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Simultaneous synthesis of dimethyl carbonate and ethylene glycol dimethacrylate using homogenous basic catalyst

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Abstract

A novel method simultaneously to prepare dimethyl carbonate and ethylene glycol dimethacrylate from ethylene carbonate and methyl methacrylate has been demonstrated in the presence of catalyst sodium methoxide and polymerization inhibitor ZJ-705. The effect of reaction parameters such as catalyst loading, polymerization inhibitor loading, concentration of reactants, reaction time, etc., on synthesis of dimethyl carbonate and ethylene glycol dimethacrylate was investigated. A reaction mechanism has been discussed with catalyst sodium methoxide.

Keywords: Dimethyl carbonate; Ethylene glycol dimethacrylate; Ethylene carbonate; Methyl methacrylate; Transesterification; CO_2 utilization

1. Introduction

Dimethyl carbonate (DMC), an environmentally benign and very useful chemical, has attracted substantial research efforts in recent years [1–4]. Among the various methods for synthesizing DMC, transesterification of ethylene carbonate with methanol is the most promising non-phosgene route for large-scale commercial industrialization. It typically involves two reactions: one is the reaction between CO_2 and ethylene epoxide with ethylene carbonate (EC) as a product; the other is the reaction between EC and methanol with DMC as a product and ethylene glycol as a by-product [3]. Because CO_2, a greenhouse gas and abundant carbon resource, is utilized as a raw material in this reaction route, transesterification process is also the most challenging and attractive from the viewpoint of "green chemistry" and "sustainable development" [4]. Ethylene glycol dimethacrylate (EGDMA) is also a very important fine chemical, which is a polymerizable monomer increasing in commercial importance and especially used as crosslinking agent to form rigid coatings which are insoluble in normally used solvents [5,6]. The very important and industrial route to produce EGDMA is the transesterification of methyl methacrylate (MMA) and ethylene glycol [6,7].

Both the transesterification of EC with methanol (1) and the transesterification between MMA and ethylene glycol (2), however, show poor atom economy. Furthermore, in both cases, ethylene glycol or methanol is produced as a very cheap by-product, which greatly reduces the efficiency of both the reagents and the reaction vessels. The major disadvantages of these above routes are the high energy consumption, high investment and high production costs. In order to solve these problems, we couple reactions (1) and (2) to utilize the total functionality of both EC and MMA, and get a new routine (3) to synthesize simultaneously DMC and EGDMA from EC and MMA with homogenous basic catalysts (see Scheme 1). The novel reaction (3) improves the atom economy in reactions (1) and (2) by avoiding the formation of by-product methanol and ethylene glycol, decreases energy consumption and investment and production costs and will accelerate the utilization of CO_2.

In the present work, the effect of various catalysts and process parameters on the synthesis of DMC and EGDMA from MMA and EC was reported.

2. Experimental

Catalyst CaO was prepared by decomposition of calcium carbonate at 900 °C for 2 h. $Pb(CH_3COO)_2$ and $Zn(CH_3COO)_2$

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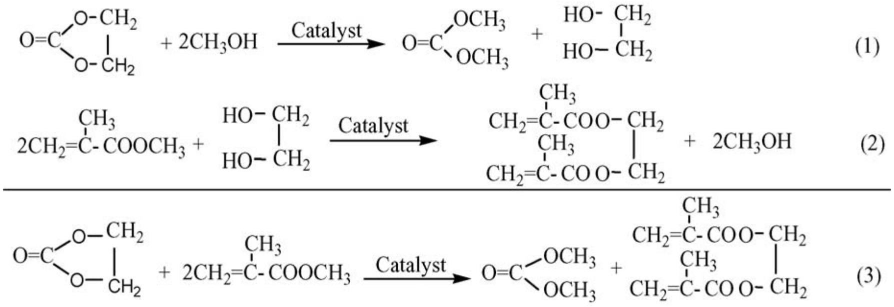


Scheme 1. Simultaneous synthesis of DMC and EGDMA from EC and MMA.

were obtained by removal of crystal water in $Pb(CH_3COO)_2 \cdot 3H_2O$ at 75 °C for 2 h and in $Zn(CH_3COO)_2 \cdot 2H_2O$ at 100 °C for 2 h, respectively. Polymerization inhibitors ZJ-705 and AR-Cu(II) were supplied by Wuxi Fuan Chemical Factory in Jiangsu Province of China. Other reagents were used as received (analytical grade).

