

Transesterification Between Diphenyl Carbonate and 1,6-Hexandiol Catalyzed by Metal-Organic Frameworks Based on Zn²⁺ and Different Aromatic Carboxylic Acids

LIPING WANG^{1,2,*}, GONGYING WANG², FAN WANG¹ and PINHUA LIU¹

¹College of Chemistry and Chemical Engineering, Qujing Normal University, Open Economic Zone Xishan, Qujing 655000, Yunnan, P.R. China

²Chengdu Institute of Organic Chemistry, Chinese Academy of Science, Chengdu 610041, Sichuan Province, P.R. China

*Corresponding author: Tel: +86 874 8998658, E-mail: wanglp_csu@163.com

(Received: 26 July 2012;

Accepted: 8 April 2013)

AJC-13212

Metal-organic frameworks based on metal ion Zn²⁺ and different aromatic carboxylic acid ligands were prepared by the solvothermal method and characterized by X-ray diffraction and Fourier transform infrared spectroscopy. They were then used as the catalysts for the preparation of polycarbonate diol *via* the transesterification between diphenyl carbonate and 1,6-hexandiol. Their catalytic activities in the transesterification process were evaluated by the yield of phenol and their catalytic activities in the polycondensation process were determined by the number-average molecular weight (M_n) and the hydroxyl value. The experimental results show that metal-organic frameworks made from Zn²⁺ with benzene-1,4-dicarboxylic acid and benzene-1,3,5-tricarboxylic acid exhibit higher catalytic activities than metal-organic frameworks made from Zn²⁺ with benzene-1,3-dicarboxylic acid and benzene-1,2-dicarboxylic acid for the preparation of polycarbonate diol.

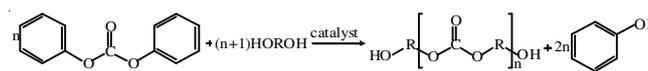
Key Words: Transesterification, Metal-organic frameworks, Aromatic carboxylic acid, Catalyst.

INTRODUCTION

Polyurethanes are well known class of valuable engineering plastics with wide applications. The structure of polyurethane can be complex and diverse containing hard and soft segments which contribute to the balance between rigid and elastomeric properties. In the conventional polyurethanes, soft segments usually originate from polyether or polyester diols. However, polyurethanes based on polyester diols are susceptible to hydrolysis and those based on polyether diols are unstable under oxidative conditions. In contrast, polyurethanes based on aliphatic polycarbonate diols are resistant both to hydrolysis and oxidation. Additionally, polyurethanes containing oligo-carbonate soft segments exhibit high tensile strength and modulus^{1,2}.

Several alternative non-phosgene methods have been proposed, including the polymerization of six and seven-membered cyclic carbonates³, the copolymerization of oxiranes with CO₂⁴ and the transesterification between organic carbonate and diol⁵⁻¹⁰. Among these methods, the transesterification between diphenyl carbonate (DPC) and aliphatic, as shown in **Scheme-I**, is regarded as a promising route to prepare polycarbonate diol. The diphenyl carbonate is an environmentally friendly chemical and widely available since it has been commercially produced *via* the transesterification between diphenyl

carbonate and phenol¹¹. Moreover, the side product phenol can be recycled to synthesize diphenyl carbonate.



Scheme-I: Synthesis of polycarbonate diol *via* the transesterification between diphenyl carbonate and aliphatic diol

Various catalysts have been developed for the transesterification between organic carbonate and aliphatic diol, including homogenous catalysts such as alkali metal alkoxides, titanium esters, organotin compounds and heterogeneous catalysts such as Mg-Al layered double hydroxides. Though the heterogeneous catalysts are easy to separate and recover for reuse, their low catalytic activities impede their industrialization. Unfortunately, the disadvantages of these homogenous catalysts are obvious. For example, alkali metal alkoxides catalysts that remain in the products frequently adversely influence the subsequent pre-polymer preparation. Titanium esters show high catalytic activities, but they are unstable and sensitive to the moisture in the air. Organotin compounds exhibit low catalytic activities and are toxic. Thus, the development of more efficient catalysts is desirable.

