Hyper-crosslinked Porous Polymer Based on Bulk Rigid Monomer for Gas and Dye Absorptions

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Abstract   Using the rigid 3,3-bis(4-hydroxyphenyl)-2-(4-tritylphenyl)isoindolin-1-one with polar functional groups as a building block and formaldehyde dimethyl acetal(FDA) as crossinglinker, a new hyper-crosslinked polymer (HCP) was synthesized *via* Friedel-Crafts alkylation reaction promoted by anhydrous $FeCl_3$. The synthesized HCP is insoluble in boiled water and common organic solvents. Moreover, it shows a good CO_2 capture capacity even if its surface area is not very high, and the absolute CO_2 uptake capacity of it is 3.05 mmol/g. This can be attributed to the introduction of polar hydroxyl and lactam groups into the skeleton of the polymer, which provides effective adsorption sites for CO_2. In addition, the synthesized HCP also exhibits good adsorption capacity for organic dyes in water, especially for crystal violet.

Keywords   Hyper-crosslinked polymer; CO_2 adsorption; Dye adsorption

1   Introduction

Porous organic polymers(POPs) as an important subclass of porous materials have attracted more and more attention not only based on their high surface area, good thermal stabilities and low skeleton densities, but also owing to their potential applications in the fields of molecular separation, heterogeneous catalysis, drug delivery and gas storage[1—5]. So far, different kinds of POPs, such as covalent organic frameworks(COFs), hyper-crosslinked polymers(HCPs), polymers of intrinsic microporosity(PIMs), conjugated microporous polymers(CMPs), and porous aromatic frameworks(PAF), have been successfully developed[6—13]. Among them, HCPs are inexpensive and can be easily synthesized on a large scale[14]. Moreover, the highly crosslinked nature, lightweight property and high surface area endow them with high thermal stability that is not commonly expected for organic polymers, and good gas storage capacity, especially in the field of carbon dioxide capture[15]. For example, HCPs based on 4,4′-bis(chloromethyl)-1,1′-biphenyl(BCMBP) with Brunauer-Emmett-Teller(BET) surface areas up to 1470 m²/g can adsorb up to 7.4%(mass fraction) CO_2 at 100 kPa and 298 K[16]. Binaphthol-based HCPs show an improved CO_2 uptake capacity of 3.96 mmol/g due to polar hydroxyl functional groups incorporated into the network of HCPs enhanceing the interaction between the pore wall and CO_2 molecules[17]. More recently, Tan and co-workers[18] utilized a three-dimensional(3D) rigid paddle wheel shape monomer, triptycene, to prepare a triptycene based HCP(THPS), which displayed good CO_2 uptake capacity and extraordinary capability for water treatment with outstanding adsorption capacities for organic solvents and dyes. Therefore, HCPs can be considered as promising materials for

the application in the fields of clean energy and environmental issues.

HCPs can be prepared from various bulk aromatic compounds *via* Friedel-Crafts alkylation promoted by inexpensive $FeCl_3$[19]. This versatile method not only avoids using noble metal catalysts to offer an opportunity for producing cost-effective POPs, but also avoids the need for monomers with specific polymerization groups when an external linker, such as formaldehyde dimethyl acetal(FDA) is employed[20]. For example, when the tetrahedral building block tetraphenylmethane is used, this "knitting" method can produce the HCPs with BET surface area being up to 1470 m²/g and CO_2 uptake capacity of 2.95 mmol/g[21].

In this work, we described the synthesis of a new HCP constructed from the rigid 3,3-bis(4-hydroxyphenyl)-2-(4-trityl-phenyl)isoindolin-1-one building block with FDA as crossing linker and anhydrous $FeCl_3$ as catalyst. This bulk building block not only possesses a rigid tetrahedral building unit, which is a versatile constructor for producing HCPs with high surface area, but also is endowed with two kinds of polar functional groups, two hydroxyl groups and one lactam group, which can improve the selectivity for CO_2 capture. In addition, the intrinsic porosity of this building block can tailor the pore size to obtain HCPs with uniform micropores. The synthesized HCP exhibits good water stability and good CO_2 capture capacity. Moreover, it shows a good adsorption capacity for organic dyes, especially for crystal violet.

