Comparison of Polycarbonate Precursors Synthesized from Catalytic Reactions of Bisphenol-A with Diphenyl Carbonate, Dimethyl Carbonate, or Carbon Monoxide

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ABSTRACT: Transesterification of bisphenol-A with diphenyl carbonate or dimethyl carbonate, and direct oxidative carbonylation of bisphenol-A were compared to obtain polycarbonate precursors for phosgene-free polycarbonate synthesis. The melt-transesterification of bisphenol-A and diphenyl carbonate occurred readily to produce reactive precursors without a significant equilibrium constraint. On the other hand, the transesterification of bisphenol-A and dimethyl carbonate showed a serious equilibrium limitation in obtaining reactive polycarbonate precursors leading to high molecular weight polymers, and coproduced a significant amount of methylated bisphenol-A. The direct oxidative carbonylation of bisphenol-A with CO produced diphenolic-ended oligomers and a significant amount of by-products, which are the least reactive in the subsequent polycondensation step of the phosgene-free polycarbonate process. A novel method to synthesize the reactive polycarbonate precursors was proposed that employed the coupled oxidative carbonylation of both bisphenol-A and phenol. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 937–947, 2002

Key words: polycarbonate precursors; phosgene-free synthesis; bisphenol-A; diphenyl carbonate (DPC); dimethyl carbonate (DMC); carbon monoxide

INTRODUCTION

Polycarbonate has been produced by the interfacial polycondensation of bisphenol-A and phosgene. The major drawbacks of the conventional phosgene process are environmental and safety problems involved in using highly toxic phosgene as the reagent and copious amounts of methylene chloride as the solvent ($\sim$ 10 times the weight of the products).[1] Phosgene-free processes for polycarbonate have been proposed that employ melt-transesterification[2–13] or solid-state polymerization[14] using bisphenol-A (BPA) and diphenyl carbonate (DPC), with the latter synthesized in a phosgene-free process.[15–24] The phosgene-free processes are mostly multistaged with prepolymerization step of BPA and DPC and subsequent polycondensation steps of the prepolymers (degree of polymerization: 1–10) produced while removing phenol under the conditions of rising temperature (450 to higher than 570 K) and lowering vacuum pressure (100 to less than 1 mmHg). As a very efficient monomer, DPC has often been synthesized by a two-step reaction of the synthesis of methylphenyl carbonate (MPC) from dimethyl carbonate (DMC) and phenol followed by the disproportionation of MPC, given that the direct synthesis of DPC is limited because of a low equilibrium constant for the forward reaction.[15,21] To overcome the equilibrium constraint in the synthesis of MPC, a gas-phase transesterification of DMC and phenol was proposed.[15–17]

As a potential substitute for DPC as a carbonylating agent, DMC would react with BPA into polycarbonate precursors. It has a great advantage that there is no need to obtain DPC, whose economical synthesis by a phosgene-free method is not easy. There are a few reports on the synthesis of polycarbonate precursor using DMC directly.[25–29] Shaikh et al.[25] and Haba et al.[29] reported that the methylcarbonate-ended oligomers from the transesterification of BPA and DMC were most reactive in producing high molecular weight polymers in the postpolycondensation step compared with hydroxyl-ended oligomers. Deshpande et al.[27] also reported that the higher content of carbonate-ended oligomer led to the higher molecular weight of the polymer in the reaction of BPA diacetate with DMC.[27,28] It was proposed to replace BPA with BPA diacetate or 1,4- bis(hydroxymethyl) cyclohexane[26] because of the low activity of the transesterification of BPA and DMC.