The transesterification reactions between EC and MMA were carried out in a 250 ml three-neck flask, equipped with a nitrogen inlet and a distillation column connected with a liquid dividing head. MMA (80.1 g, 0.8 mol), EC (17.6 g, 0.2 mol), $NaOCH_3$ catalyst (0.5 g) and polymerization inhibitor ZJ-705 (0.5 g) were added under a stream of nitrogen. When the mixture was heated to 106 °C, reflux was observed in the flask and lasted about 45 min until vapor appeared at the top of the column. The azeotrope of DMC and MMA was collected slowly in a receiver flask attached to a liquid dividing head. After reaction, the reactor was cooled to room temperature. The resulting solution was analyzed by gas chromatogram (Agilent-6890N). FTIR spectra of by-product polymers were obtained on SPECTRUM GX II apparatus from Perkin-Elmer.

3. Results and discussion

3.1. Activities of various catalysts for the transesterification

A variety of catalysts were chosen for the transesterification of MMA with EC. Preliminary experiments were carried out for their catalytic activities. The results are presented in Table 1.

These results show that a non-catalytic reaction between MMA and EC produced only trace of DMC and EGDMA after 7 h, with only a trace conversion of EC (see Table 1, entry 1) indicating that catalyst is essential for formation of DMC and EGDMA. Catalysts such as $NaOCH_3$, K_2CO_3 [7,8] often used in reaction of EC with methanol, and in reaction between MMA and glycol, were screened (see Table 1, entries 2 and 3) in which $NaOCH_3$ catalyst was found to show good activity. Catalysts such as ZnO and CaO [9,10], often used in the reaction of EC with methanol, and catalysts such as $Ti(OBu)_4$ and Bu_2SnO [6,11], often used in the reaction between MMA and glycol, were also tested (see Table 1, entries 4–7). Compared to ZnO, CaO and $Ti(OBu)_4$, Bu_2SnO shows good catalytic activity. In classical Lewis acids, $ZnCl_2$ shows better catalytic activity than $AlCl_3$ (entries 8 and 9), and polymerization happened when using $AlCl_3$ as catalyst during the reaction. Other metal derivatives such as $Zn(CH_3COO)_2$, $Pb(CH_3COO)_2$ and PbO were also found to show poor activity (entries 10–12). The results show that alkali metal alkylate such as $NaOCH_3$ gives good conversion of EC and excellent selectivities of DMC and EGDMA compared to metal oxides catalysts such as ZnO which only give poor conversion and selectivities (entries 2 and 5).

Therefore, further reactions between EC and MMA were carried out using $NaOCH_3$ as catalyst.

3.2. Effect of catalyst $NaOCH_3$ concentration

The effect of catalyst $NaOCH_3$ concentration on conversion and selectivity behaviors in transesterification between EC and MMA was investigated in the range 0.13–2% by mass (see Fig. 1a and b). A series of data show that EC conversion increases quickly with increase of $NaOCH_3$ concentration. However, with increase in $NaOCH_3$ concentration, high catalyst loading (loading > 0.5% by mass) slowly increases EC conversions, increases amounts of by-product polymer and slowly decreases selctivities of DMC and EGDMA. It can be concluded that excess $NaOCH_3$ catalyst easily leads to polymerization of EC, and is disadvantageous to produce DMC and EGDMA, which is also consistent with the literature [8].

