A NEW ROUTE TO RECOVER BISPHENOL A AND DIMETHYL CARBONATE FROM WASTE ÀPOLYCARBONATE IN IONIC LIQUIDS

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Abstract: An new strategy for methanolysis of polycarbonate (PC) to recover bisphenol A(BPA) and dimethyl carbonate(DMC) was studied in which PC could be methanolyzed in ionic liquid 1-n-butyl-3-methylimidazolium chloride([Bmim][Cl]) without any acid or base catalyst under moderate conditions. Under the conditions of m(PC):m ([Bmim][Cl]):m(CH3OH)=1:1:1.5, reaction time 2.5h and temperature 105℃, the methanolysis conversion of PC was almost 100% and the yields of both BPA and DMC were over 95%. After easily separated from the product, the ionic liquid could be reused 8 times without obvious decrease in the conversion of PC and yields of BPA and DMC. The strategy can overcome the disadvantages existed in traditional methods such as unfeasible reuse of catalyst, tedious workup procedure and environmental problem.

1. Introduction

With the rapid increase of production and consumption of polycarbonate (PC), the problem about the treatment of waste PC is now an important issue all over the world. For the purpose of chemical recycling of waste PC, there have been reported a number of methods[1-5]. In order to recover pure monomer bisphenol A (BPA) and dimethyl carbonate (DMC), the most important chemical recycling methods reported are methanolysis catalyzed by acids or bases in methanol media. However, due to the insolubility of PC in methanol, the reported methanolysis methods require high temperature and pressure and in presence of a lot amount of concentrated acids or bases. The acid or base catalysts used in traditional methods cannot be reused and result in other disadvantages such as equipment corrosion, tedious workup procedure and environmental problem. Although supercritical method can overcome some of above-mentioned shortcomings [4-8], it has its own disadvantages such as severe conditions, so its application is limited. Therefore, it is necessary to explore a new approach for methanolysis of PC.

The room temperature ionic liquid, a kind of environmentally friendly solvent and catalyst, due to its adjustable physical and chemical properties, got broadly attention of

scholars from various fields such as synthesis, catalysis and separation [9-11]. But to the best of our knowledge, no article about ionic liquid used in methanolysis of PC has been published. In this paper, we prepared several ionic liquids (Fig. 1) and used them in methanolysis of PC. To our surprise, [Bmim][Cl] was of excellent catalytic activity and reusability.

2. Experimental

2.1 Chemicals and Instruments

Pure PC pellets (3 mm length and 2.5 mm diameter with M_W. about 20000) were used as model plastics. N-Methylimidazole (MIM, 99%), n-butylchloride and other chemicals (AR) were commercially available and used without further purification. The IR spectra were recorded by a Nicolete 510P FT-IR spectrometer in the range of 4500-400cm^{-1}.

2.2 Synthesis of Ionic Liquids

2.2.1 General Procedure for Synthesis of [Bmim][Cl]

A mixture of 1-methylimidazole and n-butylchloride in a 1:1.2 molar ratio was reacted with stirring at 70℃ for 72 h. The mixture was washed by ethyl acetate for three time to remove the unreacted starting materials and then distilled at 70℃ under reduced pressure (10 mmHg) over 2 h to obtain [Bmim][Cl](yield 95%). [Bymim][Cl], [Omim][Cl], [Emim][Br], [Amim][Cl], [Cemim][Cl] and [Epydin][Br] were prepared with a similar procedure. [Bmim][BF_4] and [Omim][PF_6] were synthesized according to the references[12-14].

2.2.2 Metholysis of PC

Weighed amounts of PC(w_1), methanol and ionic liquid were added in an autoclave with a stirrer and a thermometer. The mixture was heated up to the given temperature for certain time. The reaction mixture was added an equal volume of ethyl acetate. The unreacted PC(w_2) was removed by filtration. The obtained filtrate was separated into two phases. The upper phase which is mainly composed of BPA, DMC, methanol and ethyl acetate was analyzed by a HP 5890 gas

