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The structure of organotin oxides playing a key role on the transesterification of dimethyl carbonate with hydrogenated bisphenol A

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Abstract−Transesterification of dimethyl carbonate (DMC) with hydrogenated bisphenol A (HBPA) was studied over various organotin oxides under pressured condition without removal of by-producing methanol. Bu_2SnO displayed higher activities in HBPA conversion and bis-methylcarbonate of hydrogenated bisphenol-A (BMHBPA) synthesis, and HBPA conversion and BMHBPA selectivity reached 97.4% and 84.0%. However, when Ph_2SnO was used as catalyst, HBPA conversion and BMHBPA selectivity decreased to 81.5 and 37.7%. Catalyst steric hindrance significantly influenced HBPA conversion and BMHBPA formation, and π-d interaction between phenyl ring and Sn was unfavorable for the transesterification of HBPA with DMC. Moreover, the catalytic system was further optimized.

Keywords: Transesterification, Dimethyl Carbonate, Hydrogenated Bisphenol A, Organotin Oxide, XPS

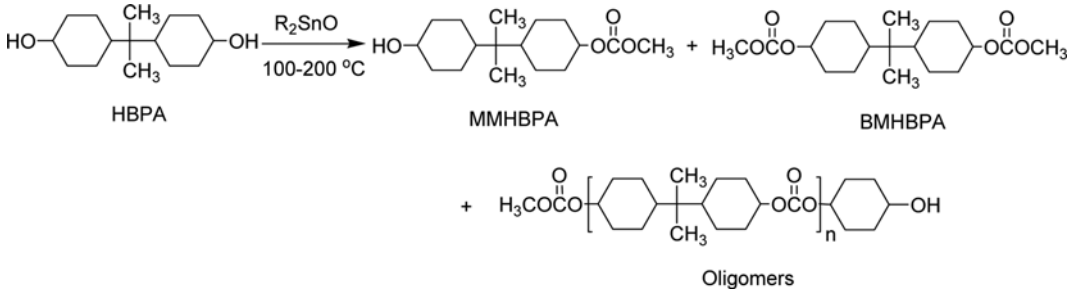
INTRODUCTION

Poly(bisphenol A carbonate) (PC) is an important thermoplastic widely used in daily products such as food containers [1]. However, the health concerns of BPA have drawn much attention in recent years since BPA is labeled as an endocrine disruptor [2]. A practical solution is to apply hydrogenated bisphenol A (HBPA), which does not contain the aromatic groups, to substitute the general usage of BPA. In addition, HBPA is not an endocrine disruptor and does not cause yellowing since there are no aromatic groups available to absorb the UV light [2].

Poly(hydrogenated bisphenol A carbonate) (PHBC) is biodegradable, biocompatible and non-toxic [3-6] which can be synthesized from DMC and HBPA through transesterification and polycondensation [7-12]. DMC first reacts with HBPA to produce mono-methylcarbonate of hydrogenated bisphenol-A (MMHBPA) and bis-methylcarbonate of hydrogenated bisphenol-A (BMHBPA), and then MMHBPA and BMHBPA are polymerized into PHBC (see Scheme 1). However, the thermodynamic stable byproduct formation coming from O-methylation of HBPA is a key factor interfering with selective transesterification and subsequently polymerization.

Lee [13] used NaH to catalyze the condensation polymerization of aliphatic diols with DMC to produce high-molecular-weight aliphatic polycarbonates under ambient pressure with continuous removal of by-producing methanol, aliphatic diols including 1,4-butanediol, 1,6-hexanediol and cyclohexane-1,4-dimethanol. For HBPA, it remained as a solid in DMC, which hampered transesterification and further condensation. Furthermore, the low solubility of the alkoxide anions in the resulting hydrophobic polymer often limited further chain growth. Pokharkar [8] reported that Bu_2SnO was the better catalyst in aliphatic polycarbonate synthesis by the melt-phase interchange reaction of aliphatic diols with DMC, such as, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol and cyclohexane-1,4-dimethanol. However, the transesterification or condensation polymerization of DMC with HBPA over organotin oxide has not been investigated.