2   Experimental

2.1   Materials and Instruments

All chemicals and solvents were commercially available

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and used as received unless otherwise stated. 3,3-Bis(4-hydroxyphenyl)-2-(4-tritylphenyl)isoindolin-1-one was prepared according to the previously reported method[22].

FTIR spectrum was recorded on a Nicolet Impact 410 spectrometer between 400 and 4000 cm^{-1} using the KBr pellet method. Thermogravimetric analysis(TGA) was conducted on a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 800 °C. Solid-state ^{1}H-^{13}C cross polarization magic angle spinning nuclear magnetic resonance(CP/MAS NMR) measurements were performed on a Bruker Avance III model 400 MHz NMR spectrometer at an MAS rate of 5 kHz. Transmission electron microscopy(TEM) was performed on a JEM-1011 microscope. A nitrogen gas adsorption experiment was carried out with a Micrometrics ASAP 2020 instrument.

2.2　Synthesis

To a solution of 3,3-bis(4-hydroxyphenyl)-2-(4-tritylphenyl)isoindolin-1-one monomer(1 mmol) and FDA(0.36 mL, 8 mmol) in 5 mL of anhydrous CH$_3$CH$_2$Cl$_2$(DCE) was added FeCl$_3$(0.65 g, 8 mmol), and then the mixture was heated at 80 °C for 24 h under nitrogen atmosphere. After cooling to room temperature, the precipitate was collected by filtration and washed thoroughly with methanol to remove unreacted monomers or catalyst residues. Further purification was carried out by Soxhlet extraction with methanol for 24 h. After drying at 60 °C, brown-yellow powders were obtained with the yield of 94%. The samples used for characterization were activated under vacuum at 120 °C for 10 h before use.

2.3　Dye Molecule Adsorption

The sample(10 mg) was added into a water solution(8 mL) of methyl orange, ctystal voilet, or rhodamine B with the concentration of 20 μg/L at room temperature, respectively. Sam-

ples for analyses were taken from the reaction suspensions and immediately centrifuged to remove the powders of HCP. The adsorption of dyes was determined using a UV-Vis spectrometer at the maximum absorbance of each dye at specified reaction time.

3　Results and Discussion

The 3,3-bis(4-hydroxyphenyl)-2-(4-tritylphenyl)-isoindolin-1-one monomer was prepared by the method reported in the literature[22]. The ^{1}H and ^{13}C NMR spectra of it are shown in Fig.S1(see the Electronic Supplementary Material of this paper) and Fig.1, respectively. Then, based on this rigid building unit, a new HCP was synthesized via the well-developed Friedel-Crafts alkylation reaction in the presence of FDA and FeCl$_3$[17,23], as outlined in Scheme 1. The experimental results indicate the polymerization reaction can proceed smoothly and the insoluble substance slowly precipitates when the molecular ratios of FeCl$_3$ to the monomer are in the range of 4—8. However, if the quantity of FeCl$_3$ is increased to 10 mmol, the solid products quickly precipitate from the reaction mixture, which is unfavorable for the polymerization.
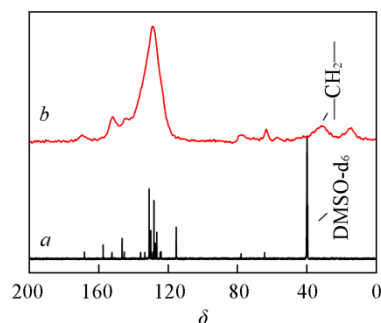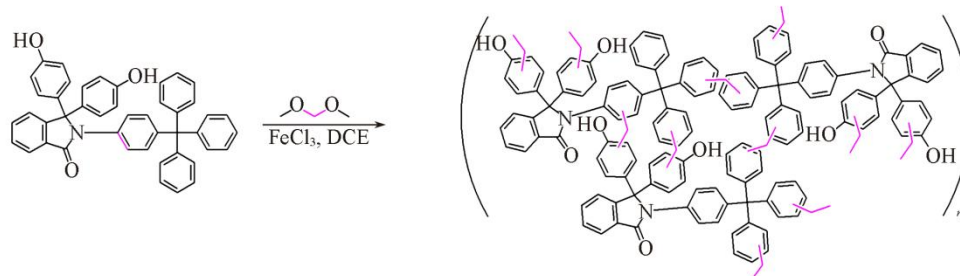