Metal-organic frameworks (MOFs) are a new class of crystalline microporous materials. They are prepared by the

copolymerization of multidentate organic ligands with transition metal ions or metal-containing inorganic clusters. They all have three-dimensional frameworks with channels and cavities in them¹². Due to their high surface areas, microporosity, well-defined structures and good chemical tenability, metal-organic frameworks are widely applied in the gas storage, separation, heterogenous catalysis, magnetism, electronics and so on¹³. Of these applications, the catalytic property of metal-organic frameworks is very fascinating. In this work, metal-organic frameworks based on Zn^{2+} and different aromatic carboxylic acid ligands were prepared and used as the catalyst in the transesterification between diphenyl carbonate and 1,6-hexandiol (1,6-HD). The experimental results shows that metal-organic frameworks made from Zn^{2+} with benzene-1,4-dicarboxylic acid (H_2BDC) and benzene-1,3,5-tricarboxylic acid (1,3,5- H_3BTC) ligands exhibit higher catalytic activities for the synthesis of polycarbonate diol.

EXPERIMENTAL

The zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.0 %, Shanghai Xinbao Fine Chemical Plant), benzene-1,4-dicarboxylic acid (H_2BDC , 99.0 %, Shanghai Runjie Chemical Reagent Co. Ltd.), benzene-1,3-dicarboxylic acid (*m*-phthalic acid) (1,3- H_2BDC , 99.0 %, Shanghai Huadong Reagent Company), benzene-1,2-dicarboxylic acid (*o*-phthalic acid) (1,2- H_2BDC , 99.0 %, Shanghai Sanai Reagent Co. Ltd.), benzene-1,3,5-tricarboxylic acid (1,3,5- H_3BTC , 99.0 %, Shanghai Bangcheng Chemical Co. Ltd.) and *N,N*-dimethylformamide (DMF, 99.0 %, Shanghai Runjie Chemical Reagent Co. Ltd.) were used to prepare metal-organic frameworks.

The diphenyl carbonate (DPC, 96.0 %, Chongqing Changfeng Chemical Plant) and 1,6-hexandiol (1,6-HD, 97.0 %, Shanghai Runjie Chemical Reagent Co. Ltd.) were used to prepare polycarbonate diol. All the reagents were used without any further purification.

Preparation of the catalyst: Metal-organic frameworks were prepared by the solvothermal method. 4.84 g $Zn(NO_3)_2 \cdot 6H_2O$ and 1.36 g H_2BDC , 1,3- H_2BDC , 1,2- H_2BDC or H_3BTC were dissolved in 100 mL DMF. The solution was sealed in a 250 mL round flask and kept at 100 °C for 24 h. The precipitate was collected by filtration and washed by DMF. The solid was dried at 90 °C in vacuum and then stored in a vacuum desiccator.

The catalysts based on H_2BDC , 1,3- H_2BDC , 1,2- H_2BDC and 1,3,5- H_3BTC ligands were denoted as MOF-A, MOF-B, MOF-C and MOF-D, respectively.

Preparation of polycarbonate diol: During the transesterification process, 0.14 mol diphenyl carbonate, 0.17 mol 1,6-hexandiol and the catalyst were introduced into a 100 mL flask equipped with a thermometer, a mechanical stirrer and a reflux condenser. The reactor temperature was gradually increased to 198 °C at the nitrogen atmosphere. This process continued until there was no phenol distilled off. During the polycondensation process, the reactor temperature was decreased to 183 °C and the pressure was reduced to 3.0×10^3 Pa over a period of 35 min. Then such conditions were remained for 3 h.

Measurements: The X-ray diffraction measurements were conducted on a Rigaku D/max 2500 PC powder X-ray diffractometer using $CuK\alpha$ radiation. The Fourier transform

infrared spectrums were recorded on a Nicolet 560 FTIR spectrometer. The specific surface area measurement and pore analysis were carried out on a Micromeritics ASAP 2020 V3.00 H (USA) surface area analyzer by N_2 adsorption at 77 K. A Shimadzu GC-2010 gas chromatograph equipped with a flame-ionization detector was used to qualitatively and quantitatively analyze the distillate. The 1H NMR and ^{13}C NMR spectrums were performed on a Bruker ACANCE III 500 MHz using deuterated chloroform ($CDCl_3$) as the solvent. The molecular weight analysis of the product was carried out on a WATERS gel permeation chromatograph in DMF solution and the calibration curve was made using a standard sample of mono-dispersed polystyrene.

