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RESEARCH NOTES

Simultaneous Synthesis of Dimethyl Carbonate and Poly(ethylene terephthalate) Using Alkali Metals as Catalysts*

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Abstract Dimethyl carbonate (DMC) and poly(ethylene terephthalate) was simultaneously synthesized by the transesterification of ethylene carbonate (EC) with dimethyl terephthalate (DMT) in this paper. This reaction is an excellent green chemical process without poisonous substance. Various alkali metals were used as the catalysts. The results showed alkali metals had catalytic activity in a certain extent. The effect of reaction condition was also studied. When the reaction was carried out under the following conditions: the reaction temperature 250℃, molar ratio of EC to DMT 3∶1, reaction time 3h, and catalyst amount 0.004 (molar ratio to DMT), the yield of DMC was 68.9%.
Keywords ethylene carbonate, dimethyl terephthalate, dimethyl carbonate, poly (ethylene terephthalate), transesterification, catalyst

1 INTRODUCTION

Dimethyl carbonate (DMC) is considered to be a benign carbonylation and methylation agent, substituting for poisonous phosgene and dimethyl sulfate. It can be used to enhance gasoline octane value and synthesize polycarbonate resins[1—3]. At present, three routes for production of DMC including the phosgene-methanol route, the oxidative carbonylation of methanol route and the transesterification route have been commercialized on a large scale[4,5]. In recent years considerable efforts have been put into the transesterification of ethylene carbonate (EC) with methanol [reaction (1) in Fig.1] due to its using simple equipment and little corrosion to equipment. Poly (ethylene terephthalate) (PET) is one of the most important engineering polymers, widely used in food packaging film and in beverage containers[6]. With the increase of demand to PET[7], there has been growing concern on the study of transesterification of ethylene glycol and dimethyl terephthalate (DMT) [reaction (2)], which is an important industrial route to produce PET.

In this paper, reactions (1) and (2) were coupled to simultaneously synthesize dimethyl carbonate and poly (ethylene terephthalate) [reaction (3)]. This method improved the atom economy by avoiding by-products of methanol and ethylene glycol and decreased energy consumption. Because ethylene carbonate is a product of the reaction between CO_2 and ethylene epoxide, this method make good use of greenhouse gas CO_2. The reaction cannot proceed without catalyst. However, there are only a few catalysts that are reported, such as $Ti(OC_4H_9)_4$[8—10], TiO_2[9], $Ti(OCH_3)_4$[9] and various metal acetates[11]. Since alkali metals compounds are often applied in reaction (1)[12,13], it is presumed that it would also have catalytic activity in a certain degree for reaction (3). Therefore, various alkali metals compounds catalysts were developed.

2 EXPERIMENTAL

2.1 Chemical reagents

Ethylene carbonate was of laboratory reagent grade. Dimethyl terephthalate was of chemical grade. The other chemicals were of analytical grade. All