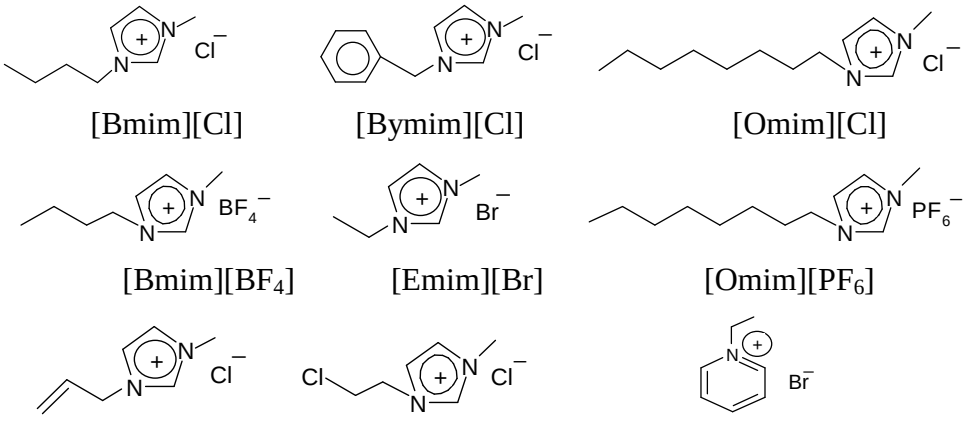

Fig. 1 Structures of ionic liquids prepared and used in this paper.

chromatograph with DB-5 glass capillary column of 50m and calculated to obtained weights of BPA(w_3) and DMC(w_4), the lower phase which is mainly ionic liquid was reused directly as solvent and catalyst. Conversion of PC and yield of BPA and DMC were calculated by following formula:Conversion of PC = $[(w_1–w_2) / w_1]$ x 100%; Yield of BPA = (w_3/ w_5)x 100%; Yield of DMC = $(w_4/ w_{6)}$ x 100%; Where w_5 and w_6 are the weights of BPA and DMC respectively that should obtained theoretically.

3. Results and Discussion

Methanolysis of PC in different ionic liquids was investigated (Tab. 1). Surprisingly, ionic liquids have a significant influence on methanolysis results of PC. Especially, [Bmim][Cl] (entry 2) exhibited an outstanding performance for methanolysis of PC under moderate conditions and without any acid or base catalyst, the conversion of PC was almost 100%. This may be due to a good dissolubility of PC in [Bmim][Cl] and the weak basicity of the ionic liquid. Methanolysis of PC did not take place in absence of ionic liquid under the given conditions (entry 1). Moreover, we can see from Tab.1 that the cations and anions of ionic liquids have significant effect on methanolysis results of PC. When the anion is [Cl], the conversion is much better (entries 2, 5) than when the anion is [BF_4](entry 7) or [PF_6] (entry 8).When using [Emim][Br] as medium, the conversion is much better (entries 3) than using [Epydin][Br] (entry 6).When using 1- R-3-methylimidazolium chloride as medium, the R group is of significant influence on methanolysis results of PC(entries 2, 4, 5, 9 10).

The effect of reaction conditions on methanolysis results was showed in Tab. 2. As can be seen from tab. 2, temperature is very important for the methanolysis of PC. When temperature is 85℃, the conversion of PC is only about 10% (entry 1) under given conditions. However, when the temperature was increased to 105℃, the methanolysis of PC almost finished (entry 3) under the same conditions. With decreasing of [Bmim][Cl] dosage from 2g to 0.5g, the conversion of PC decreased from 100%(entry 3) to 96%(entry 6), and when increasing of methanol dosage from 2g to 4g, the conversion of PC decreased from 100% (entry 5) to 90.6%(entry 8). All the results mentioned above can be explained by the difference in dissolubility of PC in the reaction mixture. The higher the temperature is, the more rapidly PC can dissolve in the reaction mixture. Moreover, both too less [Bmim][Cl] dosage and too much methanol dosage are unfavorable to improve the dissolubility of PC in the reaction mixture. It is suggested that the dissolubility of PC in the reaction mixture is the rate-determining step of the mathanolysis of PC.

Tab. 1 Effects of different ionic liquids on methanolysis reaction. [a)]

Entry	Ionic liquids	Dosage(g)	PC conversion(%)
1	-[b)]	0	0
2	[Bmim][Cl]	1.0	100
3	[Emim][Br]	1.0	64.7
4	[Amim][Cl]	1.0	38.1
5	[Omim][Cl]	1.0	2.1
6	[Epydin][Br]	1.0	0
7	[Bmim] [BF_4]	1.0	4.6
8	[Omim][PF_6]	1.0	0
9	[CEmim][Cl]	1.0	0
10	[Bymim][Cl]	1.0	0

[a)] PC 2g, CH_3OH 3g, t=2.5h, T= 105 ^oC; [b)] Using another 3g CH_3OH instead of ionic liquid.