RESULTS AND DISCUSSION

Characterization of the catalyst: The metal-organic frameworks based on Zn^{2+} and different aromatic carboxylic acid ligands were demonstrated by XRD and FTIR spectroscopy. The results are shown in Figs. 1 and 2.

As shown in Fig. 1, the main peaks of MOF-A are observed at 8.8, 14.08, 15.62, 17.64, 28.58, 30.40, 31.02 and 36.68°. The main peaks of MOF-B are observed at 9.02, 15.24, 16.88, 22.02 and 25.14°. The main peaks of MOF-C are observed at 9.04, 15.26, 16.90, 22.02 and 25.10°. The main peaks of MOF-D are observed at 10.08, 31.64, 34.32 and 36.10°. All the reflection peaks of these metal-organic frameworks are well matched with the peaks reported in Ref.¹⁴⁻¹⁷.

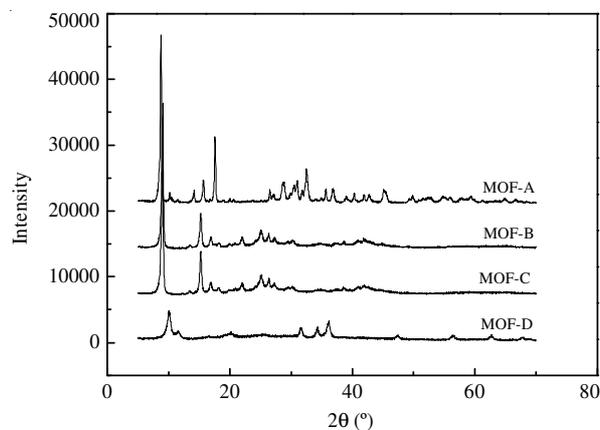


Fig. 1. XRD patterns of metal-organic frameworks

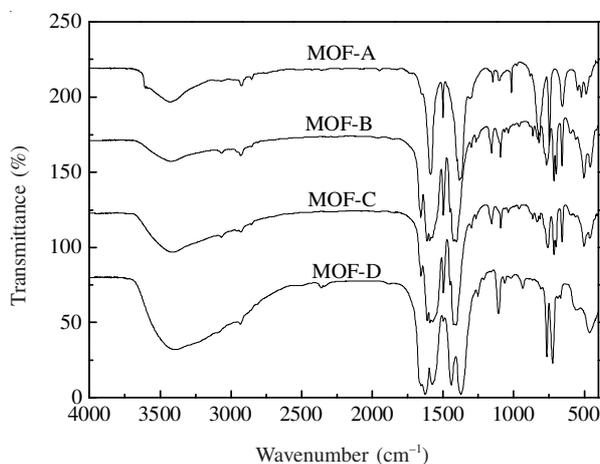


Fig. 2. FTIR spectrums of metal-organic frameworks

As shown in Fig. 2, the peaks around 1580 and 1500 cm^{-1} correspond to the asymmetric stretching vibration of $-\text{COO}^-$. The peaks at around 1400 and 1330 cm^{-1} are attributed to the symmetric stretching vibration of $-\text{COO}^-$. The peaks at 1150-1000 cm^{-1} represent the in-plane bending vibration of C-H. The peaks at 830-673 cm^{-1} correspond to the out-of-plane bending vibration of C-H.

Catalytic activity of metal-organic frameworks: The catalytic activities of metal-organic frameworks in the transesterification process is determined by the yield of phenol (y) defined as $y = (m/26.36) \times 100 \%$, where m is the amount of phenol produced and the value 26.36 is the amount of phenol produced when 0.14 mol diphenyl carbonate is completely reacted with 1,6-hexanediol. In the polycondensation process, the catalytic activities of metal-organic frameworks are evaluated by the number average molecular weight (M_n) and the hydroxyl value of polycarbonate diol.

Table-1 shows the effect of different catalysts on the process of polycarbonate diol preparation. As shown in Table-1, when metal-organic framework based on Zn^{2+} with H_2BDC or 1,3,5- H_3BTC is used as the catalyst, the yield of phenol is higher than that when metal-organic framework based on Zn^{2+} with 1,2- H_2BDC or 1,3- H_2BDC used as the catalyst. At the same time, the synthesized product has higher molecular weight and lower hydroxyl value. Thus, metal-organic framework made from Zn^{2+} with H_2BDC or 1,3,5- H_3BTC is a more efficient catalyst for the synthesis of polycarbonate diol *via* the transesterification between diphenyl carbonate and aliphatic diol.