Table 1
Activities of various catalysts for the transesterification of ethylene carbonate and methyl methacrylate[a]

Entry	Catalyst	EC conversion (%)	Yield (%)	
			DMC	EGDMA
1	None	Trace	Trace	Trace
2	$NaOCH_3$	32.8	28.6	29.3
3	K_2CO_3	20.1	7.2	8.5
4	CaO	8.0	0.8	2.5
5	ZnO	1.4	Trace	0.1
6	$(BuO)_4Ti$	6.8	5.4	5.9
7	Bu_2SnO	16.2	13.0	14.1
8	$AlCl_3$[b]	–	9.4	–
9	$ZnCl_2$	14.6	11.3	12.6
10	$Zn(CH_3COO)_2$	2.7	0.1	0.2
11	$Pb(CH_3COO)_2$	3.1	2.0	2.5
12	PbO	2.0	0.6	0.7

[a] Ethylene carbonate (0.2 mol), methyl methacrylate (0.8 mol), catalyst (2 g), polymerization inhibitor ZJ-705 (0.5 g), reaction time (7 h).

[b] All reactants were polymerized suddenly after 3 h, DMC yield was gained by the azeotrope collected.

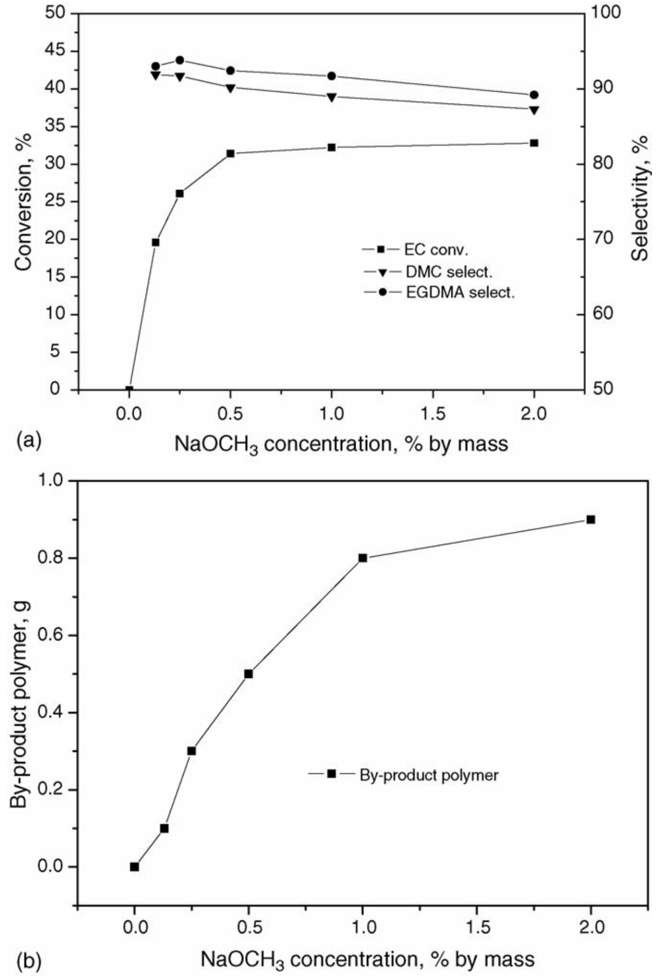


Fig. 1. (a and b) Effect of catalyst $NaOCH_3$ concentration on the transesterification between ethylene carbonate and methyl methacrylate. Ethylene carbonate (0.2 mol), methyl methacrylate (0.8 mol), inhibitor ZJ-705 (0.5 g), reaction time (7 h).

3.3. *Inhibition of various polymerization inhibitors on transesterification*

It is well-known that polymerization inhibitors have an important role in reactions including reactants such as methacrylate esters. Typical polymerization inhibitors are phenolic compounds such as hydroquinone, metal ions such as Cu(II), aromatic heterocycle such as phenothiazine and free radicals containing atoms of nitrogen and oxygen such as ZJ-705. Since inorganic Cu(II) salts have poor solubility in the mixture of EC and MMA, AR-Cu(II), a kind of organic Cu(II) salt having good solubility, was chosen. ZJ-705, hydroquinone, phenothiazine and AR-Cu(II) used as inhibitors in the transesterification were tested (see Table 2). Table 2 shows that hydroquinone has poor inhibition and significant effect on conversions and selectivities compared to inhibitor ZJ-705 and phenothiazine. The main reason that hydroquinone is a poor inhibitor for base catalysed transesterification, is that it can lower catalytic activity by reacting with $NaOCH_3$ catalyst. The results show that ZJ-705 has the best inhibition, but AR-Cu(II) has hardly inhibition. It is likely that AR-Cu(II) completely lost inhibiting ability due to its instability in basic solvent, especially containing basic $NaOCH_3$ catalyst.

