Asian Journal of Chemistry; Vol. 27, No. 8 (2015), 2967-2970

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18339

Transesterification Between Diphenyl Carbonate and 1,4-Butanediol to Polycarbonate Diol Catalyzed by Various Metal Acetylacetonates

LIPING WANG[1,*], GONGYING WANG[2] and FAN WANG[1]

[1]College of Chemistry and Chemical Engineering, Qujing Normal University, Qujing 655011, P.R. China
[2]Chengdu Institute of Organic Chemistry, Chinese Academy of Science, Chengdu, P.R. China

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

Received: 17 June 2014; *Accepted*: 4 September 2014; *Published online*: 27 April 2015; AJC-17173

The catalytic activities of various metal acetylacetonates for the synthesis of polycarbonate diol *via* transesterification between diphenyl carbonate and 1,4-butanediol were investigated. Their catalytic activities in the esterification process is monitored by measuring the amount of phenol generated and the number average molecular weight M_n and the hydroxyl value of polycarbonate diol are used as the index in polycondensation process. $Zn(acac)_2$ and $Al(acac)_3$ exhibited higher catalytic activities for transesterification between diphenyl carbonate and 1,4-butanediol. Under the optimal reaction conditions, polycarbonate diol with the M_n over 2300 and the hydroxyl value below 48.2 mg KOH/g was prepared. X-ray diffraction result shows that polycarbonate diol is a semi-crystalline and the degree of crystallinity is 73.4 %.

Keywords: Transeterification, Polycarbonate diol, Diphenyl carbonate, Metal acetylacetonate.

INTRODUCTION

Polycarbonate diol is one of key materials used in the synthesis of new polycarbonate-based polyurethane. Polyurethane produced from polycarbonate diol is superior to the ones from polyether diol or polyester diol in many physical and chemical properties such as mechanical performance, heat resistance, oil resistance, hydrolytic resistance, oxidizing resistance and weather resistance *etc*. Moreover, polycarbonate-based polyurethane is a new kind of water-borne polymer with favorable biodegradability and biocompatility and it is a kind of environmental friendly type of material[1].

The conventional phosgene process for the production of polycarbonate diol has been eliminated because of use of highly toxic phosgene[2]. Several alternative non-phosgene methods for the synthesis of polycarbonate diol have been proposed, including the polymerization of six and seven-membered cyclic carbonates[3], the copolymerization of oxiranes[4] with CO_2 and the transesterification of carbonate with diol[5-10]. The polymerization of six and seven-membered cyclic carbonate may synthesize polycarbonate diol with high molecular weight, but the commercial cyclic carbonate is mostly prepared from phosgene. The copolymerization of oxiranes with CO_2 is considered to be a prospective route for the synthesis of polycarbonate diol because CO_2 is extremely rich and low-cost C1 resources and the consumption of CO_2 leads to the reduction of the greenhouse effect, but only polycarbonate diol with a specific epoxide structure can be synthesized. The transesterification between dimethyl carbonate and aliphatic diols is regarded as a more promising method for the preparation of polycarbonate diol because dimethyl carbonate is a green chemical and has been commercially produced *via* the oxidative carbonylation of methanol instead of conventional phosgene route. However, due to lower boiling point (90 ºC) and forming azeotrope with side product methanol, dimethyl carbonate is easy to be removed from the reactor with methanol at high reaction temperature[5,6] (≥160 ºC). The synthesis of polycarbonate diol *via* the reaction between diethyl carbonate and diols has been proposed because diethyl carbonate dose not form azeotrope with the side product ethanol and the ethanol is non-toxic[7]. But diethyl carbonate can tract into the body through gastrointestinal tract, skin and respiratory for the middle-performance for toxicity. By comparison, diphenyl carbonate is not only an environmental friendly chemical but also has been commercially produced by transesterification between dimethyl carbonate and phenol[11]. Meanwhile, the side product phenol can be recycled to synthesize diphenyl carbonate. So the transesterification of diphenyl carbonate and aliphatic diol is a more promising green route to prepare polycarbonate diol.

