Synthesis and Characterization of O-Diphenol Triazine Microporous Polymer

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Abstract. A novel O-Diphenol Triazine Microporous Polymer was successfully synthesized by the one-step Friedel-Crafts reaction of cyanuric chloride and 1,2-Dihydroxybenzene (catechol) in the presence of dichloromethane and anhydrous AlCl₃ as solvents and catalyst, respectively. The polymer was characterized by FTIR, ¹³C CP/MAS NMR, XDR and TGA. The study found that the polymer is an amorphous structure containing trace amounts of quinines. The polymer has good thermal stability, and the 5% weight loss temperature is 260 °C under nitrogen conditions. The surface area of the polymer is 154.08 m²/g, the pore diameter is 5.55 nm and its distribution is mainly in the mesoporous region by adsorption-desorption of N₂ at 77 K.

Keywords: Microporous polymer of catechol triazine, free radical, anhydrous AlCl₃.

1. Introduction
Materials are the essential driving force for the development of the earth civilization, human beings play an important role in the exploration and application of new materials in the development of human civilization. Since the 21st century, with the rapid growth of population, the demand for energy is increasing. On the one hand, the increasing depletion of oil and mineral resources restricts the development of energy. On the other hand, the deteriorating living environment constantly rings the alarm for human beings, and it is urgent to solve the problem of environmental pollution. Through the unremitting efforts of researchers all over the world, a new kind of structural material porous material had been successfully discovered. Porous organic polymers (POPs) are a kind of important porous structural materials constructed by covalent bonds of C, H, O, N and other elements. Due to its high specific surface area, porosity, permeability, adsorption, low density, light weight and many other excellent physical and chemical properties, it can be widely used in adsorption and separation of gas and heavy metal ions, energy storage, heterogeneous catalysis, photoelectric materials and other fields [1-3].

In the synthetic design of POPs materials, the design of new link units can increase the surface area and pore volume, and adjust the appropriate pore size. In addition, the introduction of different functional groups, heteroatoms, unsaturated metals and other special active sites in the polymer network can improve or improve the performance and function of the material. Phenolic hydroxy group is a kind of typical functional group. Baohang Han [4] used bisphenol A and 1,2,4,5-tetrahydroxybenzene as raw materials to synthesize porous organic polymer containing polyhydroxy group. Zhimin Liu [5] reported
a template-free strategy for synthesis of phenolic azo-polymers with hierarchical porous structures based on diazo-coupling reaction in aqueous solution under mild conditions. Bhauwik[6] found that phenolic hydroxyl can make organic porous materials rich in nitrogen show stronger CO$_2$ absorption performance and CO$_2$/N$_2$ selective absorption. Mussel protein is known for its high adhesion ability under water. Most studies believe that among the adhesion proteins secreted by mussels, an amino acid residue (DOPA)[7] with 1,2-Dihydroxybenzene(catechol) groups plays a key role in strong adhesion. This kind of structure is very easy to react with oxygen to form quinone structure, so it is easier to combine with other groups[8]. In this paper, we try to use cheap and easy to get cyanuric chloride and catechol as raw materials to synthesize porous aromatic polymers with o-diphenol structure by one-step Friedel-Crafts reaction.

2. Experimental part

2.1. Experimental Materials
Cyanuric chloride was provided by Shanghai Meiruier Chemical Technology Co.Ltd., catechol was provided by Sinopharm Group Chemical Reagent Co. Ltd., and anhydrous aluminum trichloride was gifted by Shanghai Linen Technology Development Co., Ltd., which is with purity of 99% and can be for direct use. 1,2-dichloroethane, analytical pure, provided by Xilong Science Co. Ltd., dried by anhydrous magnesium sulfate, should be stored in 4 Å molecule sieves for standby.

2.2. Instrumentation and measurement
Fourier transform infrared (FTIR) spectra were recorded using the KBr pellet method on a Nicolet- iS50 spectrophotometer. $^{13}$C NMR spectra were obtained with a Bruker AVANCE III 400 MHz at an operating temperature of 25°C using a 4 mm dual channel magic angle rotating solid-state NMR probe with a rotating speed of 8 kHz, a contact time of 3.6 MS and a pulse delay of 3 ms. XRD test was carried out on the model of Ultima IV X-ray diffractometer. The scanning range of XRD is 5-60°, the scanning step is 0.02°, and the scanning speed is 10°/min. Thermogravimetric analysis (TGA) of the polymer was performed on a TA-Q50 thermogravimetric analysis instrument in a nitrogen atmosphere at a heating rate of 20°C/min$^{-1}$ from 100 to 800°C. The gas adsorption test was carried out on a physical adsorption instrument of Autosorb iQ. Before the test, the samples were degassed at 100°C for 24 h in a high vacuum system, and then the nitrogen adsorption desorption performance of the materials was tested at 77 K.

