

Synthesis of microporous organic polymers based on chloride – derivatives as structural unit

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Abstract: Microporous organic polymers are currently an important class of porous polymers that have been studied extensively. These polymers have advantages of good chemical and physical stability. The high surface area is a salient feature in comparison with traditional porous materials. Due to the predominant characteristics, they have attracted attention in a number of technological applications. In this paper, we present how these organic polymers were synthesized from aromatic compound of 4,4-Bis (chloromethyl)-1,1 Biphenyl 95% (BCMBP) in dichloroethane (DCE) or BCMBP and Dichloro-p-xylene (DCX), and their characteristics. Properties of these polymers and co-polymer were characterized by FT-IR, SEM, TGA, and BET methods. Polymer synthesized show high BET specific surface areas. S_{BET} are high from 1598.36 m²/g to 1761.34 m²/g and average pore width from 51.8 - 43.8 Å. These polymers are also stable at around 300 – 350 °C.

Keywords: Microporous Organic Polymers, BCMBP, Friedel-Craft alkylation.

1. INTRODUCTION

Microporous solids always are important materials that have been interested. Microporous organic polymers are important class, which are networks constructed from small organic building blocks. The materials exhibit a large surface areas, small pore sizes and low density. These characteristics let the microporous organic polymers have attracted attention due to their potential use in applications such as catalysis (Li B., 2012), chemical separations (Luo Y, 2012), gas storage (Chen Q., 2012), electrical energy storage (Venkata K.R., 2014). During last decades, microporous organic polymers have been developed in to different groups, such as: hypercross-linked polymers (HCPs), polymers of intrinsic microporosity (PIMs), covalent organic frameworks (COFs) and conjugated microporous polymers (CMPs) (Feng X., 2012). The design and synthesis of novel building blocks has been recognized as one of the most important driving forces for the great advance in microporous organic polymers. Thus, numerous microporous polymer based adsorbents have been developed, mainly using approaches of Friedel-Crafts alkylation, palladium catalyzed Suzuki-Miyaura reactions, Sonogashira-Hagihara and Buchwald-Hartwig cross-coupling reactions, Nickel catalyzed Ullmann coupling reactions, and oxidative coupling polymerization (Robert D., 2012). Nevertheless, it still remains a great challenge to synthesize microporous organic polymers with rational design at molecular level by using cost-effective and simple pathways for the polymerization. The hypercross-linked polymers are often synthesized from aryl halides and aromatic hydrocarbons mixture (Robert D., 2012). However, this report shows the synthesis of microporous organic polymer network directly synthesized from 4,4-Bis (chloromethyl)-1,1 Biphenyl (BCMBP) in DCE solvent under Friedel-Crafts alkylation promoted by iron (III) chloride.

2. MATERIALS AND METHODS

2.1. Materials

All chemical reagents were commercially available. 4,4-Bis (chloromethyl)-1,1 Biphenyl 95 % (BCMBP) was purchased from Aldrich. Dichloro-p-xylene (DCX) 98% and dichloroethane (DCE) 99 % were obtained from AK Scientific Inc. Iron (III) chloride 98 % and methanol 99 % were obtained from P.R.China.

2.2. Synthesis of microporous polymer network

The samples were prepared by reactions of BCMBP in solvents at various conditions of temperature and time of reactions. The scheme of these processes was shown in Figure 1. On the other hand, the synthesis of MOPs also was studied based on reaction between BCMBP and DCX at the time of 24 hours and temperature of 80°C. During this process, DCX was stirred in DCE solvent, and then mixed with BCMBP at the first step. The other steps were repeated as Figure 1. The conditions of reaction for these samples were selected in table 1.

2.3. Characterization

The FT-IR spectra were obtained using a spectrometer of Jasco FT-IR 4600 by Nujol method with KBr pellets. Size and morphology of the samples were observed under a field-emission scanning electron microscope. SEM observation was carried out using a Hitachi S-4800 microscope (Hitachi Ltd., Japan) at an accelerating voltage of 6.0 kV. Nitrogen adsorption isotherms at 77 K were measured in liquid-nitrogen baths with Micromeritics Gemini VII 2390 V1.02. TGA was performed on a LabsysEvo S60/58988 – Setaram (France) at a heating rate of 10 °C min⁻¹ with air as carrier gas.