The reaction between diphenyl carbonate and 1,4-butanediol can proceed without catalyst, but the reaction rate is somewhat slow. So the active catalyst systems are necessary for the transester-ification. So far, a variety of catalysts have been developed for the transesterification between dimethyl carbonate and aliphatic diol, which include sodium and potassium alcoholates[7,8], tin compounds[9] titanium esters[8,10] and MgAl hydrotalcites[6], *etc*. Although the sodium and potassium alcoholates such as sodium methoxide and sodium ethoxide are active catalysts, their strong alkaline can cause some side reaction. The titanium esters such as titanium tetraisopropoxide and titanium tetrabutoxide are also effective catalysts for the transesterification, but they are sensitive to the moisture and unstable in air. The MgAl hydrotalcites are heterogeneous catalysts and easy to separate from the products, but their low activities impede them from industrialization. Consequently, the development of more efficient catalyst is desirable.

The metal acetylacetonates are one kind of metallo-organic compounds containing β-dicarbonyl structure. They inherit the advantages of Zieglger-Natta and metallocene catalysts and are used widely in olefin polymerization. Due to the presence of β-dicarbonyl structure, metal acetylacetonate catalysts modified by various substituents will strongly influence the steric and electronic properties of catalytic centers, as well as their catalytic behaviors[12]. And it might be provisioned that the reaction between diphenyl carbonate and aliphatic diol might be improved by using different kinds of metal acetylacetonates. So it is of great importance to investigate the catalytic behaviours of these metal acetylacetonates for the transesterification between diphenyl carbonate and aliphatic diol.

EXPERIMENTAL

Diphenyl carbonate (DPC, CP, Chongqing Changfeng Chemical Plant), 1,4-butanediol (1,4-BD, 95 %, Shanghai Ruijie Chemical Reagent Co., Ltd.), were used without further purification. Aluminum acetylacetonate [Al(acac)$_3$, 99 %], zinc acetylacetonate [Zn(acac)$_2$, 99 %], manganese acetylacetonate [Mn(acac)$_3$, 99 %] and chromium acetylacetonate [Cr(acac)$_3$, 99 %] were purchased from Yangzhou Xingye Auxiliaries Co., Ltd.

Preparation of polycarbonate diol: The transesterification between diphenyl carbonate and 1,4-butanediol to polycarbonate diol consists of two steps: Esterification process and polycondensation process. Esterification process: diphenyl carbonate, 1,4-butanediol and the catalyst were introduced into a 100 mL round-bottomed flask equipped with thermometer, a nitrogen inlet, a mechanical stirrer and reflux condenser. The transesterification was carried out at 192 ºC under reflux collecting the distillate in a receiver. The temperature of distillation column was maintained at 180 ºC. The reaction time is about 2 h in the esterification process. Polycondensation process: The reaction temperature was maintained at 180-190 ºC under 3-4 × 10^4 Pa for 3 h to continue the reaction and remove the residual amount of the reactant and side product. Eventually, the pressure was reduced to 2-3 × 10^3 Pa for 3 h.

After completion of reaction, the product was cooled to room temperature under the protection of nitrogen. The product was dissolved in dichloromethane and precipitated in cold ethanol.

Qualitative and quantitative analyses of distillate were carried out on a Shimadzu GC-2010 gas chromatograph equipped with a flame-ionization detector. The molecular structure of polycarbonate diol was analyzed by Nicolet 560 fourier transform infrared spectroscopy, ^{1}H NMR (CDCl$_3$) and ^{13}C NMR (CDCl$_3$). The molecular weight of product was analyzed by WATERS gel permeation chromatograph in *N*,*N*-dimethylformamide solution. X-Ray diffraction measurement of the product was performed on a Rigaku D/max 2500 PC powder X-Ray diffractometer using CuK$_\alpha$ (40 Kv and λ = 0.154 nm) radiation, over a 2θ range of 10-70º with a step size of 0.02º at a scanning speed of 0.2 º/min.

