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Role of sulfonic acids in the Sn-catalyzed transesterification of dimethyl carbonate with phenol

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Abstract

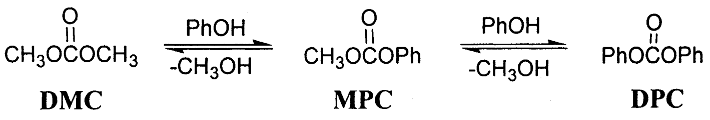
Diphenyl carbonate, the key intermediate of the non-phosgene polycarbonate manufacturing process, can be produced by the transesterification of dimethyl carbonate with phenol in the presence of dibutyltin oxide. The use of an alkyl or aryl sulfonic acid in conjunction with dibutyltin oxide significantly enhances the activity of dibutyltin oxide. ^{19}F and ^{119}Sn NMR studies suggest the formation of tin complex containing strongly electrophilic sulfonate ligand from the reaction of dibutyltin oxide with alkyl or aryl sulfonic acid. Various factors affecting the transesterification of dimethyl carbonate with phenol were investigated.

Keywords: Polycarbonate; Diphenyl carbonate; Transesterification; Non-phosgene process

1. Introduction

Polycarbonates, one of the most important engineering thermoplastics, are commercially produced by the reaction of phosgene and bisphenol-A in the presence of NaOH [1]. This conventional process has the serious environmental problems involved in the use of the highly toxic phosgene such as the formation of a stoichiometric amount of NaCl and the use a copious amount of methylene chloride as a solvent. Accordingly, there has been tremendous effort to produce polycarbonate by using non-phosgene methods [2–4].

The most practical non-phosgene process seems to be the melt polymerization of bisphenol-A with diphenyl carbonate (DPC) which can be prepared from step-wise transesterification of dimethyl carbonate (DMC) with phenol with the continuous removal of methanol as shown in Eq. (1) [5–7].



$$\underset{\textbf{DMC}}{CH_3O\overset{\overset{O}{\|}}{C}OCH_3} \underset{-CH_3OH}{\overset{PhOH}{\rightleftharpoons}} \underset{\textbf{MPC}}{CH_3O\overset{\overset{O}{\|}}{C}OPh} \underset{-CH_3OH}{\overset{PhOH}{\rightleftharpoons}} \underset{\textbf{DPC}}{PhO\overset{\overset{O}{\|}}{C}OPh} \quad (1)$$

However, due to the thermodynamically unfavorable equilibrium ($K = 3 \times 10^{-4}$ at 453 K) toward DPC, the reaction suffers from low yield and selectivity to DPC even at elevated temperatures [8]. Various catalysts have been applied as catalysts for the production of DPC by the transesterification between

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DMC and phenol [9–11], but their catalytic activities are not high enough for the industrial purpose.

During the course of our study to improve the catalytic performance of tin complexes, we have found that the use of alkyl or aryl sulfonic acid in conjunction with dibutyltin oxide significantly enhance the activity of dibutyltin oxide, producing DPC and methyl phenyl carbonate (MPC) in high yields.

We now report a highly efficient catalytic system consisting of dibutyltin oxide and an alkyl or aryl sulfonic acid for the transesterification between DMC and phenol.

2. Methods

All the transesterification reactions were conducted in a 100 ml stainless-steel bomb equipped with an electrical heater and a stainless steel column. The reactor was charged with dimethyl carbonate (3.6 g, 40 mmol), phenol (18.8 g, 200 mmol), benzene (40 ml) as a solvent, an appropriate catalyst or catalytic system, and *t*-butyl benzene (2 g) as an internal standard. Molecular sieves (30 g) were placed in a 60 ml stainless-steel column mounted to the lid of the reactor. The reactor was evacuated to remove air from the molecular sieves and then heated to 180 °C at the rate of 10 °C/min. After the reaction, the reactor was cooled to room temperature and the resulting solution was analyzed by gas chromatography (HP-6890) and gas chromatography–mass spectroscopy (GS–MS, HP-6890N GC-5973MSD). ^{19}F and ^{119}Sn NMR measurements were carried out in $CDCl_3$ using a Varian UNITYplus-300. In $CDCl_3$, CF_3CO_2H and $SnMe_4$ were used as external references for ^{19}F and ^{119}Sn, respectively.