We used the pressured condition and high temperature to pro-



Scheme 1. Transesterification of HBPA with DMC.

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mote HBPA dissolution in DMC, and organotin catalysts were introduced to selectively promote transesterification of HBPA with DMC. To provide deeper insights into the reaction process, different reaction parameters were studied.

EXPERIMENTS

1. Chemical Reagents

DMC (Tianjin Chemical Reagent Research Institute) was fractionally distilled and stored over molecular sieve (4 Å). HBPA, benzyl chloride, Ph_2SnO and Bu_2SnO were purchased from Sigma-Aldrich Company Ltd. Other chemical reagents were AR grade and used as received from local manufacturers without further purification.

2. $(C_6H_{11})_2SnO$ and $(PhCH_2)_2SnO$ Preparation

The Grignard reagent of $C_6H_{11}MgBr$ was synthesized from $C_6H_{11}Br$ and Mg in ethyl ether. After that $(C_6H_{11})_2SnCl_2$ was synthesized from $SnCl_4$ and $C_6H_{11}MgBr$ in toluene at 160 °C for 24 hours under the pressured condition, and the mole ratio of $C_6H_{11}MgBr$ to $SnCl_4$ is 2. The formed $(C_6H_{11})_2SnCl_2$ was separated from toluene solvent, and the hydrolysis of $(C_6H_{11})_2SnCl_2$ was carried out in presence of NaOH [14]. $(C_6H_{11})_2SnO$ precipitate was filtered and dried. According to the above described method, $(PhCH_2)_2SnO$ was synthesized from $PhCH_2MgBr$ and $SnCl_4$ at certain mole ratio in tandem with hydroxylation in presence of NaOH.

3. Characterization

Product structure was confirmed by GC-MS (HP5972) and compared with authentic samples. Quantitative analysis was carried on a gas chromatograph (PERSEE GC1100 with a FID detector, HP-5/DB-5 capillary column) with cetane as interior standard. Oligomers were analyzed by reversed-phase chromatography on a Varian Microsorb-MV 100-5 C18 column (250×4.6 mm, 10 : 90 H_2O/CH_3OH, 1 mL/min, 35 °C). The high performance liquid chromatograph was also equipped with evaporative light scattering detector (HPLC-ELSD 2000). The chemical states of the atoms and atom molar ratio in catalysts were characterized by X-ray photoelectron spectroscopy (XPS, ThermoFisher K-alpha).

4. Reaction Procedure

HBPA 0.01 mol, DMC 0.04 mol and catalyst 0.15 g were loaded into 20 ml stainless steel autoclave, and HBPA, DMC and catalyst suspension was heated to given temperature for certain time. After the reaction finished, the mixture was cooled and analyzed.

RESULTS AND DISCUSSION

1. The Promotion of Organotin in Transesterification of HBPA with DMC

The effects of various catalysts on the reaction were carefully studied, and results summarized in Fig. 1. HBPA conversion and BMHBPA selectivity reached 97.4% and 84.0% over Bu_2SnO. When $(C_6H_{11})_2SnO$ was used as catalyst, HBPA conversion achieved 90.6%, but BMHBPA selectivity declined to 36.0%. The major distinction between Bu_2SnO and $(C_6H_{11})_2SnO$ was their different steric hindrance, e.g., the bigger volume of $(C_6H_{11})_2SnO$ was unfavorable for transesterification. When $(PhCH_2)_2SnO$ and Ph_2SnO were used as catalyst, HBPA conversion decreased to 87.7% and 81.5%, and BMHBPA selectivity reached 48.6% and 37.7%. Comparing the performance of $(PhCH_2)_2SnO$ and Ph_2SnO, $(PhCH_2)_2SnO$ was the better catalyst in transesterification of HBPA with DMC. Those results were contrary to our early reports [13] that Ph_2SnO displays excellent catalytic performance in transesterification of DMC with bisphenol A; however, Bu_2SnO, $(PhCH_2)_2SnO$ and $(C_6H_{11})_2SnO$ exhibited weaker catalytic activity but higher selectivity for C-methylation by-product formation.