RESULTS AND DISCUSSION

Catalytic activities of metal acetylacetonates: The catalytic activities of metal acetylacetonates in the esterification process were monitored by measuring the amount of phenol generated and characterized by the yield of phenol (y), which was expressed as the following equation: y = (m/26.36) × 100 %, where m was the amount of phenol generated, the value 26.36 in the denominator was the amount of phenol produced when diphenyl carbonate of 0.14 mol completely reacted with 1,4-butanediol. While in polycondensation process, the catalytic activities of metal acetylacetonates were evaluated by the number average molecular weight (M$_n$) and the hydroxyl value. Al(acac)$_3$, Zn(acac)$_2$, Mn(acac)$_3$ and Cr(acac)$_3$ were used as the catalysts for the transesterification between diphenyl carbonate and 1,4-butanediol and their catalytic performances were investigated. As shown in Table-1, under the same reaction conditions, Zn(acac)$_2$ and Al(acac)$_3$ have much higher catalytic activities in the esterification process. Meanwhile, the catalyst has a notable effect on the property of polycarbonate diol. It can be observed from Table-1 that polycarbonate diol with higher M$_n$ and lower hydroxyl value were synthesized when Zn(acac)$_2$ or Al(acac)$_3$ used as the catalyst.

TABLE-1
CATALYTIC ACTIVITIES OF DIFFERENT CATALYSTS FOR THE TRANSESTERIFICATION BETWEEN DIPHENYL CARBONATE AND 1,4-BUTANEDIOL

Catalyst	y (%)	M$_n$	Hydroxyl value (mg KOH/g)
Zn(acac)$_2$	78.1	2400	46.8
Al(acac)$_3$	76.5	2330	48.2
Mn(acac)$_3$	71.0	1200	97.4
Cr(acac)$_3$	58.1	800	144.3

Reaction conditions: n(DPC) = 0.14 mol, n(1,4-BD):n(DPC) = 1.5, (catalyst):n(DPC) = 0.005

Reaction mechanism: The transesterification between diphenyl carbonate and 1,4-butanediol is similar to the reaction of dimethyl terephthalate with ethylene glycol. The previous work has shown that the transesterification between dimethyl terephthalateand ethylene glycol may proceed by the nucleophilic attack of hydroxyl group in ethylene glycol upon ester carbonyl group in dimethyl terephthalate[13]. Similarly, it may be considered that the transesterification between diphenyl carbonate and 1,4-butanediol may proceed by the nucleophilic attack of hydroxyl group in 1,4-butanediol upon carbonyl group in diphenyl carbonate. In the presence of metal acetylacetonate, the coordination of central atom M to carbonyl oxygen in diphenyl carbonate may enhance the positive charge of carbonyl carbon in diphenyl carbonate and accelerate the reaction of diphenyl carbonate and 1,4-butanediol.

The stronger eletrophilicity or L acidity of central atom M and the smaller steric hindrance are helpful for M to coordinate with carbonyl oxygen in diphenyl carbonate. So the catalytic activity of metal acetylacetonate may depend on the eletrophilicity or L acidity of central atom M and its stereo configuration. The L acidity of M is known to be Al^{3+} (3.042) > Mn^{3+} (1.698) > Zn^{2+} (0.656) > Cr^{3+} (0.473)[14]. As shown in Table-1. $Al(acac)_3$ and $M_n(acac)_3$ with higher L acidity exhibit lower catalytic activites than $Zn(acac)_2$. The acetylacetonate anion forms complexes with central atom M wherein both oxygen atoms bind to central atom M to form a six-membered chelate ring. Al^{3+}, Mn^{3+} and Cr^{3+} have coordination numbers of 6 and the structures of $Al(acac)_3$, $M_n(acac)_3$ and $Cr(acac)_3$ are octahedral, while the coordination number for Zn^{2+} is 4 and the structure of $Zn(acac)_2$ is tetrahedral. The ionic radii is Zn^{2+} (0.74 Å) > Mn^{3+} (0.65 Å) > Cr^{3+} (0.62 Å) > Al^{3+} (0.54 Å)[15]. The higher coordination number and smaller size of Al^{3+} and Mn^{3+} are unfavorable for them to coordinate with carbonyl oxygen in diphenyl carbonate. At the same time, due to Jahn-Teller effect[16], the distorted octahedral structures of $Mn(acac)_3$ and $Cr(acac)_3$ are not beneficial for Mn^{3+} and Cr^{3+} to coordinate with carbonyl oxygen in diphenyl carbonate. So $Zn(acac)_2$ has the highest activity of the tested catalysts. The possible reaction mechanism was shown in **Scheme-I**.