Fig.1　^{13}C NMR spectra of the monomer(*a*) and the synthesized HCP(*b*)

Scheme 1　Synthetic pathway of HCP

The chemical structure of the synthesized HCP can be confirmed by solid-state ^{13}C NMR spectra. As shown in Fig.1, the strong signals in the range of δ 152—128 are attributed to the aromatic carbon atoms. The signals at approximately δ 63 and 78 can be assigned to the quaternary carbon atoms in the tetrahedral building units and the cardo groups, respectively. This demonstrates that the structure of the monomer has been successfully introduced into the skeleton of the polymer. The signal near δ 30 is related to the methylene carbon atoms, further indicating that FDA participated in the reaction.

FTIR spectrum can further confirm the polymerization of the monomer and FDA. As shown in Fig.2, the weak peaks for
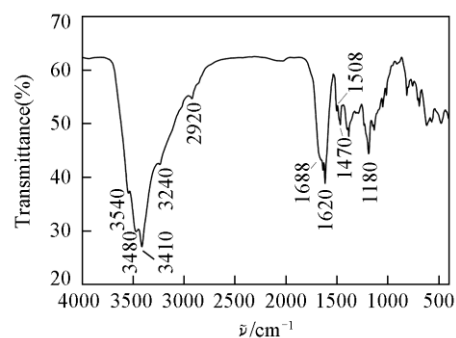

Fig.2　FTIR spectrum of the synthesized HCP

C—H stretching and bending vibrations at *ca.* 2920 and 1508 cm^{-1}, respectively, and the appearance of peaks for stretching vibrations of the methylene group at 2920 cm^{-1} reveal that the monomers are linked by methylene groups as desired. The peaks for aromatic C=C bands at *ca.* 1688 and 1620 cm^{-1} show the presence of phenyl rings in the HCPs, which is consistent with the expected networks. Additionally, the FTIR spectrum also clearly shows the presence of hydroxyl(*ca.* 3410 cm^{-1}) and lactam group (*ca.* 1700 cm^{-1}) in the network, respectively, indicating that the functional groups were well-retained.

The PXRD pattern(Fig.3) shows that the resulting polymeric materials are in an amorphous phase, which is common in kinetics-controlled irreversible coupling processes[24,25].
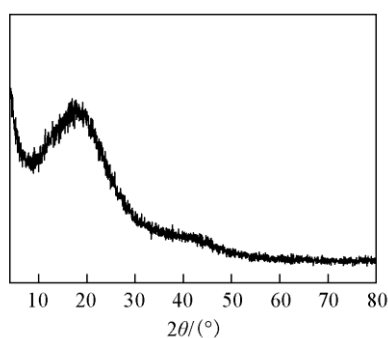

Fig.3 PXRD pattern for the synthesized HCP

The stability of HCPs is a vital factor for gas absorption and separation because HCPs with high stability can efficiently increase the recyclability to reduce the energy consumption and cost per cycle. The obtained HCP was insoluble in boiled water as well as common organic solvents such as hexane, methanol, acetone, chloroform, tetrahydrofuran(THF) and dimethylformamide(DMF). It indicates the synthesized HCP possesses good solvent resistance, which also confirms the occurrence of the crosslinking. The thermal stability of the synthesized HCP was studied by TGA, which was performed under air with a heating rate of 10 °C/min from the ambient temperature up to 800 °C. As shown in Fig.4, the synthesized HCP undergoes a rapid mass loss from 210 °C which can be attributed to the prior decomposition of the functional groups in the networks. It further confirms the high crosslinking degree of the synthesized HCP.
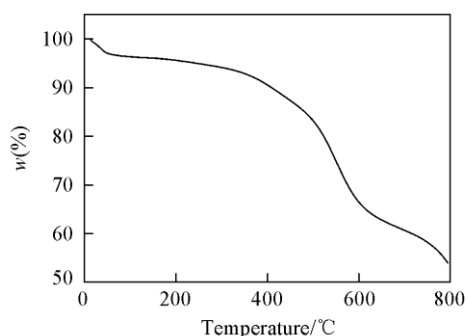