TABLE-1
EFFECT OF DIFFERENT CATALYSTS
ON THE SYNTHESIS OF PCDL

Catalyst	y (%)	M_n	Hydroxyl value/mg KOH/g
MOF-A	88.6	5370	23.5
MOF-B	82.3	4610	26.3
MOF-C	80.7	3470	34.4
MOF-D	86.4	5170	23.7

Reaction conditions: $n(\text{DPC}) = 0.14$, $n(1, 6\text{-HD})/n(\text{DPC}) = 1.2$, $w(\text{catalyst}) = 0.03 \text{ wt. } \%$

The transesterification between diphenyl carbonate and 1,6-hexanediol to polycarbonate diol is an oligomerization process and the size of polycarbonate diol molecule can grow with the progress of the reaction. Thus, the pore size of metal-organic framework may play an important role on its catalytic activity. As shown in Tables 1 and 2, MOF-A with the highest pore volume and highest average pore diameter exhibits the most efficient catalytic activity. Besides, the surface area of metal-organic framework may affect strongly its catalytic activity. For example, MOF-B and MOF-D have similar average pore diameter, but MOF-D with higher surface area shows higher catalytic activity than MOF-B. Moreover, the frameworks of MOF-A and MOF-D have the better symmetric properties and stronger stabilities than those of MOF-B and MOF-C because the symmetric properties of H_2BDC and H_3BTC molecular structures are better than those of 1,2- H_2BDC and 1,3- H_2BDC molecular structures. Consequently, the catalytic activity of metal-organic framework may be greatly influenced by its pore size, surface area and unique molecular structure.

TABLE-2
TEXTURAL PROPERTIES OF MOFs BASED ON Zn^{2+} AND DIFFERENT AROMATIC CARBOXYLIC ACID LIGANDS

Catalyst	BET surface area/ m^2/g	Pore volume/ cm^3/g	Average pore diameter/nm
MOF-A	206.7	0.100	28.6
MOF-B	61.6	0.020	10.9
MOF-C	22.0	0.007	8.4
MOF-D	137.4	0.050	9.8

Comparison of catalytic activity of MOF-A with that of other catalysts: To better illustrate the catalytic activity of metal-organic framework made from Zn^{2+} with H_2BDC , we also compared the catalytic activities of metal-organic framework made from Zn^{2+} with H_2BDC with those of triethylenediamine ($\text{C}_6\text{H}_{12}\text{N}_2$), Mg-Al layered double hydroxide (Mg-Al LDH), sodium ethoxide ($\text{C}_2\text{H}_5\text{ONa}$) and sodium methoxide (CH_3ONa) in a refluxing batchwise reactor. The results are listed Table-3.

TABLE-3
COMPARISON OF CATALYTIC ACTIVITIES OF MOF MADE FROM Zn^{2+} WITH H_2BDC WITH THOSE OF OTHER CATALYSTS

Catalyst	y (%)	m.w.	Hydroxyl value/mg KOH/g	Colour of PCDL
MOF-A	88.6	5370	23.5	White
$\text{C}_6\text{H}_{12}\text{N}_2$	64.6	1150	108.7	Yellowish
Mg-Al LDH	73.4	2060	59.3	White
$\text{C}_2\text{H}_5\text{ONa}$	81.2	3400	37.6	Yellowish
CH_3ONa	83.7	3540	34.2	Yellowish

Reaction conditions: $n(\text{DPC}) = 0.14$, $n(1, 6\text{-HD})/n(\text{DPC}) = 1.2$, $w(\text{catalyst}) = 0.03 \text{ wt. } \%$

As shown in Table-3, compared to $\text{C}_6\text{H}_{12}\text{N}_2$, Mg-Al LDH, $\text{C}_2\text{H}_5\text{ONa}$ and CH_3ONa , metal-organic framework made from Zn^{2+} with H_2BDC exhibits highest catalytic activity in the transesterification process. Meanwhile, the product polycarbonate diol is light-coloured and shows highest molecular weight and lowest hydroxyl value when metal-organic framework made from Zn^{2+} with H_2BDC is used as the catalyst, indicating that metal-organic framework made from Zn^{2+} with H_2BDC is the most efficient catalyst for the preparation of polycarbonate diol.