TABLE-2
EFFECT OF $n(Zn(acac)_2):n(DPC)$
ON THE TRANSESTERIFICATION

$n(Zn(acac)_2):n(DPC)$	M_n	Hydroxyl value (mg KOH/g)
0.001	1490	75.3
0.003	2100	56.1
0.005	2400	46.8
0.007	2410	46.8
0.009	2450	45.8

Reaction conditions: n(DPC) = 0.14 mol, n(1,4-BD):n(DPC) = 1.5

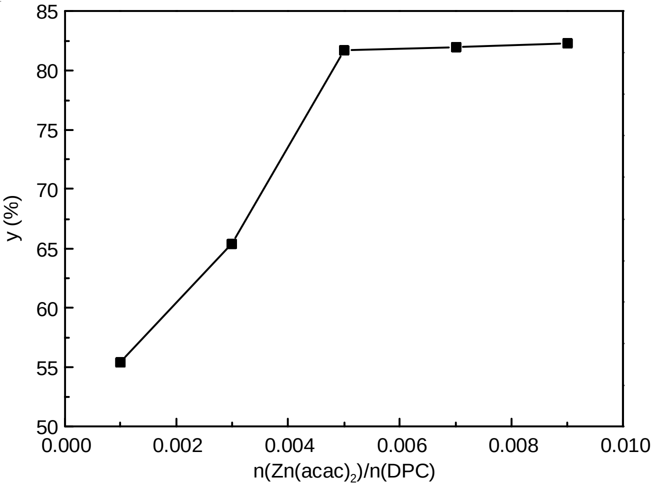
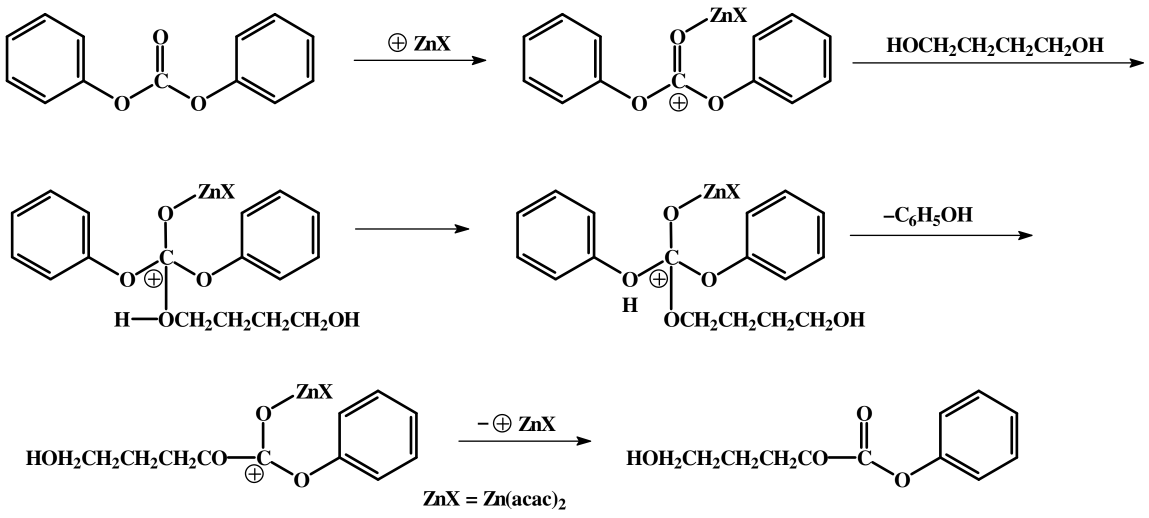


