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Study on the reaction between bisphenol A and dimethyl carbonate over organotin oxide

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Abstract

Organotin oxide was used to catalyze the reaction between BPA (bisphenol A) and DMC (dimethyl carbonate), and Ph₂SnO (diphenyltin oxide) displays the excellent catalytic performance in transesterification and O-methylation. However, Bu₂SnO (dibutyltin oxide), (PhCH₂)₂SnO (dibenzyltin oxide) and (C₆H₁₁)₂SnO (dicyclohexyltin oxide) exhibited weaker catalytic activity but higher selectivity for C-methylation product formation. The π - π function between Ph₂SnO and BPA provided more chances for their interaction, and π -d interaction between phenyl ring and Sn resulted in catalyst having higher activity in transesterification and O-methylation. O-methylation product formation over Ph₂SnO comes from transesterification product decomposition not from direct methylation of BPA with DMC.

Keywords: Transesterification; Methylation; Organotin oxide; Dimethyl carbonate; Bisphenol A.

1 Introduction

Bisphenol-A polycarbonate (PC) is one of the most widely used engineering thermoplastics because of its excellent properties such as high-impact strength, heat resistance, flame retardancy, dimensional stability, and high optical transparency [1]. PC is often produced by the interfacial polycondensation of BPA and phosgene. In an attempt to devise a phosgene free PC synthesis process, diphenyl carbonate (DPC) [2-5], CO [6-8] and DMC [9-11] were used as carbonylating agents to replace phosgene. The transesterification of DMC with BPA is of significant interest as a green route to aromatic polycarbonates. Shaikh et al [12, 13] had synthesized the bis-methylcarbonate bisphenol-A of (BMBPA) and found **BMBPA** melt-polycondensation to achieve high molecular weight PC. Therefore, the selective synthesis of BMBPA from BPA and DMC has become particularly important. However, BMBPA synthesis from DMC and BPA suffers from low yield and selectivity even at elevated temperature due to a thermodynamically unfavorable process. Apparently, In the PC synthesis by the transesterification of DMC with BPA, the major challenge subjects were to improved target compound selectivity, and the byproducts formed from O-methylation of BPA or C-methylation of BPA with DMC must be eliminated because the methylation byproducts especially C-methylation hindered BMBPA polycondensation [14-17] (see scheme 1). Organotin catalyst had been considered as fine catalyst for transesterification [18], but the design of new active catalytic systems was prerequisite to promote BMBPA synthesis. BMBPA synthesis from BPA and DMC was often catalyzed by Lewis acid catalysts, for

example, TiO₂/SBA-15[14], TiO₂/SiO₂ [15], (Bu₂SnCl)₂O [16], Bu₂SnO and titanium alkoxides [16]. The development of heterogeneous catalysts with better performance was highly desirable in view of regeneration and separation. The transesterification of BPA with DMC can be promoted by TiO₂/SBA-15 [14, 19], however, the yield and selectivity of BMBPA over TiO₂/SBA-15 were still far from satisfaction in comparison with those over homogeneous organotin catalyst. Li et al [17] found that heterogeneous organotin modified SBA-15 can promote BMBPA synthesis, but the methylation is still an important side-reaction. Because the synthetic procedure for BMBPA is a thermodynamically unfavorable process and the high reaction temperature will result in methylation byproduct formation, apparently, it is a challenge problem to selectively promote the transesterification of BPA with DMC. Apparently, in order to keep BPA and DMC from methylation, the methylation reaction between BPA and DMC need to be well studied over organotin oxide catalyst, which provides deeper insights into the methylation by-product formation process.

Herein, we introduced a several organotin oxide to selectively catalyze the reaction between BPA and DMC. Diphenyltin oxide displays the excellent catalytic performance in the selective transesterification even at 120 °C, however, it can catalyze the O-methylation product formation at high reaction temperature (>180 °C). Compared to diphenyltin oxide, dialkyltin oxide such as Bu₂SnO, (PhCH₂)₂SnO and $(C_6H_{11})_2$ SnO showed a better activity for direct C-methylation. In order to provide deeper insights into the reaction process, different reaction parameters were studied.

2. Experiment

2.1. Chemical Reagents

DMC (Tianjin Chemical Reagent Research Institute) was fractionally distilled and stored over 4A molecular sieve. BPA and other chemical reagents were AR grade and used as received from local manufactures without further purification. Ph₂SnO and Bu₂SnO were purchased from Sigma-Aldrich.

2.2. Phenyl tinoxide preparation

 $(PhCH_2)_2SnO$ and $(C_6H_{11})_2SnO$ were synthesized from Grignard reagents and stannic tetrachloride at certain mole ratio in tandem with hydroxylation in presence of NaOH.

2.3. Characterization

Fourier transform infrared spectra (FT-IR) of the samples were measured through a FTIR TENSOR 37 (BRUKER Corporation, Germany) operated by Attenuated Total Reflectance (ATR) in the wavenumber range of 4000-500 cm⁻¹. 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. The HPLC analyses were carried out by a reverse-phase method on a Waters 2690 separation module (Waters Associates, Milford, MA). As an UV detector, a Waters 2487 Dual Absorbance Detector was used at the wavelength of UV 254nm. The reverse-phase C18 column was Waters Lichrosorb adjusted with a gradient mode of CH₃OH and water from 80/20 to isocratic CH₃OH.