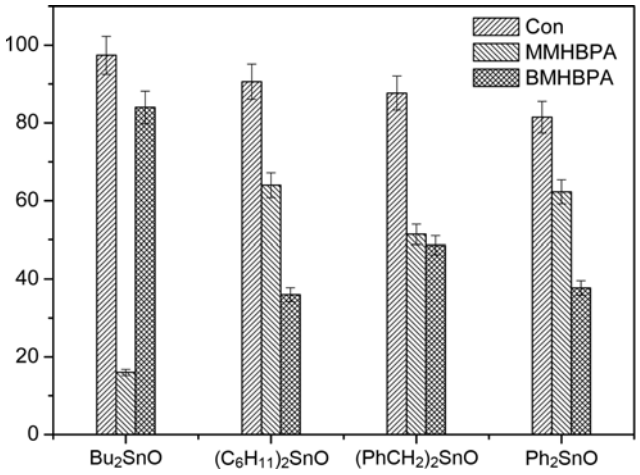


Fig. 1. The transesterification of HBPA with DMC over various organotin catalysts (Reaction condition: 160 °C, 6 h, molar ratio of HBPA/DMC=1 : 4, HBPA 0.01 mol, catalyst 0.15 g).

To investigate why the reaction of DMC and HBPA is different from that of DMC and BPA, the chemical states of Sn and O in catalysts were characterized by XPS (Fig. 2). In Fig. 2(a), the O electron binding energy in $(PhCH_2)_2SnO$, Bu_2SnO and $(C_6H_{11})_2SnO$ appeared around 531 ev, but oxygen electron binding energy of Ph_2SnO increased to 538 ev, which indicates that the oxygen of Ph_2SnO has weaker nucleophilic property. In Fig. 2(b), the electron binding energy of Sn $3d_{3/2}$ and Sn $3d_{5/2}$ in Ph_2SnO was 502 ev and 493 ev, but the electron binding energy of Sn $3d_{3/2}$ and Sn $3d_{5/2}$ in Bu_2SnO and $(C_6H_{11})_2SnO$ was much lower, which indicates that the phenyl ring

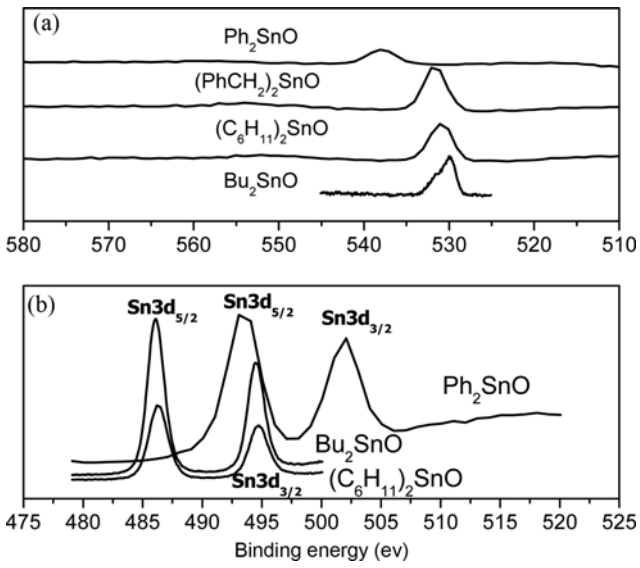


Fig. 2. XPS survey spectrum of organotin oxides.