Fig. 1. Effect of molar ratio of $Zn(acac)_2$ to diphenyl carbonate on the transesterification

Effect of the molar ratio of $Zn(acac)_2$ to diphenyl carbonate on the transesterification: As shown in Fig. 1, the yield of phenol increased rapidly with the increase of the molar ratio of $Zn(acac)_2$ to diphenyl carbonate. When the molar ratio of $Zn(acac)_2$ to diphenyl carbonate was increased to 0.005 from 0.001, the yield of phenol reached the maximum. Above 0.005, however, the yield of phenol remained almost unchanged. Table-2 shows the effect of molar ratio of $Zn(acac)_2$ to diphenyl carbonate on the polycondensation. Table-2 showed that with the increase of molar ratio of $Zn(acac)_2$ to diphenyl carbonate, the property of polycarbonate diol is improved. When the molar ratio of $Zn(acac)_2$ to diphenyl carbonate increased to 0.005, the molecular weight of polycarbonate diol was as high as 2400 and the hydroxyl value decreases to 46.8 mg KOH/g, while the bigger molar ratio of $Zn(acac)_2$ to diphenyl carbonate did not result in more improvement of the property of polycarbonate diol any more.

Combined with results in Fig. 1 and Table-2, the optimal molar ratio of $Zn(acac)_2$ to diphenyl carbonate was 0.005.

FTIR Spectra, ^{1}H NMR and ^{13}C NMR of polycarbonate diol: The FTIR spectra of polycarbonate diol (Fig. 2). The band at 3560 and 3460 cm^{-1} is the absorption of -OH, the bands at 2970, 2950, 2890, 1460 and 1400 cm^{-1} are the characteristic absorption of CH_2, the band at 1740 cm^{-1} is the absorption of



Scheme-I: Possible reaction mechanism

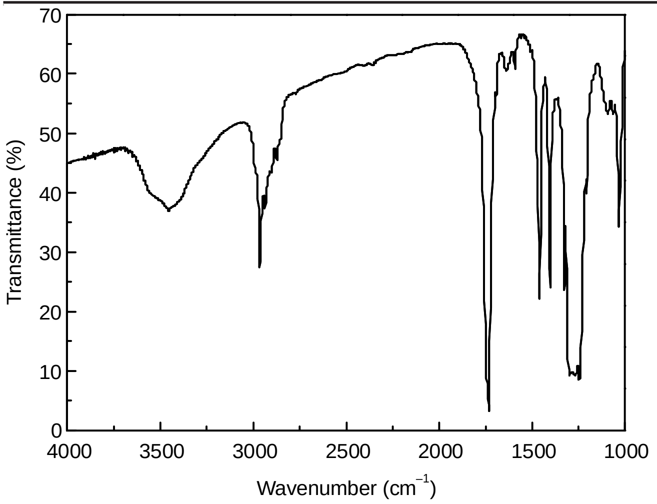


Fig. 2. FTIR spectra of polycarbonate diol

carbonate C=O, the bands at 1260 and 1240 cm^{-1} are the absorption of aliphatic carbonate O-C-O.

^{1}H NMR ($CDCl_3$): $\delta = 4.17$ (t, $OC(O)OCH_2$), $\delta = 3.66$ (t, $HOCH_2$), $\delta = 1.63$ (t, $OC(O)OCH_2CH_2$), $\delta = 1.55$ (t, $HOCH_2CH_2$). ^{13}C NMR ($CDCl_3$): $\delta = 155.20$ (C=O), $\delta = 67.8$ ($C(O)OCH_2$), $\delta = 62.3$ ($HOCH_2$), $\delta = 25.2$ ($C(O)OCH_2CH_2$), $\delta = 28.9$ ($OHCH_2CH_2$). These three data showed that the product was polycarbonate diol.