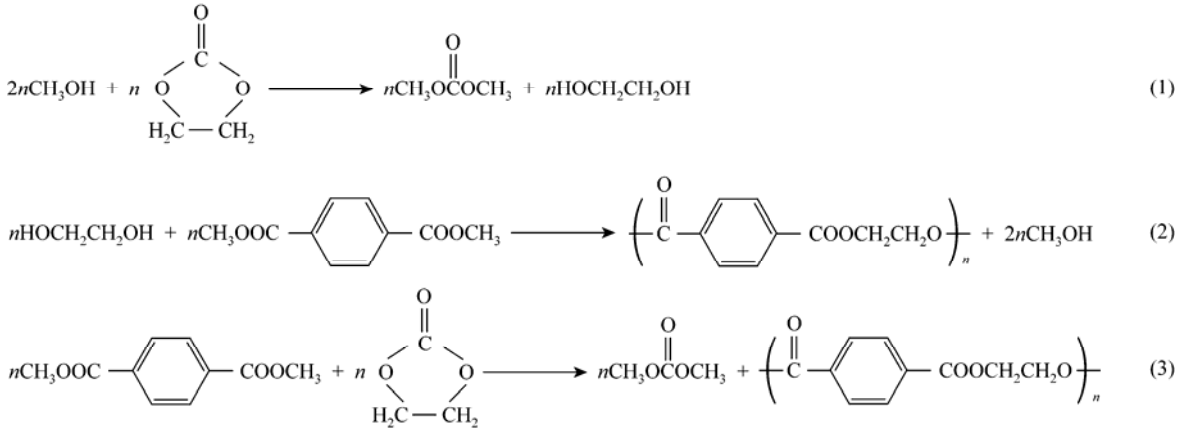

Figure 1 Simultaneous synthesis of DMC and PET from EC and DMT

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reagents were purchased from local manufactures and used without any pretreatment.

2.2 General procedure

The reaction was carried out in a 100ml three-neck round-bottomed flask, equipped with a thermometer, a nitrogen inlet, and a fractionating column connected to a liquid dividing head. After ethylene carbonate, dimethyl terephthalate and catalyst were introduced into the flask, nitrogen was let in to drive away the air. The reaction mixture was under refluxing condition and the reaction temperature was kept at 250℃. During the reaction, distillate of DMC was collected slowly in a receiver flask attached to the liquid dividing head for further analysis. After the reaction, the mixture was cooled to room temperature.

2.3 Product analysis

Identification analysis of the reaction product was conducted on a HP 6890/5973 GC-Mass spectrometer (GC-MS). Quantitative analysis of DMC was carried out by a Shimadzu GC-14B gas chromatograph equipped with a SE-30 capillary column and flame ionization detector (FID). The reaction mixture was solid after cooling, it was dissolved in 50/50 (mass percentage) mixture of phenol/1,1,2,2-tetrachloroethane, then precipitated in voluminous methanol. The product obtained was analyzed on a Nicolet560 Fourier Transform Infrared (FT-IR).

3 RESULTS AND DISCUSSION

3.1 Catalytic behavior

To investigate the reaction of ethylene carbonate with dimethyl terephthalate, several experiments were carried out first to screen the catalysts. The reaction conditions are: temperature 250℃, molar ratio of EC/DMT＝1, molar ratio of catalyst/DMT＝0.002, reaction time 3h, amount of DMT 0.05mol. The results are presented in Table 1.

Table 1 Reaction of EC and DMT in the presence of different catalysts

No.	Catalyst	Yield of DMC, %
1	LiOH	29.1
2	$LiNO_3$	38.6
3	Li_2CO_3	28.9
4	LiCl	41.7
5	NaOH	34.7
6	CH_3ONa	38.8
7	C_2H_5ONa	38.4
8	$NaNO_3$	38.4
9	Na_2CO_3	26.9
10	$NaHCO_3$	37.4
11	NaCl	31.4
12	Na_2SO_4	15.9
13	KOH	30.6
14	KCl	21.3
15	KNO_3	35.0
16	K_2CO_3	35.3
17	K_2SO_4	7.9

Table 1 shows alkali metals compounds are active in the reaction, indeed. The catalytic activity of $LiNO_3$, LiCl, CH_3ONa, C_2H_5ONa, $NaNO_3$ and $NaHCO_3$ is close to each other and their yields of DMC are above 37%. A small amount of methanol was also detected by the GC-MS analysis. Methanol might be intermediate product and was distilled slightly with DMC when the oligomerization of poly (ethylene terephthalate) occurred during the transesterification.

LiCl is chosen as the catalyst and studied the effect of reaction conditions in detail.

3.2 Effect of catalyst amount on the reaction

It can be seen from Table 2 that the catalytic activity was increased with increasing LiCl amount, but when the molar ratio of LiCl was above 0.004, the catalytic activity dropped to a slightly lower level. It seems likely that excess LiCl catalyst leads to polymerization of EC, disadvantageous to produce DMC. So, the optimal catalyst amount may be 0.004.