2.4. Reaction procedure

Reactions were carried out in two methods, at ambient pressure with continuous

removal of by-producing methanol and under pressured condition without removal of by-producing methanol. Ambient pressure reactions were carried out in a four neck flask which was equipped with a thermometer, a nitrogen inlet, a dropping funnel and a fractionating column connected to a liquid dividing head. BPA and catalyst were charged into a flask under nitrogen atmosphere. During the reaction, a distillate of DMC and methanol was collected slowly in a receiver flask. Pressured reaction was carried out in polytetrafluoroethylene reaction kettles. After the reaction finished, the mixture was cooled and analyzed.

3. Results and Discussion

3.1. Characterization of organotin oxide catalysts

FT-IR spectra of the samples are presented in Fig.1. The characteristic absorption band at 1472 cm⁻¹ was caused by stretching vibration of benzene skeleton, and the bending vibration at 698 cm⁻¹ was caused by =C-H of benzene. The absorption bands for Sn=O bond stretching vibration occurred at 1072cm⁻¹. 2920 cm⁻¹ was attributed the presence of CH₂. The weight loss was carried out under an air atmosphere in muffle furnace at 900 °C for 3 h. (PhCH₂)₂SnO, (C₆H₁₁)₂SnO and Ph₂SnO catalysts exhibited 48.7%, 52.3% and 55.6% SnO₂ residue at 900 °C. Those data match very well with the theory value 47.6%, 50.2% and 55.2%.

3.2 The organotin oxide catalyzed the reaction between DMC and BPA

The catalytic performance of organotin catalysts was systematically summarized in Table. 1. When reactions were carried out at 120 °C at ambient pressure with continuous removal of by-producing methanol, BPA conversion over Ph₂SnO reached

33.7%, the selectivity of transesterification products achieved 100%, and no methylation byproducts were detected. Although transesterification was a thermodynamically unfavorable process, the high temperature was still benign to DMBPA synthesis [13]. When reaction was carried out at 180 °C over Ph₂SnO at ambient pressure, BPA conversion came up to 51.9%. But the selectivity of transesterification products declined to 76.3%, and O-methylation byproduct selectivity reached 23.2%. If reactions were carried out at 220 °C over Ph₂SnO under pressured condition without removal of by-producing methanol, the yields of O-methylation products came up to 95.5-97.5%, however, nearly no MMBPA and C-methylation products were detected. Contrary to expectation, (C₄H₉)₂Sn=O, (C₆H₁₁)₂SnO and (PhCH₂)₂SnO show lower activity in BPA conversion, and much more C-methylation byproducts appeared. On the basis of those studies, we can hypothesize that the aromic ring appearance in organotin might have π - π function with BPA, which provided more chances for phenolic hydroxyl group and Sn=O bond to contact. Most importantly, phenyl ring in Ph₂SnO has a strong π -d interaction with Sn. The positive Sn cation has higher ability to activate DMC and well promotes the reaction of BPA with DMC. Additionally, Ph₂SnO can be precipitated from reaction mixture by adding CH₃OH, and the refreshed catalytic can be recycled without loss in activity.

3.3 Effect of temperature on transesterification and methylation

Ph₂SnO can catalyze transesterification at low temperature, but much more O-methylation byproduct formed at high temperature, therefore the O-methylation

byproduct formation mechanism need to be explored. Herein, temperature effects on reaction selectivity were investigated under pressured condition without removal of by-producing methanol. As obviously exhibited in Fig.2, temperature plays a great role on product distribution and BPA conversion. The selectivity of MMBPA declined from 66.9 to 0.5% as reaction temperature rising from 160 to 240 °C, but MBPA ether and DMBPA ether increased to 82.6% and 13.9%. In addition, elevating reaction temperature can well inhibit C-methylation of BPA. Those results suggested that high temperature was benign to MBPA ether and DMBPA ether formation.

3.4 Effect of reaction time on transesterification and methylation

Transesterification product disappearance process and O-methylation byproduct formation mechanism need to be further explored. Here, effects of reaction time on product selectivity were studied, and results were showed in Fig.3. When reaction time increased from 6 to16h, BPA conversion increases from 72.7 to 100%, and MBPA ether and DMBPA ether increased from 22.2% and 4.8% to 82.0% and 13.7%, however, MMBPA selectivity declined from 70.0 to 4.9%. Base on those results, we confirmed that O-methylation byproducts mainly come from MMBPA and DMBPA decomposition not from direct O-methylation of BPA with DMC (see scheme 2).