3. Results and discussion

The catalytic activities of dibutyltin oxide with or without the presence of sulfonic acids were tested for the transesterification between DMC and phenol. As can be seen in Table 1, dibutyltin oxide gave low yields of MPC and DPC. When triflic acid or *p*-toluenesulfonic acid was used as a catalyst, only MPC was produced with considerable amount of anisole as a by-product. However, when an alkyl or aryl sulfonic acid was used in conjunction with dibutyltin oxide, the yields of MPC and DPC increased significantly: approximately five times for DPC and 2 times for MPC. Furthermore, the formation of anisole was greatly reduced. No appreciable change in catalytic activity of dibutyltin oxide was observed with the variation of sulfonic acids (entry 4–7).

Various factors affecting the transesterification of DMC and phenol were investigated.

The effect of molar ratio of dibutyltin oxide to DMC on the transesterification of DMC with phenol was studied in the presence of triflic acid ($Bu_2SnO/CF_3SO_3H = 1/1$) at 180 °C. As shown in Fig. 1, yields of MPC and DPC increased rapidly with increasing molar ratio of dibutyltin oxide/DMC = 0.02. Above 0.02, however, the yields of MPC and DPC remained unchanged. It is likely that certain amounts of catalyst might transform into less active species at higher catalyst concentration.

Table 1
Activities of various catalytic systems for the transesterification of dimethyl carbonate with phenol[a]

Entry	Catalyst	Sulfonic acid	DMC conversion (%)	Yield (%)		
				DPC	MPC	Anisole
1	Bu_2SnO	–	21.0	4.0	16.7	0.3
2	–	CF_3SO_3H	13.0	–	9.7	2.8
3	–	$CH_3C_6H_4SO_3H$	12.8	Trace	10.5	3.7
4	Bu_2SnO	CF_3SO_3H	58.5	18.3	39.8	Trace
5	Bu_2SnO	CH_3SO_3H	56.5	19.7	36.5	Trace
6	Bu_2SnO	$CH_3C_6H_4SO_3H$	60.4	20.8	39.4	Trace
7	Bu_2SnO	$C_6H_5SO_3H$	57.9	19.4	38.2	0.2

[a] Dimethyl carbonate (40 mmol), phenol (200 mmol), Bu_2SnO (0.4 mmol), sulfonic acid (0.4 mmol), benzene (40 ml), molecular sieves (30 g), 180 °C, $t = 3$ h.

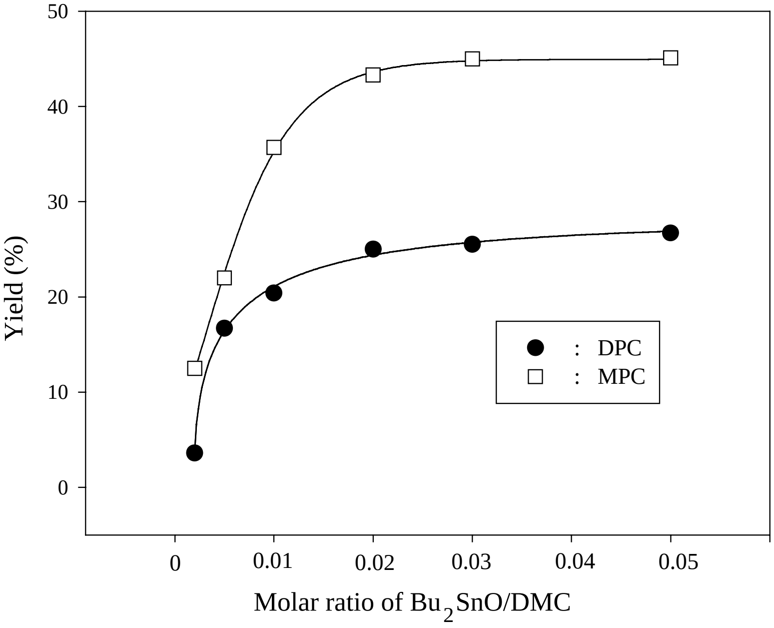

Fig. 1. Effect of molar ratio on the transesterification of DMC with phenol. Dimethyl carbonate (40 mmol), phenol (200 mmol), benzene (40 ml), molecular sieves (30 g), $Bu_2SnO/CF_3SO_3H = 1/1$, 180 °C, 3 h.