X-ray diffraction spectra of polycarbonate diol: Fig. 3 shows the X-ray diffraction result of polycarbonate diol. As shown in Fig. 3, two sharp reflection peaks were observed at $2\theta = 21.32°$ and $24.44°$, which were uplifted. This indicates that there is clear difference between crystalline and amorphous in the sample and polycarbonate diol is a semi-crystalline. The degree of crystallinity is 73.4 %.

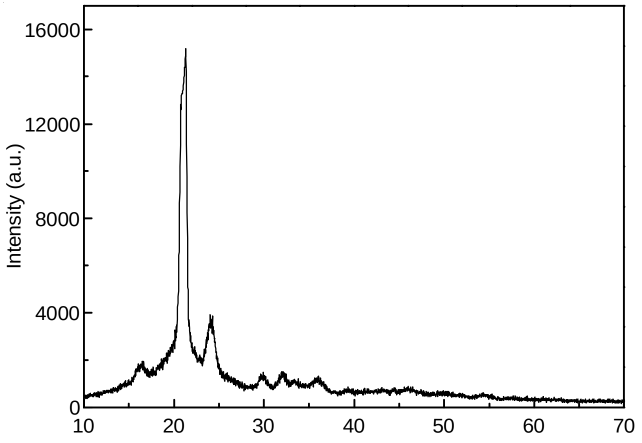


Fig. 3. X-ray diffraction spectra of polycarbonate diol

Conclusion

$Zn(acac)_2$ and $Al(acac)_3$ were found to be efficient catalysts for transesterification of diphenyl carbonate and 1,4-butanediol. Under the optimal reaction conditions, the yield of phenol was above 76 % in the esterification process. Meanwhile, the properties of polycarbonate diol were improved. Moreover, due to the presence of β-dicarbonyl structure, $Zn(acac)_2$ and $Al(acac)_3$ catalysts modified by various substituents will strongly influence the steric and electronic properties of catalytic centers, as well as their catalytic behaviors. So they are promising catalysts for transesterification between diphenyl carbonate and aliphatic diol and further study on the details of $Zn(acac)_2$ and $Al(acac)_3$ modified by different substituents are underway in our lab and will be reported separately.

ACKNOWLEDGEMENTS

This work was supported by the Key Projects in the National Science & Technology Pillar Program during the Twelfth Five-Year Plan Period (20116BAZ03281), Yunnan Provincial Basic & Applied Research Program (2013FZ108) and the Key Research Program of Qujing Normal University (2011ZD004), China.

REFERENCES

1. L.A. Matheson, R.S. Labow and J.P. Santerre, *J. Biomed. Mater. Res.*, **61**, 505 (2002).
2. H. Schnell, Chemistry and Physics of Polycarbonates, Wiley, New York, p. 9 (1964).
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. A. Rokicki and W. Kuran, *J. Macromol. Sci. Rev. Macromol. Chem. C*, **21**, 135 (1981).
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. X.Y. Xie, J.H. Li, C.S. He, C.R. Fan and Y.P. Zhong, *Polym. Mater. Sci. Eng.*, **18**, 169 (2002).
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. Tech.*, **3**, 346 (2010).
12. S.T. Chen and Y.L. Hu, *Petrochem. Tech.*, **6**, 896 (2006).
13. K. Tomita and H. Ida, *Polymer*, **14**, 55 (1973).
14. Y.H. Zhang, *Inorg. Chem.*, **21**, 3889 (1982).
15. D.N. Ye, D.S. Ai and R.S. Zen, *Sci. China Series B Chem.*, **9**, 303 (1999).
16. F.A. Cotton, G. Wilkinson, C.A. Murillo and B. Manfred, Advanced Inorganic Chemistry, Wiley-Interscience New York, edn. 6, p. 168 (1999).