

Catalytic activity of metal acetate in transesterification of diphenyl carbonate and 1,4-butyldiol

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Abstract. Synthesis of polycarbonate diols from diphenyl carbonate and 1,4-butyl diol has been demonstrated in the presence of metal acetate catalysts. Alkali metal acetate and alkaline earth metal acetate catalysts showed much higher catalytic activity, of them, lithium acetate was the most active. And the catalytic mechanism was discussed.

Introduction

Aliphatic polycarbonate diols (PCDL) is a polymer whose terminal group is hydroxyl group, main chain containing sub-alkyl and carbonate-based repeating unit. It is widely used in synthetic leather, TPU, SPANDEX, adhesives, paint and other areas [1]. Its important downstream product of polyurethane material with excellent performance and a wide variety of characteristics, is widely used in construction, chemical industry, light industry, mechanical and electrical, metallurgical, medical and health and other fields. Its demand for an annual growth rate is 6% ~ 8%, the global consumption of polyurethane materials has reached more than 11 million tons in 2006, forming a large category of synthetic materials, and has been ranked No. 6 of synthetic materials [2]. Polyurethane produced from PCDL is superior to the ones from polyether diol or polyester diol in mechanical performance, heat resistance, oil resistance, hydrolytic resistance, oxidizing resistance, abrasion resistance, chemical resistance and weather resistance. PCDL performs excellently with respect to hydrolytic resistance and aging resistance, its outstanding properties enables it be used extensively in each area of polyurethane [3]. Therefore, PCDL is a broad development prospect of the chemical.

PCDL can be prepared by various methods: the reaction of phosgene with diol[4], the copolymerization of oxiranes with CO₂[5], the polymerization of six- and seven-membered cyclic carbonates[6] and the transesterification of carbonate with diol[7-9]. As a result of using highly toxic phosgene and large numbers of byproducts hydrogen chloride causing serious corrosion of equipment, the method of phosgene reaction with diol has been basically eliminated. CO₂ is the most abundant and cheap resources of C₁. But PCDL with specific epoxide structure is only synthesized. The cost of synthesis of cyclic carbonate is much higher, so the polymerization of six- and seven-membered cyclic carbonates is of little value for industrial application. Compared with other methods, the advantages of the transesterification include greater flexibility for the synthesis of all possible structures and controlled programming of the molecular weight of the target products [12]. Carbonate used in the transesterification includes dimethyl carbonate (DMC)[7-8], diethyl carbonate (DEC)[9] and diphenyl carbonate (DPC)[10]. Due to lower boiling point and forming azeotrope with side product methanol, DMC is easy to be removed from the reactor. DEC is unable to form azeotrope with byproduct ethanol, and ethanol is non-toxic. But DEC can tract into the body through gastrointestinal tract, skin and respiratory for the middle-performance for toxicity. Besides, DEC is easy to form an explosive mixture with air. In constant, DPC is not only environmentally friendly compound but has higher boiling point. Though the side product phenol is toxic, but it can be recycled to synthesize DPC by ester interchange with DMC. So the transesterification of DPC and aliphatic diol is a more promising route to prepare PCDL.

The transesterification of DPC with 1,4-butyl diol (BD) can proceed without catalyst, but the reaction is quite slow. So use of catalyst is necessary in this reaction. There are a few catalysts used in transesterification of DMC or DEC and diol [7-9]. But few catalysts reported are used to catalyze DPC

reaction with BD. Metal acetate catalysts are active catalysts for ester exchange reaction [12-13]. In this work, the activities of various metal acetate catalysts were evaluated, and the catalytic mechanism was discussed.

Experimental

The reaction was carried out in a 100mL round-bottomed flask equipped with thermometer, a nitrogen inlet, a mechanical stirrer and reflux condenser. DPC, BD and the catalyst were introduced into the flask under nitrogen atmosphere. The reaction temperature was kept between 186 and 196 °C. The temperature of distillation column was maintained at 180°C. The byproduct phenol was collected in a flask.

Qualitative and quantitative analyses of distillate were carried out a Shimadzu GC-2010 gas chromatograph equipped with a flame-ionization detector. The yield of phenol was expressed in percent of its theoretical value, which was calculated based on the 100% conversion of DPC. The reaction residue was a yellow solid, after cooling, then it was dissolved in dichloromethane and precipitated by addition of ethyl alcohol. IR spectra of the product obtained were recorded on a Nicolet 460 Fourier transform infrared spectroscopy. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer.

The IR spectra of PCDL: the band at 3454.8 cm⁻¹ is the absorption of -OH, the bands at 2965.8 cm⁻¹, 2936.3 cm⁻¹, 2873 cm⁻¹, 1459.0 cm⁻¹ and 1403.6 cm⁻¹ are the characteristic absorption of CH₂, the band at 1732 cm⁻¹ is the absorption of carbonate C=O, the bands at 1269 cm⁻¹ and 1246.2 cm⁻¹ are the absorption of aliphatic carbonate O-C-O (see Fig1).

¹H NMR (CDCl₃): δ=4.17(t, OC(O)OCH₂), δ=3.66 (t, HOCH₂), δ=1.63 (t, OC(O)OCH₂CH₂), δ=1.55 (t, HOCH₂CH₂).

¹³C NMR (CDCl₃): δ=155.20 (C=O), δ=67.8 (C(O)OCH₂), δ=62.3 (HOCH₂), δ=25.2 (C(O)OCH₂CH₂), δ=28.9 (OHCH₂CH₂).

The progress of the reaction was followed by measuring the yield of phenol expressed in percent of its theoretical value which was calculated based on the 100% conversion of DPC. As shown in Table 1, alkali metal acetate and alkaline earth metal acetate catalysts showed much higher catalytic activity. The order of the activity of alkali metal acetate is lithium acetate > sodium salt > potassium acetate. The order of the activity of alkaline earth metal acetate is magnesium acetate > calcium acetate > barium acetate. Of them, lithium acetate is the most active.