The high catalytic activity of metal-organic framework made from Zn^{2+} with H_2BDC may be related to its framework structure. In this framework structure, a single O atom bonds with four Zn atoms to form a inorganic group $[\text{Zn}_4\text{O}]^{6+}$ and this inorganic group is connected with $[\text{CO}_2\text{-C}_6\text{H}_4\text{-CO}_2]^2$ to form a three-dimensional framework. The three-dimensional framework would lead to a structure with high surface area and high pore volume. As shown in Fig. 3, the polar Zn-O1 band in the organic group $[\text{Zn}_4\text{O}]^{6+}$ is similar with that in zinc oxide. Although the polarity of Zn-O2 band is weaker than that of Zn-O1 band, O₂ atom becomes more negative because of the donation of π -electrons from benzene ring¹⁷. The Zn atom becomes more positive because of the stronger electron-attracting ability of the conjoint O atoms. This would lead to the formation of positive regions spread around the Zn_4O inorganic groups and the formation of negative regions localized around O₂ atoms. Further, the negative regions are slightly above the aromatic rings because of the electrons. Thus, there are Lewis acid and basic sites on the surface of this framework.

Moreover, the high surface area and high porosity may also contribute to the high catalytic activity of metal-organic framework made from Zn^{2+} with H_2BDC .

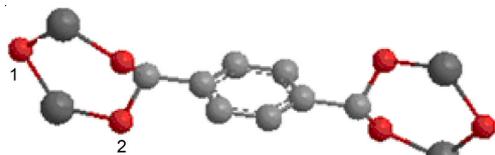


Fig. 3. Fragment of metal-organic framework made from Zn^{2+} with H_2BDC structure with atomic labels (Zn, dark grey; O, red; C, grey)

Effect of the amount of the catalyst on the synthesis of polycarbonate diol: The effect of the amount of metal-organic framework made from Zn^{2+} with H_2BDC used in the reaction on the process of polycarbonate diol preparation was investigated at 198°C . As shown in Fig. 4, the amount of metal-organic framework made from Zn^{2+} with H_2BDC has an evident effect on the transesterification process. It can be seen that the yield of phenol increases rapidly with the increase in the amount of metal-organic framework made from Zn^{2+} with H_2BDC when the total metal-organic framework made from Zn^{2+} with H_2BDC mass fraction is less than 0.03 wt. %. When the mass fraction is above 0.03 wt. %, the further increase in the amount of metal-organic framework made from Zn^{2+} with H_2BDC does not lead to the increase in the yield of phenol.

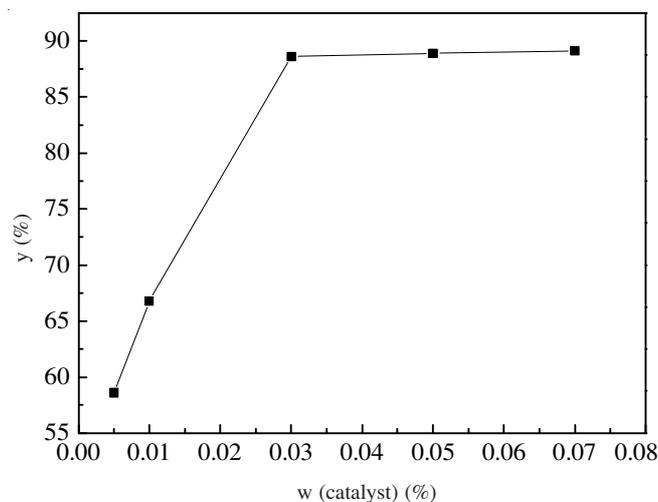


Fig. 4. Effect of the amount of the catalyst on the transesterification process Reaction conditions: $n(\text{DPC}) = 0.14$, $n(1, 6\text{-HD})/n(\text{DPC}) = 1.2$

The amount of metal-organic framework made from Zn^{2+} with H_2BDC has a notable effect on the polycondensation process. As shown in Fig. 5, when the amount of metal-organic framework made from Zn^{2+} with H_2BDC increases from 0.005 wt. % to 0.03 wt. %, the molecular weight rises from 1200 to 5360 and the hydroxyl value decreases from 117.5 to 23.6 mg KOH/g. However, the further increase in the amount of metal-organic framework made from Zn^{2+} with H_2BDC causes the decrease in the M_n and the increase in the hydroxyl value.