2.3. Examples of polymer synthesis
A typical polymer was prepared by cyanuric chloride (1.884 g, 10.0 mmol), catechol (1.652 g, 15.0 mmol) in anhydrous aluminum trichloride (6.667 g, 50.0 mmol) as a catalyst, and 1,2-dichloroethane (50 mL) as a solvent. The experimental conditions were that the reaction was carried out at room temperature for 2 hours, and then the temperature was raised up to reflux for 7 hours under the protection of nitrogen. The product was immersed in deionized water, followed by Soxhlet extraction with acetone, tetrahydrofuran, and absolute ethanol, followed by vacuum drying to obtain a purple-black solid powder sample, COF-CAT, with a yield of 21%.

3. Results and discussion
The FTIR spectrum was shown in Fig. 1. The results show that there were obvious characteristic absorption peaks at 1602 cm$^{-1}$, 1520 cm$^{-1}$, 1488 cm$^{-1}$, 1401 cm$^{-1}$ and 1376 cm$^{-1}$, which indicate the existence of triazine skeleton in the polymer, 1120 cm$^{-1}$ and 800 cm$^{-1}$ correspond to the characteristic absorption peak of C-Ar aromatic group and this shows that the substitution reaction between cyanuric chloride and catechol monomer has taken place. The $^{13}$C solid-state NMR spectrum was shown in Fig. 2. The absorption peak of 173 was the chemical shift of carbon in the triazine skeleton, and the absorption peaks of 125, 144, and 123 corresponded to the chemical shift of carbon in the catechol group,
respectively. A weak absorption peak appeared at 183, indicating that a small amount of phenol was oxidized to quinone.

![Figure 1. FTIR spectrum.](image1)

![Figure 2. $^{13}$C NMR spectrum](image2)

In this experiment, the effects of the amount of AlCl$_3$ catalyst and the reaction time on the polymerization yield were discussed. The study found that the yield increased first and then decreased with the increase in the amount of anhydrous AlCl$_3$. When the feed molar ratio of anhydrous AlCl$_3$ and cyanuric chloride reaches 5:1, the yield reaches the maximum value. Because catechol first reacts with anhydrous AlCl$_3$ to form a catechol aluminum complex, then it reacts with electron-rich cyanuric chloride to form the target polymer. The complex needed acidic conditions to dissociate the hydroxyl group, and finally the target ortho-hydroxyl group was obtained. The recycling efficiency of the catalyst was very low, so the reaction needed to add excess anhydrous AlCl$_3$. With the further increase of the amount of anhydrous AlCl$_3$, the concentration of the reaction system increased, the side reactions increased, and the polymer agglomeration, the difficulty of separation increased, and ultimately the yield decreased. Considering comprehensively, the optimum amount of anhydrous AlCl$_3$ and cyanuric chloride is to be 5:1. The polymerization yield increased with the reaction time, and the yield reached the maximum value at 7 h.
The thermal stability of the polymers was investigated using TGA at a heating rate of 20°C/min under nitrogen atmosphere. Their onset temperatures of 5% weight loss are above 260°C, and the amount of residual slag is about 42% at 800°C, indicating good thermal stability of the polymers. The XRD spectrum of the polymer shows no obvious strong diffraction peak, which indicates that the polymer is amorphous. The pore structure of the material was analyzed by N₂ adsorption-desorption curve adsorption behavior at 77K. The specific surface area of the polymer is calculated by the multi-layer adsorption theory to be 154.08 m²/g, the pore diameter is 5.55 nm and the distribution is mainly in the mesopore area. The isotherm is characterized by a mixture of typical Class I and Class IV adsorption curves. There is a significant hysteresis loop between the desorption curve and the adsorption curve, which indicates that the polymerization reaction has insufficient crosslinking density and forms a large number of mesoporous structures.
4. Conclusion
In this paper, the O-diphenol triazine microporous polymer was successfully synthesized by one-step Friedel Crafts reaction using cheap and easily available cyanuric chloride and catechol as raw materials. The polymer was characterized by FTIR, $^{13}$C CP/MAS NMR, XDR and TGA. The study found that the polymer contained a small amount of quinoid structure, which was shown to have good thermal stability, a large amount of mesoporous structure, and a specific surface area of 154.08 m$^2$/g. This type of polymer has potential application value in the fields of gas adsorption / separation.

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