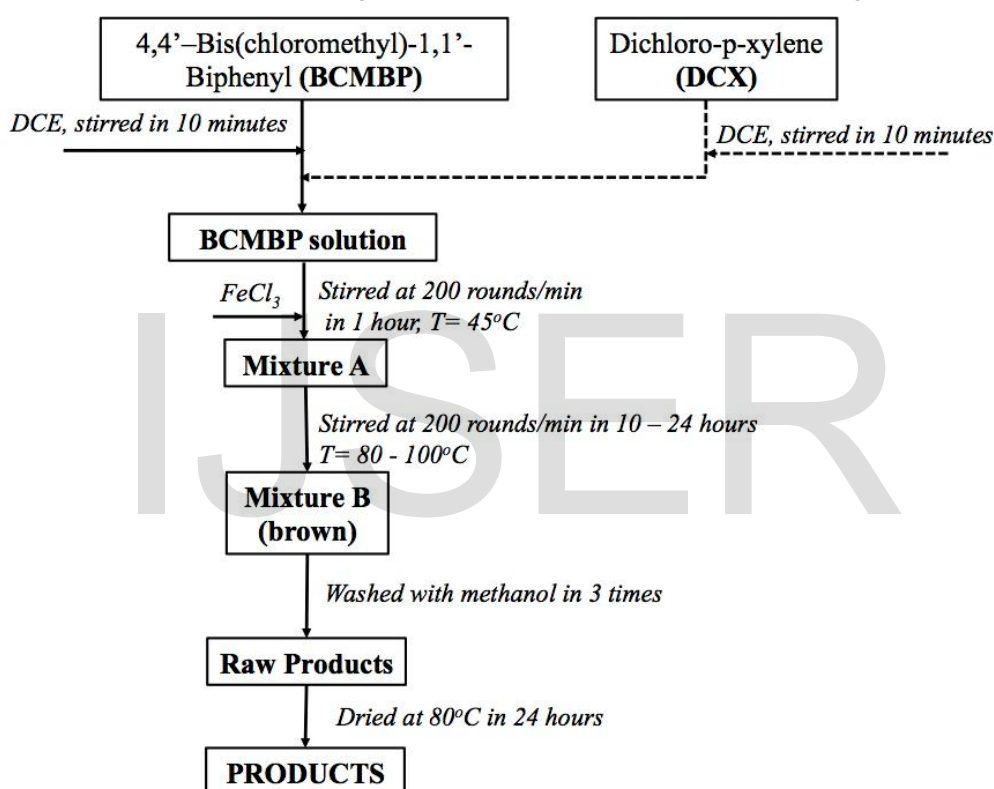


Figure 1: Scheme of MOPs synthesis from BCMBP (or BCMBP and DCX)

Table 1: Polymers synthesized

Sample	Reaction substances (molar ratio)			Time of reaction (hours)	Temperature of reaction (°C)
	BCMBP	DCX	DCE		
BC-DX_1.3	1	3	10	12	80
BC-DX_1.1	1	1	10	12	80
BC-DX_3.1	3	1	10	12	80
BC-DX.1	1	0	10	24	80
BC-DX.2	1	0	10	20	80
BC-DX.3	1	0	10	10	80

BC-DX.4		1		0	10	24	100
BC-DX.5		1		0	10	24	90
BC-DX.6	1	0	10	24	80		

3. RESULTS AND DISCUSSION

The polymerization of BCMBP or BCMBP and DCX in DCE solvent at various conditions of temperature and time give products of light brown to dark brown insoluble powders after cleaning and drying. These compounds could be contributed base on the aromatic ring blocks (Shujun X., 2013).