Fig.4 TG curve for the synthesized HCP

The porous property of the synthesized HCP was investigated by nitrogen adsorption analysis at 77 K. As shown in Fig.5, the synthesized HCP shows a typical Type I nitrogen gas sorption isotherm, indicating the existence of micropores in its network. The sorption isotherm of it shows a steep rise at high relative pressures(p/p_0>0.9), which might be attributed to the surface absorption of assembled small particles[25]. The apparent surface area calculated from the BET model is 382 m^2/g. Significant hysteresis observed in the desorption branch of the isotherm for the sample is consistent with elastic deformations or swelling as a result of gas sorption[26]. The median pore width calculated using the Horvath-Kawazoe(HK) method is 0.845 nm as listed in Table S1(see the Electroic Supplementary Material of this paper). The TEM image(Fig.6) shows the clearly porous textures in the synthesized HCP.
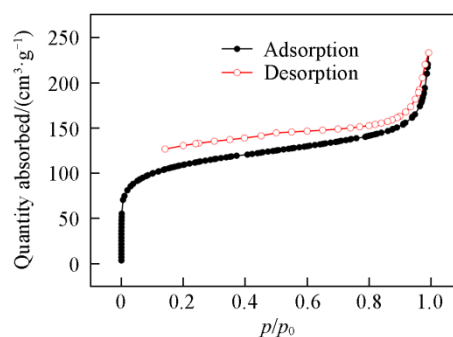

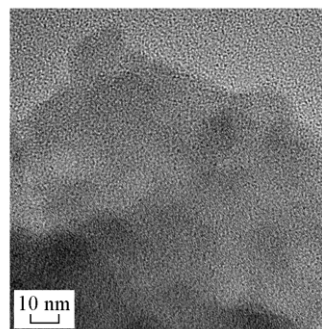**Fig.5 N$_2$ adsorption-desorption isotherm at 77 K of the synthesized HCP**

Fig.6 TEM image of the synthesized HCP

As is well known, the incorporation of electron-rich functional groups into a framework may provide polar adsorption sites, which could result in strong dipole-quadrupole interactions with CO$_2$ molecules, thus effectively improving the CO$_2$ adsorption capability of the material[27]. The CO$_2$ uptake of the synthesized HCP was also measured up to 100 kPa at 273 K. As shown in Fig.7, the absolute CO$_2$ uptake capacity of the synthesized HCP is 3.05 mmol/g, much higher than those of PAF-32(1.66 mmol/g) and its functionalized analogues(1.62 and 2.27 mmol/g)[25], MOP-A[21] with the surface area of 4077 m^2/g(2.65 mmol/g) and the covalent organic framework COF-102[28] with the surface area of 3620 m^2/g(1.56 mmol/g) at 100 kPa and 273 K. It demonstrates that the molecular structure and chemical nature of the monomer play significant roles in the CO$_2$ uptake capacity for HCPs besides the surface area.

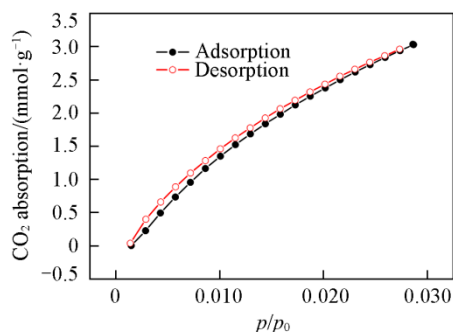Thus, the selection of suitable monomer are important in the design and synthesis of POPs.