Table 2
Inhibition of various polymerization inhibitors on transesterification of ethylene carbonate with methyl methacrylate[a]

Entry	Inhibitor	EC conversion (%)	By-product polymer (g)	Selectivity (%)	
				DMC	EGDMA
1	ZJ-705	31.4	0.5	90.2	92.4
2	Phenothiazine	32.0	1.1	88.4	89.2
3	Hydroquinone	25.9	8.4	83.0	76.8
4	AR-Cu(II)[b]	–	–	–	–

[a] Ethylene carbonate (0.2 mol), methyl methacrylate (0.8 mol), catalyst $NaOCH_3$ (0.5 g), inhibitor (0.5 g), reaction time (7 h).

[b] All reactants were polymerized suddenly after 0.5 h.

3.4. *Effect of polymerization inhibitor ZJ-705 concentration*

The effect of polymerization inhibitor ZJ-705 concentration on transesterification of MMA with EC was studied over $NaOCH_3$ catalyst. As shown in Fig. 2, amounts of by-product polymer decrease rapidly with increasing concentration of inhibitor ZJ-705. Above 0.13% by mass, however, amounts of by-product polymer remained almost unchanged, so the best concentration of inhibitor ZJ-705 is about 0.13% by mass.

3.5. *Effect of molar ratio of MMA to EC*

The effect of molar ratio of MMA to EC was also studied with $NaOCH_3$ catalyst. The molar ratio of MMA to EC was varied in the range of 1–6 and results are shown in Fig. 3a and b. Conversions of EC increased steadily up to the molar ratio of 4, then remained almost constant. With the increase

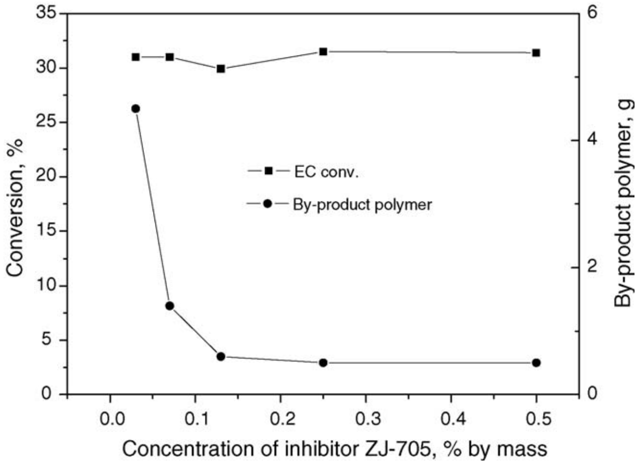


Fig. 2. Effect of inhibitor concentration on the transesterification between ethylene carbonate and methyl methacrylate. Ethylene carbonate (0.2 mol), methyl methacrylate (0.8 mol), catalyst $NaOCH_3$ (0.5 g), reaction time (7 h).