Table 2 Effect of molar ratio of lithium chloride to DMT on the reaction①

No.	Catalyst amount n(LiCl)∶n(DMT)	Yield of DMC, %
1	0.001	34.7
2	0.002	41.7
3	0.004	46.8
4	0.006	43.4
5	0.008	42.8
6	0.01	43.1

① Reaction conditions: temperature: 250℃, the molar ratio of EC/DMT: 1, reaction time: 3h, the mole of DMT: 0.05mol.

3.3 Effect of molar ratio of EC/DMT on the reaction

Table 3 presents the yield of DMC *versus* the molar ratio of EC to DMT. When EC and DMT were added according to the stoichiometric reaction, the yield of DMC is the lowest. This may ascribe that the reaction is reversible. It is more favorable to the yield of DMC when EC is in excess compared with the amount of DMT. When the molar ratio of EC/DMT was increased to 3∶1, the yield of DMC increased greatly, but the increase thereafter became negligible. The appropriate molar ratio of EC to DMT was about 3∶1.

Table 3 Effect of molar ratio of EC/DMT on the reaction①

Entry	n(EC)∶n(DMT)	Yield of DMC, %
1	1∶1	46.8
2	2∶1	64.4
3	3∶1	68.9
4	4∶1	69.1
5	1∶2	53.1
6	1∶3	58.0
7	1∶4	59.1

① Reaction condition: temperature: 250℃, reaction time: 3h, the molar ratio of catalyst/DMT: 0.004, the mole of DMT: 0.05mol.

3.4 Effect of reaction time on the reaction

To investigate the catalytic activity at different time, more experiments was conducted in the range of 1—7h. The result is shown in Table 4. It can be seen that the yield of DMC increased with the reaction time, but the change was not significant after about 3h. So, the optimal reaction time for the reaction is 3h.

Table 4 Effect of reaction time on the reaction①

Entry	Time, h	Yield of DMC, %
1	1	63.6
2	2	65.7
3	3	68.9
4	5	69.4
5	7	69.5

① Reaction conditions: temperature: 250℃, molar ratio of catalyst/DMT: 0.004, molar ratio of EC/DMT: 3, amount of DMT: 0.05mol.

3.5 FT-IR spectra about oligomer of PET

The FT-IR spectra about PET are shown in Fig.2. The FT-IR spectrum of most PET produced by the transesterification of ethylene glycol and dimethyl terephthalate is shown as spectrum (1)[14]. The FT-IR spectrum (2) is the product that obtained using LiCl as catalyst and the reaction conditions were the same with those in section 3.1. It is interesting to see that spectrum (2) is almost identical to spectrum (1) and it can be concluded that the present product is the oligomer of PET. In spectrum (2), the characteristic bands are mainly derived from ester and aromatic ring groups. 1267cm^{-1} and 1128cm^{-1} are due to stretching vibration of C—O. The bands at 1719cm^{-1} and 728cm^{-1} are characteristic of C═O and benzene ring, respectively [14]. The band at 3432cm^{-1} indicates the oligomer of PET contains hydroxyl.

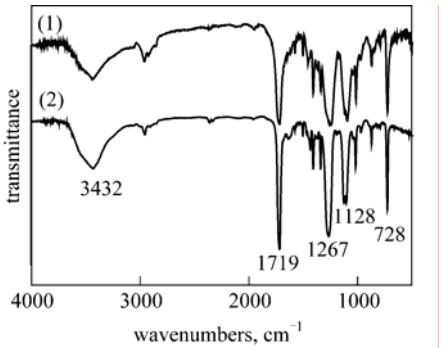

Figure 2 FT-IR spectra of PET

In this work, the oligomer of PET was obtained, and the study of further polymerization is under way.

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