The direct insertion of carbon monoxide to the *para* position of BPA is also possible. Recently, Goyal et

al.[30,31] reported a successful synthesis of polycarbonate oligomers from the direct oxidative carbonylation of BPA. They utilized a catalyst system that has been found effective in the extensive works on the synthesis of DPC from phenol and CO directly as a phosgene-free synthesis.[32–39] Conceptually, oxidative carbonylation of BPA is the most promising method of phosgene-free polycarbonate synthesis because it involves the least number of reaction steps. However, the oligomers produced from the oxidative carbonylation of BPA were end-uncapped oligomers and those phenolic end groups made the polymers extremely unstable.[4,40]

We compared these three different preparation methods of polycarbonate precursors. As carbonylating agents, DPC, DMC, and CO were reacted separately with BPA to investigate the reaction characteristics and to compare the nature of precursors obtained from each reaction process under similar reaction conditions of batch system. We performed preliminary screening of the catalyst system for each reaction. The characteristics of each reaction are discussed and a novel method of the one-step synthesis of reactive polycarbonate precursors is proposed that employs simultaneous oxidative carbonylation of both BPA and phenol.

EXPERIMENTAL

Reaction procedures

For the melt-transesterification of BPA (Aldrich Chemicals, Milwaukee, WI) and DPC (Aldrich), a 100-cm³ autoclave (Parr Inst. Co., Moline, IL) with a magnetic stirrer was employed as a batch reactor. BPA and an aqueous catalyst solution of alkali metal hydroxides (or carbonates) were added into the reactor containing molten DPC with a catalyst concentration of 10^{-5} to 10^{-3} mol cat/mol BPA. After the reactor was purged by dinitrogen three times and pressurized to 1 MPa, the temperature was ramped to 433 K with an electric heater. Sampling was performed every hour by using sampling valves attached to the reactor. In the transesterification of BPA and DMC (Aldrich), the reaction was carried out in the same manner as the reaction between BPA and DPC. The catalysts of titanium alkoxides or silica-supported titanium oxides were employed here, which have been found effective for the transesterification of phenol and DMC.[15]

For the direct oxidative carbonylation of BPA, the reaction system and procedure were based on the oxidative carbonylation of phenol.[37] A homogeneous Pd catalyst, an inorganic cocatalyst as a reoxidant of Pd, tetrabutylammonium bromide as a base, quinones as organic cocatalysts, methylene chloride as a solvent, and BPA were charged into the 100-cm³ autoclave

(Parr). After purging the reactor with O_2 three times, 5 MPa of CO and 0.5 MPa of O_2 were charged successively and the reaction temperature was adjusted to 373 K. The reaction was quenched after a desired reaction time by cooling the reactor with ice water.

Product analyses

Reaction products were analyzed by high-performance liquid chromatography (HPLC), gas chromatography (GC), and GC–mass spectrometry (GC/MS) to identify and quantify the polycarbonate precursors and by-products. We adopted the methods of Bailly et al.[41] and Kim et al.[4] in separation and identification of polycarbonate oligomers by HPLC under similar analysis conditions. The HPLC analyses were carried out by a reverse-phase method on a Waters 2690 separation module (Waters Associates, Milford, MA) equipped with an autosampler. As an UV detector, a Waters 2487 Dual λ Absorbance Detector was used at the wavelength of UV 240 nm. The reverse-phase LC column was Waters Lichrosorb RP18 analytical column (5-μm particle size; 4.6 × 250 mm). A mobile phase flow rate of 1 mL/min was adjusted with a gradient mode of acetonitrile and water from 65 : 35 to isocratic of acetonitrile. The reaction samples were diluted 50 times with acetonitrile and 5 μL was injected by an automatic injector. The Millenium[32] software was used for data reduction and integration. It gave a good separation and UV sensitivity to polycarbonate precursors and BPA, but phenol and DPC showed a poor sensitivity, in agreement with the report of Bailly et al.[41] Moreover, DMC and solvent were not detected under these conditions.

We combined GC and GC/MS analyses with HPLC to identify and quantify UV-insensitive and/or light molecules such as DMC, phenol, DPC, and by-products. An HP 5890II gas chromatograph (GC) equipped with a flame ionization detector (FID) and a GC–mass spectrometer of HP 5890–HP 5972 MSD were used (Hewlett-Packard, Palo Alto, CA). Products were separated by an HP PONA capillary column (50 m × 0.2 mm × 0.5 μm) for GC and GC/MS analyses.