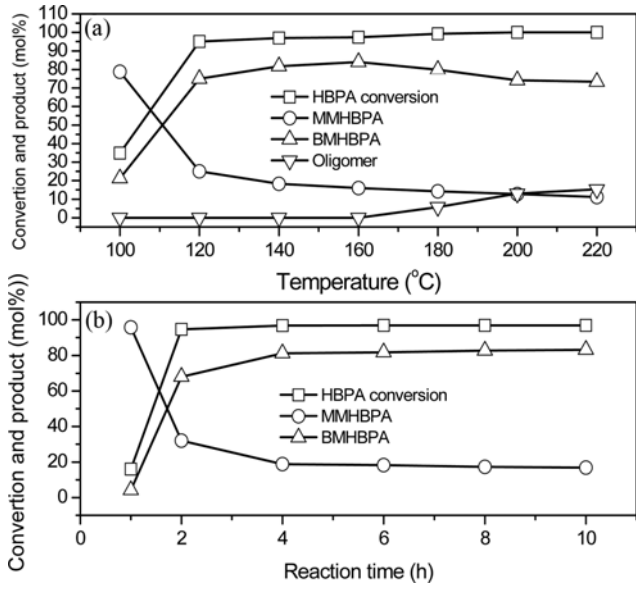


Fig. 3. Effect of temperature and reaction time on transesterification of DMC with HBPA ((a) reaction condition: 6 h, molar ratio of HBPA/DMC=1 : 4, HBPA 0.01 mol, Bu_2SnO 0.15 g; (b) reaction condition: 140 °C, molar ratio of HBPA/DMC =1 : 4, HBPA 0.01 mol, Bu_2SnO 0.15 g).

has a strong π-d interaction with Sn to result in Ph_2SnO having the higher positive Sn cation. Therefore, the different reaction between HBPA and BPA was attributed to the fact that the hydroxyl of HBPA displays weak bases which cannot be well activated by the weaker nucleophilic oxygen of Ph_2SnO through the hydrogen bonding. However, BPA is a kind of weak acid, and BPA and DMC over Ph_2SnO can be simultaneously activated by the weaker nucleophilic oxygen and positive Sn cation.

2. Effect of Temperature and Reaction Time on Transesterification DMC with HBPA

As Fig. 3(a) clearly shows, temperature played a great role on HBPA conversion and product distribution. When reaction was conducted at 100 °C for 6 h, HBPA conversion reached 34.9%, and the major product was MMHBPA. As reaction temperature increased to 140 °C, HBPA conversion and BMHBPA selectivity reached 96.9% and 75.0%. MMHBPA selectivity was decreased to 16.0% at 160 °C, and many oligomers were observed at 180 °C, which suggests that high reaction temperature is in favor of oligomer formation. Therefore, to get a better BMHBPA yield, the optimized temperature is 160 °C.

As for the oligomer formation, two types of polymerization reactions responsible for chain growth are proposed: (1) reaction between the hydroxyl terminal group and the methyl carbonate terminal group, and (2) transesterification between two methyl carbonate terminal groups [11]. The reaction between the hydroxyl terminal group and the methyl carbonate terminal group played a key role on oligomer formation. Additionally, when the [-OH]/[-OCH_3] ratio of the oligomers deviated from 1, it was difficult to attain a high molecular weight PHBC [13].

Fig. 3(b) shows the effect of reaction time on transesterification of DMC with HBPA. HBPA conversion and MMHBPA selectivity were 16.0% and 4.2% at 1 h. When reaction was conducted at

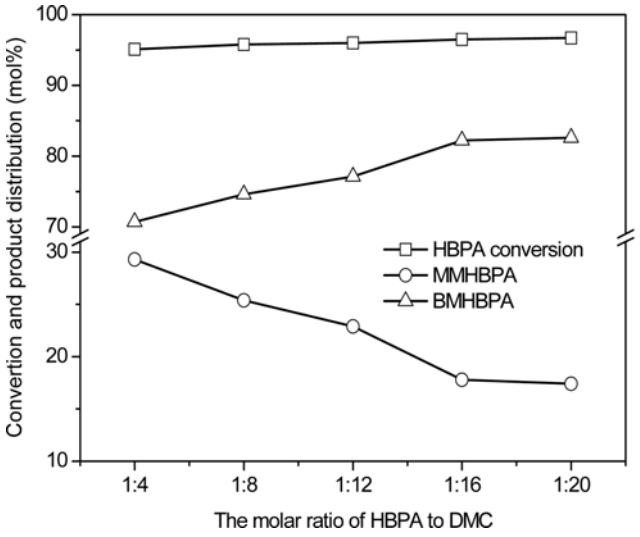


Fig. 4. Effect of molar ratio on transesterification HBPA with DMC (Reaction condition: 140 °C, 3 h, HBPA 0.01 mol, Bu_2SnO 0.15 g).