Table 1 Yield of phenol formed with various metal acetates as catalysts

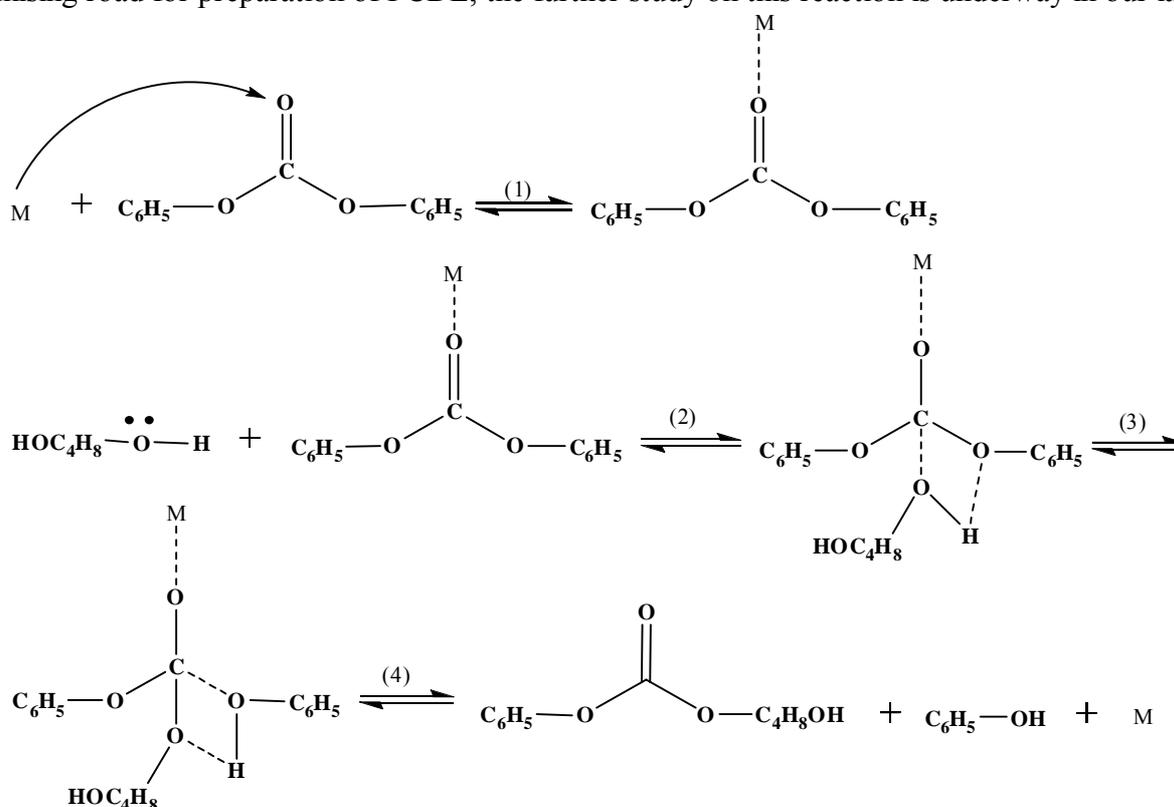
No	Catalyst Name	Yield of Phenol (%)
1	None	4.6
2	Lithium acetate	70.5
3	Sodium acetate anhydrous	66.2
4	Potassium acetate	59.6
5	Magnesium acetate	50.3
6	Calcium acetate	44.4
7	Barium acetate	38.6
8	Lead acetate	32.2
9	Manganese acetate	24.1
10	Cobaltous acetate	24.3
11	Cupric acetate	31.7
12	Zinc acetate	35.6

Reaction temperature: 196 °C, molar ratio of BD and DPC: 1.2, the mole ratio of catalyst to DPC: 0.002, reaction time: 4 h, the mole of DPC: 0.23 mol

Oxygen is more electronegative than carbon, and thus pulls electron density away from carbon. So the carbonyl group is polar, the partial positive charge on carbonyl carbon causes it be attacked by

nucleophiles, the partial negative charge on carbonyl oxygen causes it be attacked by electrophiles. And the carbonyl carbon with positive charge has a greater reactivity than carbonyl oxygen with negative charge. The transesterification may proceed by the nucleophilic attack of hydroxyl group in BD upon carbonyl group in DPC. The phenoxy group is an electron-donating group, it can increase negative charge of carbonyl carbon and thus reduce electrophilic capacity of carbonyl carbon, and it increases steric hindrance and thus makes it difficult for carbonyl carbon to close with nucleophiles.

In presence of metal acetate, the reaction intermediate is considered as a complex formed by coordination of the carbonyl group to the metal species. This coordination increases the positive charge of carbonyl carbon and facilitates the nucleophilic attack of hydroxyl group upon this positively polarized carbon atom (Scheme 1). In conclusion, all of metal acetate catalysts tested had catalytic activity to the reaction of DPC with BD. Among them, alkali metal acetate and alkaline earth metal acetate catalysts had much higher activity, and lithium acetate was the most active. The small quantity of crystal water in the catalysts could not affect the reaction, so the catalyst can be directly used without any pretreatment. And metal acetate catalysts are commercial available and inexpensive. As a promising road for preparation of PCDL, the further study on this reaction is underway in our lab.



Scheme 1 Possible reaction mechanism

Conclusions

Lithium acetate shows higher catalytic activity for the synthesis of PCDL via the transesterification between DPC and BD. And the crystal water in the lithium acetate could not affect the reaction, so lithium acetate catalyst can be directly used without any pretreatment.

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