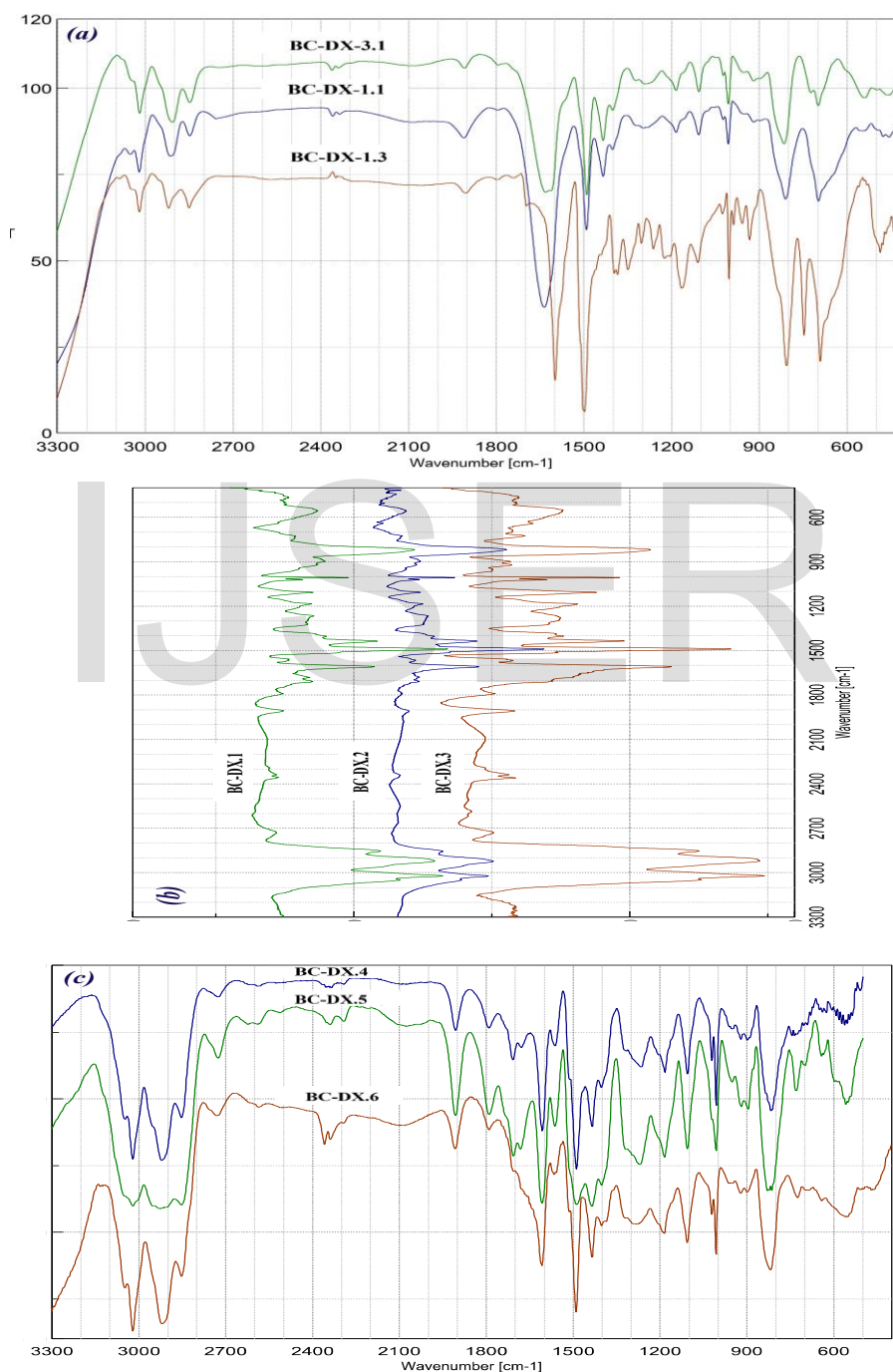


Figure 2: FT-IR spectra of the networks at various time and temperature samples synthesized with BCMBP, DCX