According to Figs. 3 and 4, the optimal amount of metal-organic framework made from Zn^{2+} with H_2BDC is 0.03 wt. %.

Characterization of the product: The product was characterized by the FTIR spectroscopy. As shown in Fig. 6, the

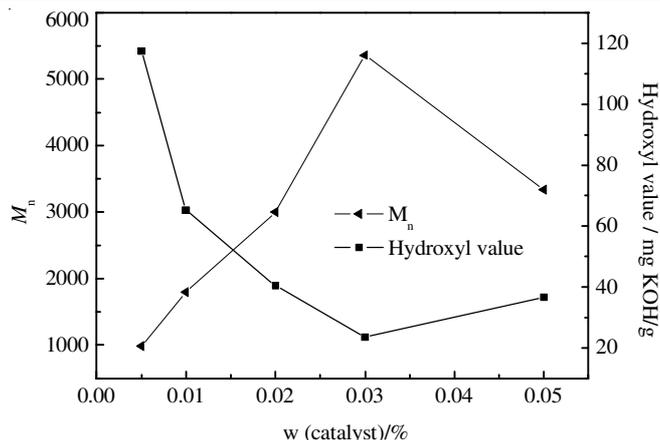


Fig. 5. Effect of the amount of catalyst on the property of polycarbonate diol. Reaction conditions: $n(\text{DPC}) = 0.14$, $n(1, 6\text{-HD})/n(\text{DPC}) = 1.2$

peak observed at 3455 cm^{-1} is attributed to the stretching vibration of hydroxyl group. The peaks at 2940 and 2870 cm^{-1} correspond to the asymmetric and symmetric stretching vibration of methylene group. The peaks at 1482 and 1408 cm^{-1} are attributed to the bending vibration of methylene group. The peak at 1742 cm^{-1} represents the stretching vibration of carbonate $\text{C}=\text{O}$. The peak at 1251 cm^{-1} reflects the stretching vibration of aliphatic carbonate $\text{O}-\text{C}-\text{O}$.

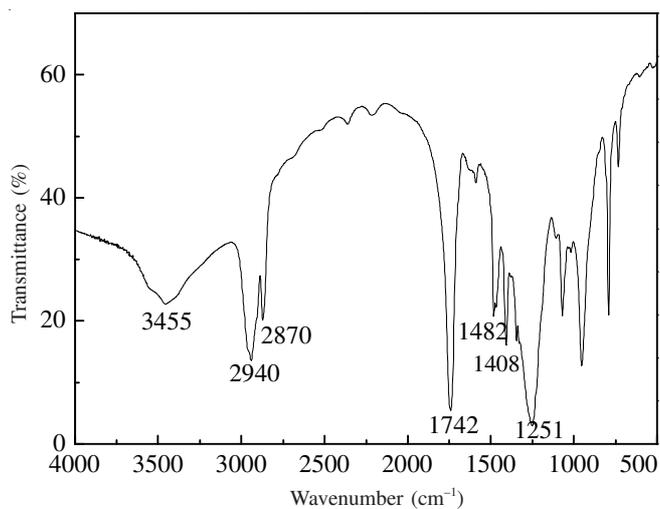


Fig. 6. FTIR spectrum of polycarbonate diol

The product was characterized by the ^1H NMR. The peaks at 4.22, 1.64, 1.45 ppm correspond to the protons in the $\text{OC}(\text{O})\text{OCH}_2$, $\text{OC}(\text{O})\text{OCH}_2\text{CH}_2$ and HOCH_2CH_2 , respectively. The ratio of these three peak areas is 1:1:1. Since the area of each peak is proportional to the number of proton in the related group. The peak at 1.55 ppm is attributed to the proton in the HOCH_2CH_2 . The peak at 3.68 ppm represents the proton in the CH_2 adjacent to OH end group. There are no peaks at 7.30, 7.41 and 7.27 ppm corresponding to the protons in the terminal phenyl group in the ^1H NMR spectrum, indicating that there is no terminal phenyl group in the molecular chain of polycarbonate diol.

The product was characterized by the ^{13}C NMR. The peak at 155.3 ppm is attributed to the $\text{C}=\text{O}$. The peak at 67.8 ppm reflects the CH_2 adjacent to the carbonyl group $\text{C}=\text{O}$. The peak

at 62.3 ppm corresponds to the CH₂ adjacent to OH end group. The peaks at 32.6, 28.9 and 25.1 ppm are attributed to the HOCH₂CH₂, C(O)OCH₂CH₂ and OHCH₂CH₂CH₂, respectively. There are no peaks at 121.8, 126.0, 129.3 and 151.2 ppm corresponding to the terminal phenyl group in the ¹³C NMR spectrum, indicating that there is no terminal phenyl group in the molecular chain of polycarbonate diol.

