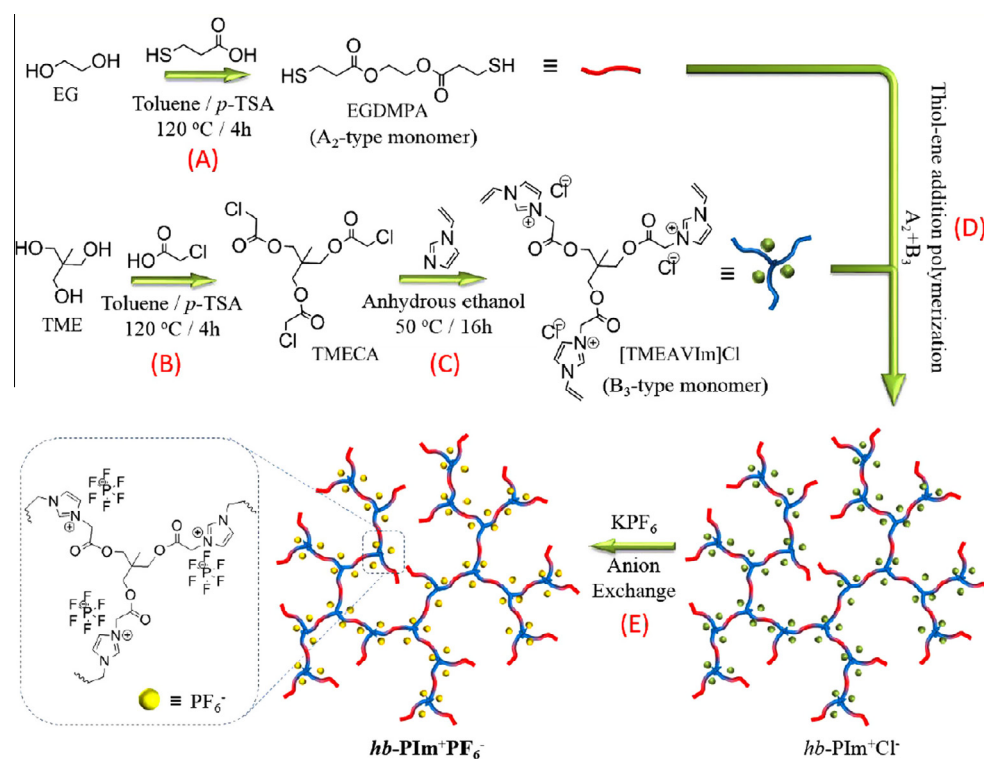
2. Experimental

2.1. Materials

2,2-azobisisobutyronitrile (AIBN, 98%) and trimethylolethane (TME, 97%), Acros; 3-mercaptopropionic acid (>99%), Sigma-Aldrich; N-vinyl imidazole (VIm, >98%), TCI. Potassium hexafluorophosphate (KPF₆, 99%), Aladdin Chemistry. Co. Ltd.; ethylene glycol (EG) and chloroacetic acid (CAA), Sinopharm Chemical Reagent Co. Ltd.; para-toluenesulfonic acid (*p*-TSA), Tianjin Kemiou Chemical Reagent Co. Ltd. (Tianjin City, China); congo red (CR), methyl orange (MO), acid fuchsin (AF), thymol blue (TB), methyl violet (MV), and malachite green (MG), Tianjin Hongyan Chemical Co. Ltd. (Tianjin City, China); and methylene blue (MeB), SERVA Electrophoresis GmbH. Co. Ltd. AIBN was recrystallized from methanol prior to use.

2.2. Characterizations

Nuclear magnetic resonance (¹H NMR) spectra were recorded using a Bruker Ascend 400 MHz spectrometer in CDCl₃ or D₂O. Fourier transform infrared (FTIR) spectra of the samples were recorded using a NICOLET iS10 spectrometer (Nicolet, USA) in the range 4000–400 cm⁻¹. Polymer samples for FTIR observation were prepared by casting thin polymer films on a KBr holder. UV-vis spectra were recorded using a spectrophotometer UV-2550 model (Shimadzu, Japan). The BET surface area and total pore volume of



Scheme 1. Synthesis route of the hyperbranched polymeric ionic liquid *hb*-PIm⁺PF₆⁻.

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