Fig. 2 shows the effect of temperature on the transesterification of DMC and phenol to give MPC and DPC in the temperature range 120–220 °C. The yields of MPC and DPC increased gradually with the increase of the reaction temperature, implying that our catalytic systems are thermally stable up to 220 °C. The formation of by-product, anisole was negligible even at elevated temperature of 220 °C.

The effect of molar ratio of phenol/DMC was also studied at 180 °C in the presence of a catalytic system consisting of dibutyltin oxide and triflic acid. The molar ratio of phenol to DMC was varied in the range of 3–10, and the results are shown in Fig. 3. The yields of MPC and DPC increase steadily up to the molar ratio of 7, but thereafter remained almost constant.

The yields of MPC and DPC were also monitored with reaction time using a catalytic system consisting of dibutyltin oxide and triflic acid at 180 °C. Fig. 4 shows that the formation of DPC continuously increases with reaction time, whereas the formation of MPC increased with the reaction time up to 10 h and then decreased thereafter. After 27 h of reaction, the conversion of DMC reached 98.4% and the yields of DPC and MPC were 95.4 and 2.5%, respectively.

The reason for the activity enhancement of dibutyltin oxide by the presence of alky or aryl sulfonic acid can be ascribed to the in situ formation of highly active tin species containing sulfonate ligand [12]. As a result of a sulfonate bonding, the Sn atom becomes more electrophilic or Lewis acidic in comparison with that of dibutyltin oxide, thereby coordination of DMC to electron-deficient Sn center, the first step of the transesterification, would take place more easily.

To confirm the in situ formation of triflato bonded tin species, ^{19}F NMR and ^{119}Sn experiments were conducted in $CDCl_3$.

As shown in ^{19}F NMR spectra in Fig. 5, the sample (A) containing dibutyltin oxide, triflic acid, phenol, and DMC show the peak at −1.63 ppm which is downfield shifted from that of triflic acid at −0.49 ppm as shown in the sample (B). ^{119}Sn NMR spectra also show that the peaks associated with Sn in sample (A) shifted to downfield from −178.5 and −177.8 ppm to −126.9, −139.1 and −151.6 ppm (Fig. 6). These results strongly suggest the in situ formation of active tin species containing electron withdrawing ligand like CF_3SO_3 by the interaction of dibutyltin oxide with triflic acid in the presence of phenol.

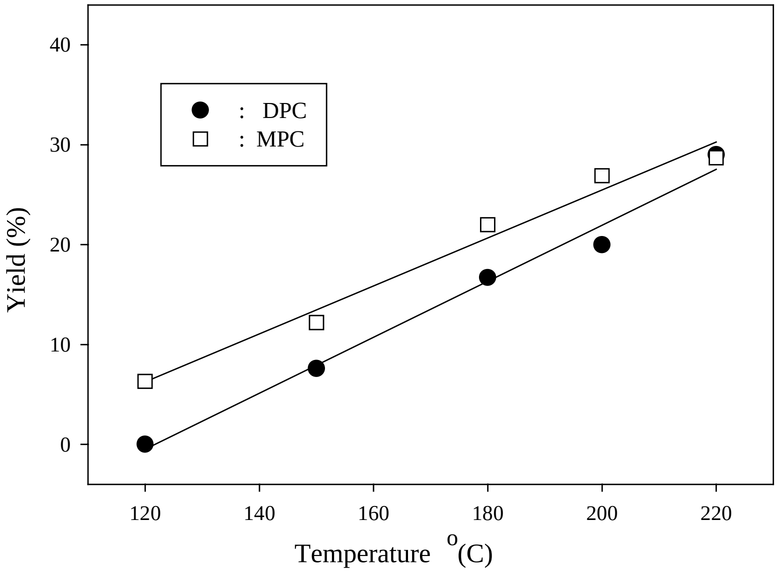

Fig. 2. Effect of temperature on the transesterification of DMC with phenol. Dimethyl carbonate (40 mmol), phenol (200 mmol), dibutyltin oxide (0.2 mmol), triflic acid (0.2 mmol), benzene (40 ml), molecular sieves (30 g), 3 h.