FT-IR

The FT-IR of samples synthesized at the ratio of BCMBP : DCX of 1:3, 3:1, and 1:1 are presented on Figure 2a. The samples synthesized with BCMBP in DCE at various time from 10 hours to 24 hours and temperature from 80 °C to 100 °C presented in Figure 2b, 2c. As shown in Figure 2, FT-IR spectroscopy revealed that there was indeed a true co-polymerization. For instance, the spectra of samples exhibited unsaturated C = C vibration at 1500 cm⁻¹, 1600 cm⁻¹, and the characteristic vibration of 1,4-substitution at 810 cm⁻¹, that meaning the containing of para-substitution compound based on BCMBP and DCX. The band at 2915 cm⁻¹ ascribed to C - H stretching vibrations originating from - CH₂ - of BCMBP and DCX, and the band at 3030 cm⁻¹ ascribed to vibrations of - C - H in aromatic rings. The conversion of the functional groups of BCMBP and DCX can be derived from the intensity of the characteristic bands at 1190 cm⁻¹ and 690 cm⁻¹, which are attributed to the wagging and stretching vibration of the CH₂ - Cl group, respectively. As only minor bands were observed in the spectra of all the samples at these wavenumbers, it can be supposed that the crosslinking was almost quantitative.

SEM

The morphologies of the samples were investigated by scanning electron microscope (SEM) (Figure 3). As in Figure 3, all samples consist of spheres, with regular large particles. However, BC-DX.4 sample shows a little fused particles. This could be this sample was synthesized at higher temperature than the others.

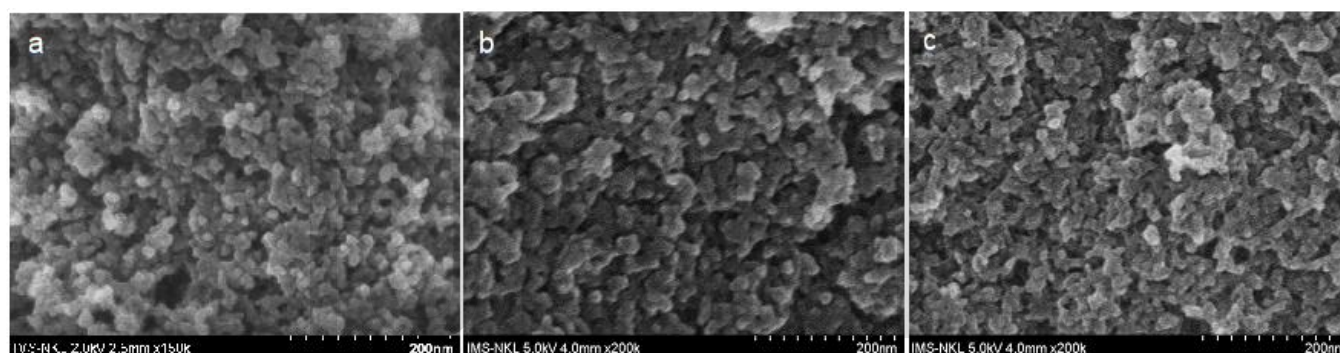


Figure 3: SEM images of the surface of samples: (a) BC-DX.3, (b) BC-DX.1, (c) BC-DX.4

TG-DTA

The TGA results of samples under air condition are presented in Figure 4. As shown in Figure 4, thermal gravimetric analysis (TGA) indicated that all samples were thermally stable up to a temperature of 350 °C in air and were completely destroyed at 520 °C. Due to weaker stability of methylene linkers compared with aromatic rings, these samples began to degrade at approximate 350 °C.