All those data verify that the product is polycarbonate diol.

Conclusion

The metal-organic frameworks made from Zn²⁺ with H₂BDC and 1,3,5-H₃BTC exhibit more effective catalytic activities than metal-organic frameworks made from Zn²⁺ with 1,2-H₂BDC and 1,3-H₂BDC for the preparation of polycarbonate diol *via* the transesterification between diphenyl carbonate and aliphatic diol. Compare to triethylenediamine, Mg-Al layered double hydroxide, sodium ethoxide and sodium methoxide, metal-organic framework made from Zn²⁺ with H₂BDC is the most efficient catalyst for the preparation of polycarbonate diol. The high catalytic activity of metal-organic framework based on Zn²⁺ with H₂BDC may be attributed to its high surface area, high porosity and unique molecular structure.

ACKNOWLEDGEMENTS

This work was supported by the Key Projects in the National Science and Technology Pillar Program during the Twelfth Five-Year Plan Period (20116BAZ03281), Jiangsu

Provincial Science and Technology Pillar Program (BE2010065) and the Key Research Program of Qujing Normal University (2011ZD004), China.

REFERENCES

1. A. Eceiza, M.D. Martin, K. de la Cala, G. Kortaberria, N. Gabilondo, M.A. Corcuera and I. Mondragon, *Polym. Eng. Sci.*, **48**, 297 (2008).
2. V. García-Pacios, V. Costa, M. Colera and J.M. Martin-Martinez, *Int. J. Adhes. Adhes.*, **30**, 456 (2010).
3. H. Hocker and H. Heul, in ed.: J.C. Salomone, *Cyclic Carbonates (Ring-Opening Polymerization)*. Polymeric Materials Encyclopedia, CRC Press, Boca Raton, Florida, p. 16 (1996).
4. H. Sugimoto and A. Ogawa, *React. Funct. Polym.*, **67**, 1277 (2007).
5. Y.X. Feng, N. Yin, Q.F. Li, J.W. Wang, M.Q. Kang and X.K. Wang, *Ind. Eng. Chem. Res.*, **47**, 2140 (2008).
6. H. Steffen, B. Rolf and B. Lotar, US Patent 20050065360 (2005).
7. M. Shuichi, H. Satoshi and T. Kazunobu, *Macromol. Chem. Phys.*, **201**, 1632 (2000).
8. J. Tillack and J. Laue, WO Patent 03002630A3 (2003).
9. H.J. Buysch and H. Krimm, DE Patent 2523352A1 (1976).
10. T. Murai and T. Fujii, EP Patent 0343572A2 (1989).
11. P. Cao, W.B. Shi, X.G. Yang, T. Kang, Y. Ch. Lei and G.Y. Wang, *Petrochem. Technol.*, **3**, 346 (2010).
12. M. Dincă and J.R. Long, *Angew. Chem. Int. Ed.*, **47**, 6766 (2008).
13. Y.X. Zhou, Sh. G. Liang, J.L. Song, T.B. Wu, S.Q. Hu, Zh. H. Liu, T. Jiang and B.X. Han, *Acta. Phys. Chim. Sin.*, **26**, 939 (2010).
14. Z.Q. Li, M. Zhang and L.G. Qiu, *Chin. J. Lumines.*, **31**, 421 (2010).
15. K. Schlichte, T. Kratzke and S. Kaskel, *Micopor. Mesopor Mater.*, **73**, 81 (2004).
16. Q.R. Fang, G. Sh. Zhu, M.H. Xin, D.L. Zhang, X. Shi, G. Wu, G. Tian, L.L. Tang, M. Xue and Sh. L. Qiu, *Chem. J. Chin. Univ.*, **6**, 1026 (2004).
17. G. Tian, X.J. Liu and Q.R. Fang, *Chem. J. Chin. Univ.*, **4**, 784 (2004).
18. B. Civalieri, F. Napoli, Y. Noël, C. Roetti and R. Dovesi, *Cryst. Eng. Commun.*, **8**, 364 (2006).