Fig.7 CO_2 adsorption-desorption isotherm at 273 K of the synthesized HCP

As a result of rapid industrial development, dye molecules have been frequently observed pollutants of water and most of them are toxic and even carcinogenic[29,30]. Most dye molecules are stable to light and oxidants, thus it is difficult for them to be degraded in natural environment. Currently, the adsorption is a prominent strategy in dye removal due to its high efficiency, low cost and simple operation[31]. With the intrinsic pores and broad size distribution as well as good stability in water, HCPs can be used as promising adsorbents for dyes in wastewater[18]. Therefore, the capability of the synthesized HCP to capture dyes in water was also investigated.

We chose three organic dyes with different charges and sizes for this study: negatively charged methylene orange(MO^-) and positively charged crystal violet(CV^+) and rhodamine B(RD^+)(Table S2, see the Electronic Supplementary Material of this paper). First, we selected MO^- and CV^+ as models to evaluate the capability of the synthesized HCP for absorbing dyes in water. These two dyes possess similar sizes and molecular weights but different charges as summarized in Table S2.

Typically, 10 mg of the synthesized HCP was soaked in 8 mL of the water solution of MO^- or CV^+ without further disturbing, respectively. The dye-adsorbing capability of the synthesized HCP in the solution was estimated at certain time intervals using UV-Vis absorption spectroscopy. As shown in Fig.8(A) and (B), the synthesized HCP shows obvious adsorption for the two dyes, and compared with the anionic dye MO^-, the cationic dye CV^+ can be quickly and efficiently adsorbed. This may be attributed to the well-match of the charges between the dye and the synthesized HCP. Moreover, the absorption peak of the solution declines quickly up to 160 min, suggesting almost all the CV^+ is absorbed by the synthesized HCP. In contrast, the corresponding absorption of the RD^+ solution disposed by the synthesized HCP decreases gradually with the increase of the time and the RD^+ can be efficiently adsorbed with longer time, 430 min[Fig.8(C)]. The main reason for it is that RD^+ possesses larger size, thus the size effect is more obvious. These results demonstrate the synthesized HCP can be considered as a potential absorbent for the treatment of waste water.
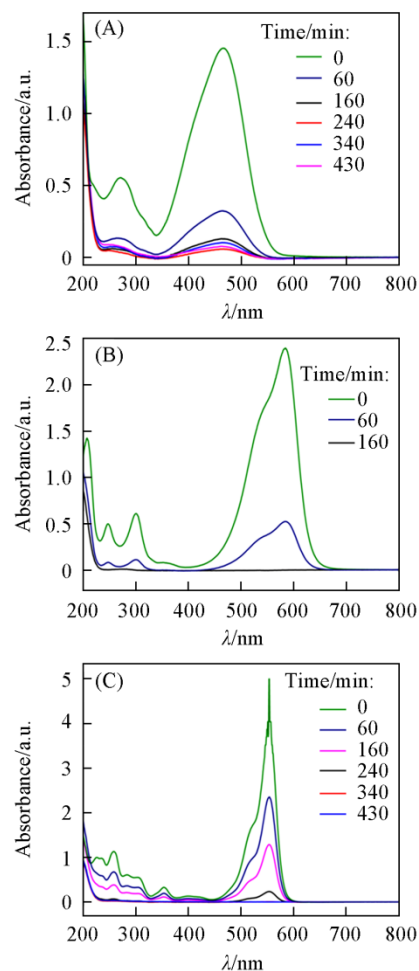

Fig.8   UV-Vis spectra of aqueous solution of MO^-(A), CV^+(B) and RD^+(C) with the synthesized HCP

4   Conclusions

In summary, using a rigid monomer, 3,3-bis(4-hydroxyphenyl)-2-(4-tritylphenyl)isoindolin-1-one, we have prepared a new HCP with good solvent resistance. Due to the introduction of hydroxyl and lactam groups into the skeleton of the polymer, the synthesized HCP displays a good adsorption capacity for CO_2 even if its surface area is not very high. In addition, the synthesized HCP shows a good adsorption ability for organic dyes in water. Thus, combined with the advantages of low cost, easy availability and water resistance, the synthesized HCP can be considered as a potential adsorbent for the application in the fields of clean energy and environmental issues. Further studies will focus on the design of other rigid monomers to prepare new functional POPs.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at http://dx.doi.org/10.1007/s40242-017-6467-5.

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