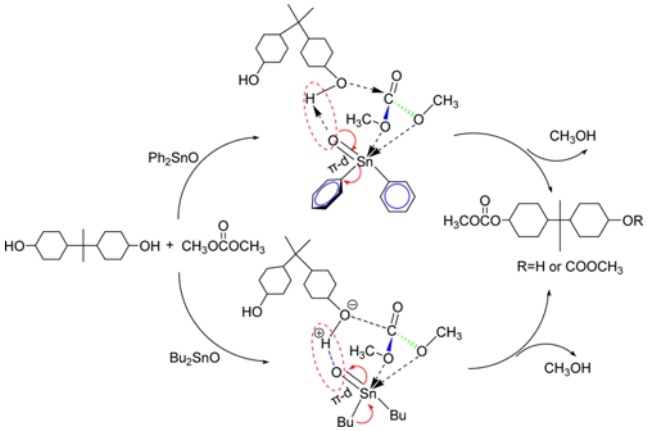
140 °C for 2 h, HBPA conversion and BMHBPA selectivity reached 94.7% and 68.0%. After 4 h period, HBPA conversion and BMHBPA selectivity almost remained the same because transesterification nearly reached equilibrium conversion.

3. Effect of Molar Ratio on Transesterification of DMC with HBPA

Effects of HBPA/DMC molar ratio on transesterification were investigated and results shown in Fig. 4. HBPA conversion gradually increased from 95.1% to 96.7% as the mole ratio increased from 4 to 20, due to the availability of additional DMC for reaction. Although HBPA conversion increased slowly above a molar ratio of 1 : 4, a significant increase in the selectivity of BMHBPA was observed, and MMHBPA selectivity was reduced significantly. This result suggests that excess DMC loading has the advantage of BMHBPA formation.

4. Suggested Mechanism

We suggest the following mechanism for our process (Scheme 2). DMC was attacked by Sn=O on two oxygen atoms of CH_3-O moiety, which increased the positive character of the carbonyl group.



Scheme 2. The suggested mechanism for transesterification of HBPA with DMC over Bu_2SnO and Ph_2SnO.

At the same time, the hydroxyl of BPA could also be activated by the hydrogen bonding with the oxygen of Sn=O, which increases the nucleophilicity of oxygen. Therefore, the oxygen of HBPA may easily attack carbonyl carbon of DMC to form transesterification products. The oxygen of Ph_2SnO has weaker nucleophilic property than that of Bu_2SnO, which leads to Ph_2SnO having lower activity in transesterification of DMC with HBPA.

CONCLUSIONS

Bu_2SnO and Ph_2SnO were used as catalyst, HBPA conversion achieved 97.4% and 81.5%, and BMHBPA selectivity reached 84.0% and 37.7%, respectively. Comparing the performance of Bu_2SnO and Ph_2SnO, Bu_2SnO was the better catalyst in transesterification of HBPA with DMC. XPS characterization indicated that the O electron binding energy of Bu_2SnO and Ph_2SnO appeared around 531 ev and 538 ev, which indicated that the oxygen of Bu_2SnO has better nucleophilic capacity; however, Sn electron binding energy of Bu_2SnO is lower than that of Ph_2SnO, indicating Ph_2SnO has the higher positive Sn cation. The nucleophilic oxygen of organic tin oxide plays a key role in transesterification because the weak base hydroxyl of HBPA can be well activated by Bu_2SnO.

When reaction was conducted at 140 °C for 2 h, HBPA conversion and BMHBPA selectivity reached 94.7% and 68.0%, but HBPA conversion and BMHBPA selectivity almost remained the same after 4 hours because transesterification nearly reached equilibrium conversion; however, the excess DMC loading has the advantage of BMHBPA formation. The optimized BMHBPA selectivity reached 84.0% at 160 °C, but many oligomers were observed above 160 °C. The reaction mechanism was given that DMC was attacked by Sn=O on two oxygen atoms of CH_3-O moiety; at the same time BPA can also be activated by the nucleophilic oxygen of Sn=O through hydrogen bonding, which resulted in HBPA being easily attacked by carbonyl carbon of DMC to form transesterification products.

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