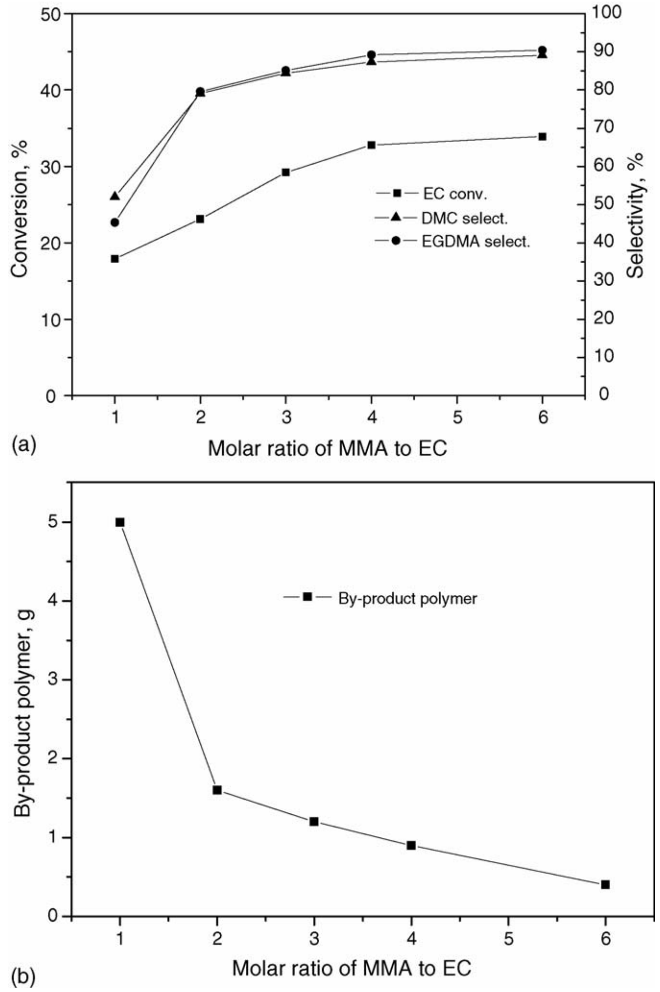


Fig. 3. (a and b) Effect of molar ratio of MMA to EC on the transesterification between ethylene carbonate and methyl methacrylate. Methyl methacrylate (0.8 mol), catalyst $NaOCH_3$ (2% by mass), inhibitor ZJ-705 (0.5 g), reaction time (7 h).

of MMA concentration, selectivities of DMC and EGDMA increased and amounts of by-product polymer decreased. One reason is that with higher EC concentration, reaction temperature also increases and higher temperature easily causes polymerization of methacrylate esters. During these experiments, it was found that the highest reaction temperature in each reaction increased slowly from 108 to 115 °C when the molar ratio of MMA to EC decreased from 6 to 2. But when the molar ratio of MMA to EC was 1, the highest reaction temperature reached 128 °C. Therefore, polymerization of MMA and EGDMA increased and EGDMA selectivity was caused to be lower than DMC selectivity. Another reason is that higher EC concentration is favorable to polymerization of EC, not to synthesis of DMC and EGDM, which will be explained in reaction mechanism.

3.6. Effect of reaction time on transesterification

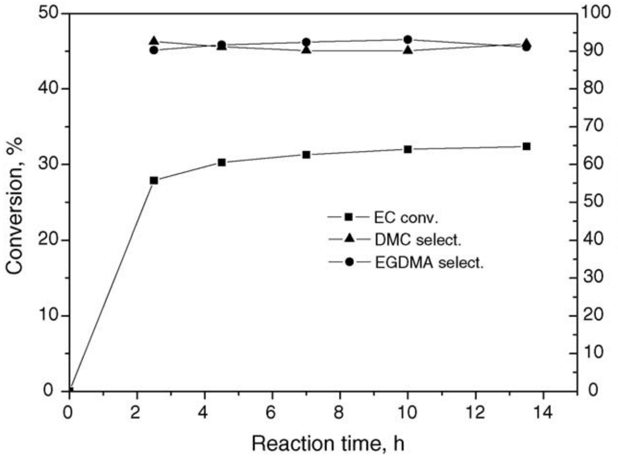


Fig. 4. Effect of reaction time on the transesterification between ethylene carbonate and methyl methacrylate. Methyl methacrylate (0.8 mol), ethylene carbonate (0.2 mol), catalyst $NaOCH_3$ (0.5 g), inhibitor ZJ-705 (0.5 g).

Conversions of EC were also studied versus reaction time using $NaOCH_3$ catalyst. As shown in Fig. 4, conversions of EC rapidly increase with reaction time up to 2.5 h, but only a little after that. Selectivities of DMC and EGDMA are both excellent and almost constant during all reaction time.