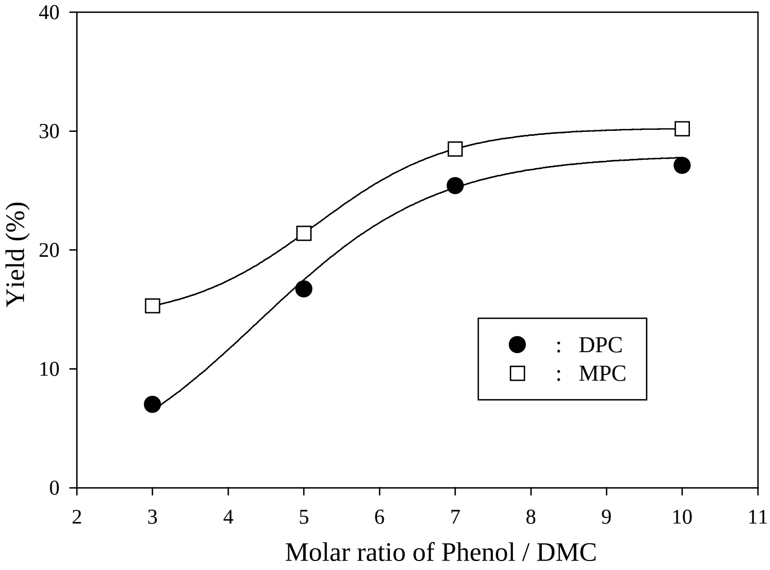

Fig. 3. Effect of molar ratio of phenol/DMC on the transesterification of DMC with phenol. Dimethyl carbonate (40 mmol), Bu_2SnO (0.2 mmol), CF_3SO_3H (0.2 mmol), benzene (40 ml), molecular sieves (30 g), 130 °C, 3 h.

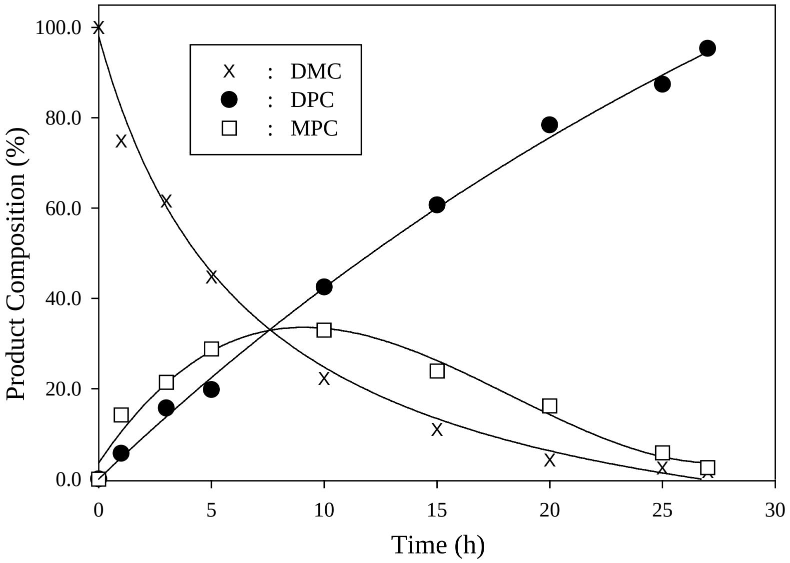

Fig. 4. Variation of product composition with the reaction time for the transesterification of DMC with phenol. Dimethyl carbonate (40 mmol), phenol (200 mmol), Bu_2SnO (0.2 mmol), CF_3SO_3H (0.2 mmol), benzene (40 ml), molecular sieves (30 g), 180 °C.