Tab. 2 Effects of reaction conditions on methanolysis results.[c)]

Entry	Temp.(^oC)	CH_3OH Dosage(g)	[Bmim][Cl] Dosage(g)	PC conversion(%)
1	85	2.0	2.0	10.4
2	95	2.0	2.0	30.5
3	105	2.0	2.0	100
4	105	2.0	3.0	100
5	105	2.0	1.0	100
6	105	2.0	0.5	96.0
7	105	3.0	1.0	100
8	105	4.0	1.0	90.6

[c)] PC 2g, t=2.5h

Tab. 3 Reusability results of [Bmim][Cl] [d)]

Cycle	1	2	3	4	5	6	7	8
PC conversion (%)	100	100	100	100	100	100	100	100
Yield of BPA (%)	95.6	95.8	94.5	96.0	95.4	95.7	95.4	94.7
Yield of DMC (%)	96.5	96.8	96.4	96.3	95.9	94.7	95.6	95.3

[d)] PC 2g, CH_3OH 3g, [Bmim][Cl] 2g, t=2.5h, T= 105 ^oC

Fig. 2 shows the effects of reaction time on PC conversion at different temperature. At 105°C, the conversion of PC was almost 100% when methanolysis was carried out for about 2.5h. However, at 95 °C, the conversion of PC was still lower than 75% after 5.5h.

The reusability of ionic liquid [Bmim][Cl] for methanolysis of PC was examined and the results were showed in tab. 3. It is showed that the ionic liquid can be reused for 8 times without obvious decrease in the conversion of PC and yields of BPA and DMC under given conditions. Therefore, the ionic liquid has excellent reusable performance in methanolysis of PC. It is well known that the main factor which affects the reuse performance of ionic liquid is its stability under the reaction temperature and reaction fluid surroundings. Because ionic liquid [Bmim][Cl] itself is of a good thermal stability, the reaction mixture is almost neutral and the reaction temperature is only 105 °C, it is reasonable that it has good reusable performance in the methanolysis of PC.

The obtained BPA was characterized by IR using a Nicolet 510P FT-IR spectrometer in the range of 4000–400 cm^{-1}, using KBr powder containing ca. 1 wt% of sample. The IR spectrum was showed in Fig. 3 and the spectra data were as follows: ν(cm^{-1})3362,2964,

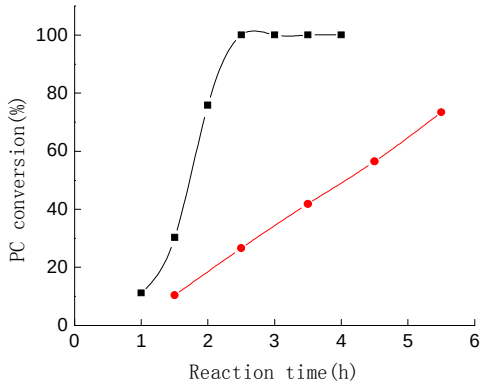

Fig. 2 Changes of PC conversion with reaction time at 105 °C(■) and 95 °C(●).

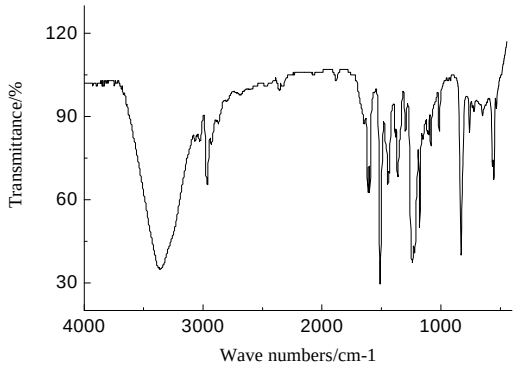

Fig. 3 IR spectrum of obtained BPA product

1612,1598,1510,1446,1362,1239,1221,1178,829,553. The IR spectrum and spectra data are identical with those of standard BPA. It is demonstrated that PC is completely depolymerized into BPA and DMC monomers and no intermediates of oligomers exist.

4. Conclusion

PC can be methanolysized to its starting monomer BPA and DMC in presence of ionic liquid [Bmim][Cl] without any acid or base catalyst under moderate conditions. Under the conditions of PC 2g, CH_3OH 3g, [Bmim][Cl] 2g, reaction time 2.5h and temperature 105 °C, the methanolysis conversion of PC was almost 100% and the yields of both BPA and DMC were over 95%. The ionic liquid could be reused 8 times without obvious decrease in the

conversion of PC and yields of BPA and DMC. The strategy can overcome the disadvantages existed in traditional methods such as unfeasible reuse of catalyst, tedious workup procedure and environmental problem.

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