3.7. Effect of number of additions of $NaOCH_3$ catalyst

When 1 g $NaOCH_3$ catalyst was divided into two parts or three parts, the second of two parts was put into reactor when reaction time reached 4 h in one reaction and one of three parts was put into reactor every 2 h in another reaction. Reaction time was 7 h. The results are shown in Fig. 5. If 1 g $NaOCH_3$ catalyst was added in three equal amounts, at intervals of 2 h, conversions of EC increased from 32.2 to 43.2%, while the selectivities of DMC and EGDMA were almost constant. Total amounts of catalyst $NaOCH_3$ added to one reaction were constant, but different results were obtained by different number of additions of catalyst $NaOCH_3$. The possible reason is that the increase of number

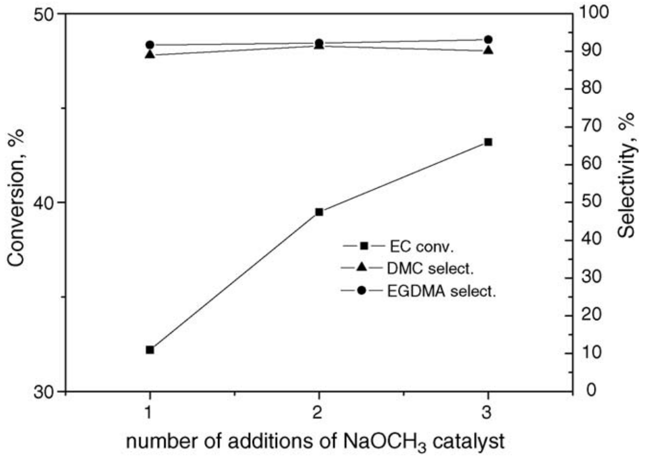


Fig. 5. Effect of number of additions of catalyst $NaOCH_3$ on the transesterification between ethylene carbonate and methyl methacrylate. Methyl methacrylate (0.8 mol), ethylene carbonate (0.2 mol), catalyst $NaOCH_3$ (1 g), inhibitor ZJ-705 (0.5 g), reaction time (7 h).

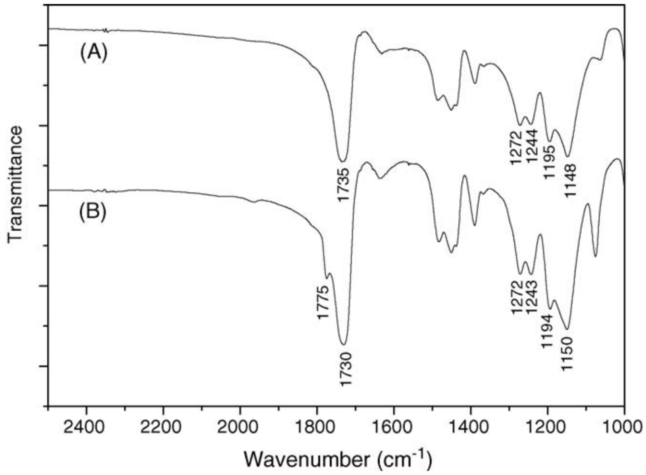


Fig. 6. FTIR spectra of by-product polymers.

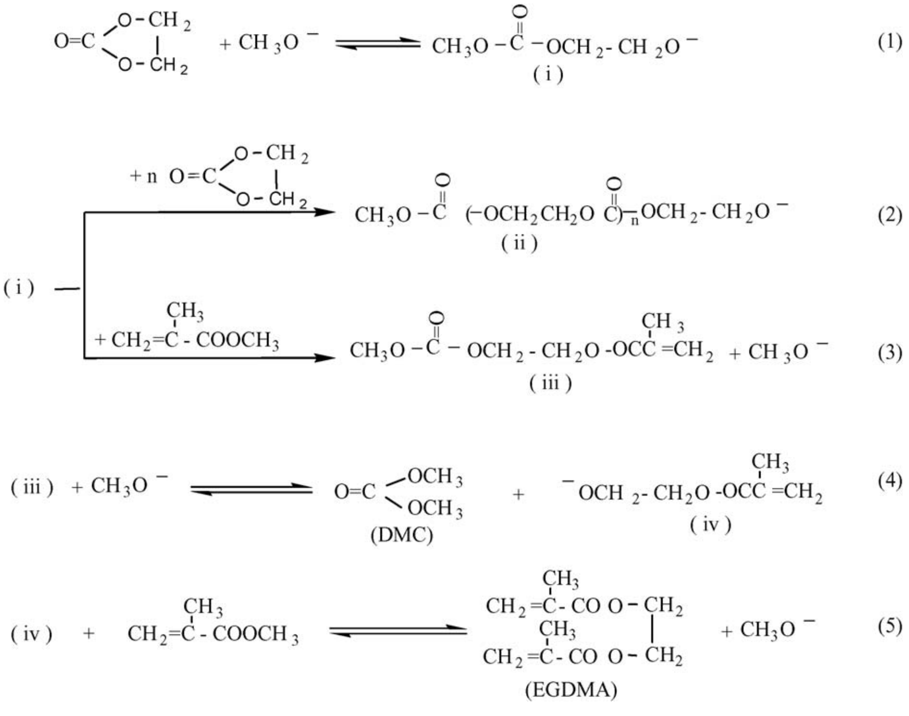
of additions of $NaOCH_3$ can avoid the participation of excess $NaOCH_3$ in other reactions and slows the decrease of the catalytic activity.