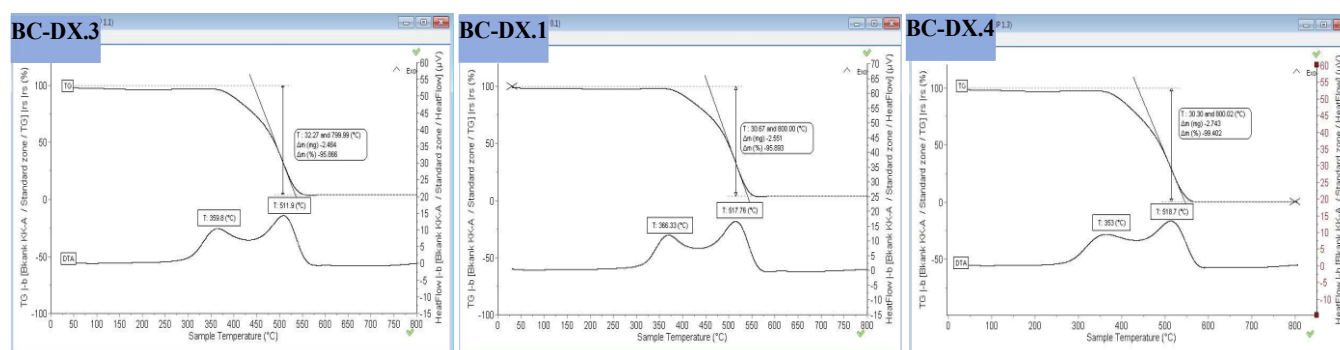


Figure 4: TGA data of samples: (a) BC-DX.3, (b) BC-DX.1, (c) BC-DX.4

BET - Surface area and pore size distribution

The polymers were based on blocks of aromatic rings (Shujun X., 2013). The crosslinking leaves the polymer chains locked in an expanded form. When the solvent is removed from the system, the space that it had previously occupied becomes pore volume and a network of intercommunicating pores is left behind (Germain J., 2009). The nitrogen adsorption and desorption isotherms at 77.3 K and pore size distribution analysis of samples were calculated and shown in table 2. This table summarizes the information about surface area followed by Brunauer-Emmett-Teller (BET) and Barrett-Joiner-Halenda (BJH) procedures, pore volume properties of these samples.

Table 2: Porosity properties of microporous polymers

Sample	BET surface area (m ² /g)	BJH adsorption surface area, (m ² /g)	BJH desorption average pore width, Å
BC-DX_1.3	1476.36	1389.82	55.63
BC-DX_1.1	1656.04	1558.18	50.36
BC-DX_3.1	1663.02	1557.52	43.49
BC-DX.3	1635.31	1595.71	48.21
BC-DX.1	1761.84	1717.18	43.78
BC-DX.6	1739.06	1686.26	45.46
BC-DX.5	1598.36	1489.62	51.36

Listed in Table 2 are the keys structural properties derived from the isotherm data such as BET surface area data, BJH adsorption specific surface area data, and pore volumes. The BET specific surface area values for these polymers range from 1598.36 m²/g to 1761.34 m²/g, which are calculated in commonly used relative pressure (P/P₀) ranging from 0.05 to 0.2. Along the increasing of temperature in the reaction, surface areas of the samples decreased systematically. The higher temperature of synthesis could get the particles lightly fusion. So the temperature was selected is 80°C. On the other hand, time of reaction also lightly affect to the products. At 24 hours, polymer shows the best specific surface area. In comparison, the sample was contributed base on two kinds of halides aromatic show lower BET surface areas than polymer from substance of BCMBP. A reasonable explanation for this result was that DCX content changed the polymer crosslinking levels, which in turn led to lower porosities and surface areas (Wood C., 2007).

4. CONCLUSION

Microporous polymer was synthesized from 4,4-Bis-(chloromethyl)-1,1-Biphenyl (BCMBP) or BCMBP and Dichloro-p-xylene (DCX) using a Friedel-Crafts alkylation process promoted by anhydrous FeCl₃. These samples were light brown to dark brown powders, which were not soluble in any common organic solvents. They remained stable up to 300°C – 350 °C in air. The BET specific surface areas for the obtained networks were high from 1598.36 m²/g to 1761.34 m²/g and pore width average from 51.8 – 43.8 Å. The polymers were synthesized from BCMBP show greater surface areas than sample synthesized from BCMBP and DCX. The advantage conditions for the synthesis are temperature of 80 °C, and time duration of 24 hours. With high surface area, and stability in chemical and medium temperature environment, these microporous polymers are promising candidates for potential application for adsorption such as capture of CO₂, H₂ or gas separation.

ACKNOWLEDGMENTS. The present research was financially supported by the Ministry of Education Training (MOET).

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