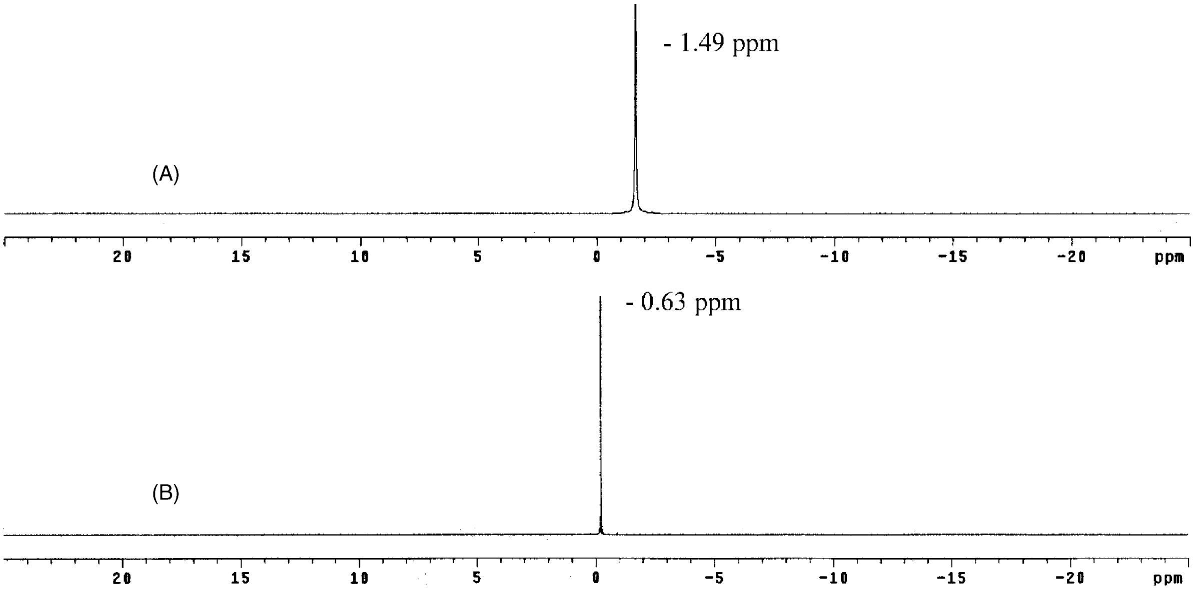

Fig. 5. ^{19}F NMR spectrum of sample (A) $Bu_2SnO + CF_3SO_3H$ + phenol + DMC; sample (B) CF_3SO_3H + phenol + DMC.

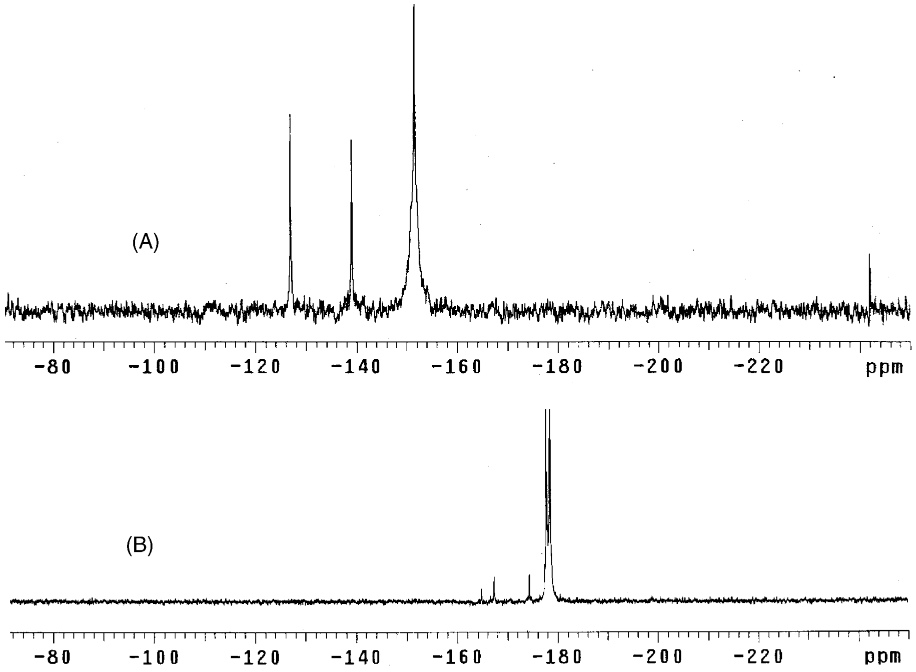

Fig. 6. ^{119}Sn NMR spectrum of sample (A) $Bu_2SnO + CF_3SO_3H$ + phenol + DMC; sample (B) Bu_2SnO + phenol + DMC.

Further studies are in progress to clearly elucidate the active species.

4. Conclusions

The use of alkyl or aryl sulfonic acids in conjunction with dibutyltin oxide significantly enhances the activity of dibutyltin oxide and suppresses the formation of the side product, anisole to a great extent in the transesterification of DMC with phenol. ^{19}F and ^{119}Sn NMR experiments reveal that dibutyltin oxide interacts with triflic acid to form active tin species containing triflato ligand in the presence of phenol. Therefore, the reason of the activity enhancement of dibutyltin oxide by the presence of alkyl or aryl sulfonic acid can be ascribed to the in situ formation of sulfonate bonded tin species.

Acknowledgements

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