3.8. FTIR spectra of by-product polymers

The FTIR spectra of by-product polymers are shown in Fig. 6. The FTIR spectrum of most by-product polymers is shown in spectrum A. The FTIR spectrum B is that of by-product polymers formed when $NaOCH_3$ concentration increases to about 1% by mass and molar ratio of EC and MMA increases to about 1/4. In spectrum A, the band at 1735 cm^{-1} due to stretching vibration of the C=O bond and the bands at 1272, 1244, 1195 and 1148 cm^{-1} are characteristic bands of poly(MMA) [15]. In spectrum B, besides characteristic bands of poly(MMA), the band at 1775 cm^{-1} is consistent with the stretching vibration of C=O bond of R–OCOO–R′ [16], which indicates the by-product polymers with spectrum B contain poly(EC). The band at 1775 cm^{-1} is much smaller than the band at 1735 cm^{-1}, which indicates the amounts of poly(EC) is much smaller than that of poly(MMA) in the by-product polymers with spectrum B.

4. Plausible reaction mechanism (Scheme 2)

$NaOCH_3$ is well-known to catalyze reaction of EC with methanol via a nucleophilic substitution mechanism [3], indicating transesterification between MMA and EC with $NaOCH_3$ catalyst is likely to be a nucleophilic substitution reaction. Firstly, $NaOCH_3$ as nucleophile attacks EC to produce hydroxyethyl methyl carbonate (HEMC) which exists only for short time [10–13]. And the second step is a key step, in which there is a competition between reactions (2) and (3) [14]. $NaOCH_3$ concentration has significant effect on the competition. Higher $NaOCH_3$ concentration is favorable to produce compound (i), and higher compound (i) concentration is advantage to both reactions (2) and (3). Because $NaOCH_3$ is produced in reaction (3), higher $NaOCH_3$ concentration is more favorable to reaction (2), which was testified in Fig. 1b and was also consistent with the literature [8]. Molar ratio of MMA to EC also acts as an important role for the competition. From reactions (2) and (3), it can be seen that high EC concentration is more advantageous to reaction (2) which produces polyethylene carbonate (PEC), but high MMA concentration



Scheme 2. Mechanism of transesterification between EC and MMA with $NaOCH_3$ catalyst.

is more advantageous to reaction (3) which is a very important step to produce DMC and EGDMA, which was testified in Fig. 3b.

5. Conclusions

A new method to synthesize simultaneously dimethyl carbonate and ethylene glycol dimethacrylate from ethylene carbonate and methyl methacrylate has been investigated. This route avoids the formation of by-product methanol and ethylene glycol and greatly improves the atom economy in reaction. The catalyst screening studies showed that basic homogenous catalyst $NaOCH_3$ had the best activity. In various polymerization inhibitors, ZJ-705 showed the best inhibition. Under the conditions of 0.8 mol methyl methacrylate, 0.2 mol ethylene carbonate, 0.5 g inhibitor ZJ-705, 1 g $NaOCH_3$ catalyst adding one-third every 2 h, reaction time 7 h and protection with nitrogen, the conversion of EC was 43.2%, with selectivity for DMC and EGDMA being 90.1 and 93.1%, respectively.

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