3.5 Effect of Ph₂SnO catalyst usage amount on transesterification and methylation

A series of reactions using different catalyst usages were conducted, and the results were showed in Fig.4. Ph₂SnO usage plays a great role on BPA conversion and product distribution. Conversion of BPA increased gradually with the rising amount of catalyst. When catalyst usage was 0.05g, BPA conversion and MBPA ether yield are

33.9% and 77.2%, and much more transesterification product MMBPA existence whose selectivity reached 10.6%. The selectivity of MBPA ether reached as high as 90.8% when Ph₂SnO dosage was 0.1g, but BPA conversion was 47.8% and no MMBPA was detected. This result implied that MMBPA or DMBPA decomposition rate is high than the transesterification rate of BPA with DMC. The similar results were obtained with the increase of catalyst dosage from 0.3 to 0.4g. Much more catalyst was loaded, the high selectivity of DMBPA ether achieved, and the selectivity of DMBPA ether increased to 25.0% when Ph₂SnO dosage was 0.4g.

4 Conclusions

Ph₂SnO displayed high activity to catalyze transesterification and O-methylation, and MBPA ether and DMBPA ether mainly come from MMBPA and DMBPA decomposition not from direct O-methylation of BPA with DMC. Alkyltin oxide, such as $(C_4H_9)_2Sn=O$, $(C_6H_{11})_2SnO$ and $(PhCH_2)_2SnO$, shows lower activity for BPA conversion but higher selectivity for C-methylation product formation. The π -d effect in phenyltin oxide and π - π function between BPA and Ph₂SnO promote the reaction of BPA with DMC, and π -d interaction between phenyl ring and Sn result in Sn having higher activity in the transesterification of BPA with DPC and decomposition of MMBPA or DMBPA into MBPA ether or DMBPA ether. However, transesterification products are more stable in presence of alkyltin oxide.

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Captions

- Fig.2. Effect of temperature on yield (5gBPA, 50ml DMC, 0.3g ph₂SnO and16h)
- Fig.3 Effect of reaction time on product distribution and BPA conversion (5gBPA,

50ml DMC、 0.3g Ph₄Sn₃O₄、 220 °C)

Fig.4 Effect of Ph₂SnO catalyst amount on reaction (5g BPA, 50ml DMC, 220 °C,

16h)

Scheme 1 The product distribution of dimethyl carbonate (DMC) reaction with bisphenol-A

Scheme 2 MBPA ether and DMBPA ether come from MMBPA and DMBPA decomposition not from directing O-methylation of BPA with DMC



Fig .1 FT-IR spectra of organotin oxide catalysts



Fig.2 Effect of temperature on yield (5gBPA, 50ml DMC, 0.3g ph₂SnO and16h)



Fig.3 Effect of reaction time on product distribution and BPA conversion (5gBPA,

50ml DMC, 0.3g Ph₄Sn₃O₄, 220 °C)



Fig.4. Effect of Ph₂SnO catalyst amount on reaction (5g BPA, 50ml DMC, 220 °C,

16h)



Scheme 1 The product distribution of dimethyl carbonate (DMC) reaction with

bisphenol-A



Scheme 2 MBPA ether and DMBPA ether come from MMBPA and DMBPA decomposition not from directing O-methylation of BPA with DMC

Catalyst	Tem (°C)	Con (%)	Product distribution (mol %)				
			MMBPA	BMBPA	MBPA C-Me		DMBPA
					e me	ether	ether
^a Ph ₂ SnO	120	33.7	89.3	10.7			
^a Ph ₂ SnO	180	51.9	71.1	5.2	0.5	23.2	
^b Ph ₂ SnO	220	99.5	0.7	6	1.8	62.4	35.1
^b Ph ₂ SnO (0.2)	220	65.5		-	2.8	88.1	9.2
^b Ph ₂ SnO (0.1)	220	47.8	0.1		2.0	90.8	7.1
^b R-Ph ₂ SnO	220	99.1	0.9		2.0	66.2	31.8
^b Bu ₂ Sn=O	220	56.1	58.9		23.8	8.8	8.5
^b (PhCH ₂) ₂ SnO	220	74.7	36.5		36.1	16.8	10.6
$^{b}(C_{6}H_{11})_{2}SnO$	220	68.8	30.8		46.9	16.7	5.6

Tab.1 Effects of catalysts on reaction between BPA and DMC

Reaction conditions: 5g BPA, 50ml DMC, 0.3 g catalyst, 16 h. 0.2 and 0.1 indicated 0.2 g and 0.1 g catalyst usage. ^a indicated that reactions were carried out at ambient pressure with continuous removal of by-producing methanol. ^b indicated that reactions were carried out under pressured condition without removal of by-producing methanol. R-Ph₂SnO was the refreshed catalyst. C-Me indicated the methylation at phenyl ring. Tem and Con indicated Temperature and Conversion.

 $-OH + CH_3OCOCH_3 \xrightarrow{Ph_2SnO} HO -$ O −OCOCH₃ + H₃COCO-√ но-{ 160-200 °C MMBPA BMBPA BPA DMC 180-240 °C CO_2 DMCor CH₃OH -OCH₃ + H₃CO≺ OCH₃ но-{ DMBPA ether MBPA ether Graphical abstract Chilling and the second

Highlights

 Ph_2SnO selectively catalyzes O-methylation product formation from BPA and DMC.

Alkyltin oxide catalyzes C-methylation of BPA with DMC.

Ph₂SnO catalyzes transesterification products decomposition into O-methylation

products.

Transesterification products are more stable over alkyltin oxide.

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