RESULTS AND DISCUSSION

HPLC chromatograms of polycarbonate precursors from different carbonylating agents

Figure 1 shows typical HPLC spectra of the products from the reactions of BPA with DPC, DMC, and CO. For the reaction of BPA and DPC, there are three kinds of precursors with respect to their end-group functionality of oligomers produced. The oligomer that is mono phenylcarbonate-ended on one side and hydroxy (of phenolic)-ended on the other side is as-
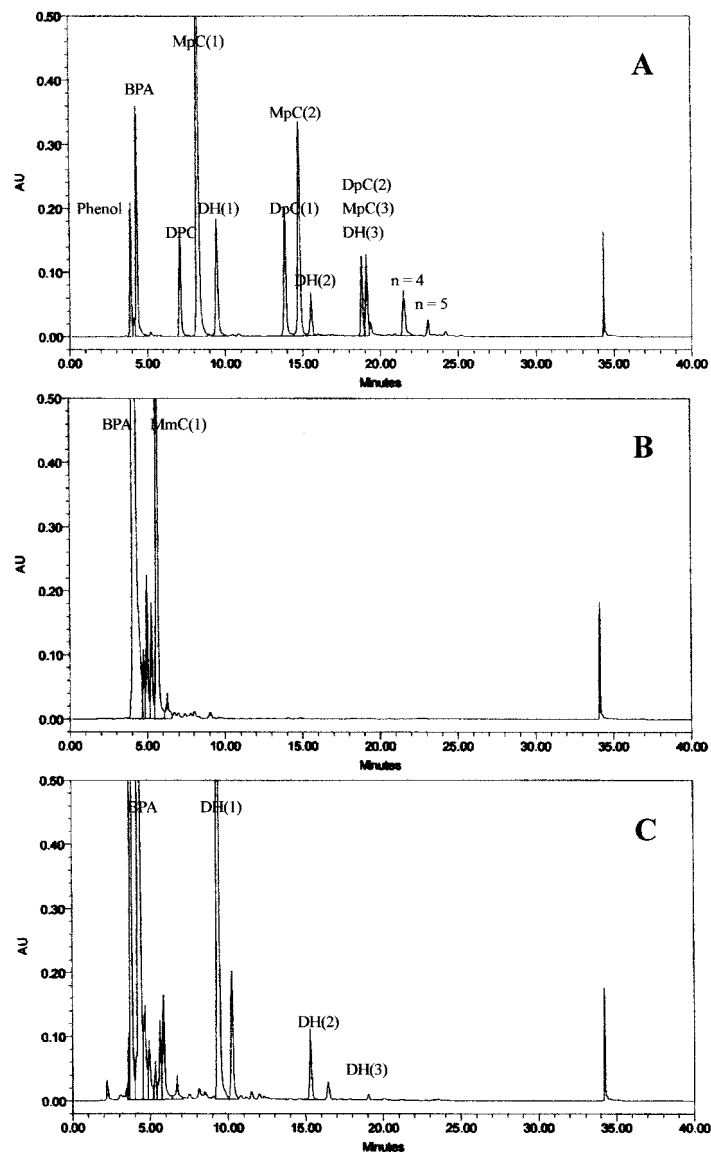
Figure 1 Typical HPLC chromatograms for the products obtained from the reactions of bisphenol-A with diphenyl carbonate (A), dimethyl carbonate (B), and carbon monoxide (C).

signed as MpC(n), with n being the number of repeating units of BPA carbonate. The second type precursor is dihydroxy-ended oligomer on both sides and the third is diphenylcarbonate-ended, assigned as DH(n) and DpC(n), respectively. As suggested by Kim et al.[4] and Bailly et al.,[41] oligomers having the same number of carbonate groups eluted at similar retention times as a group and the bulkier oligomer in the group eluted later in the reverse-phase HPLC analysis. Under our experimental conditions, the precursors were well separated, as illustrated in Figure 1(A), and grouped according to the number of carbonate groups. We could detect oligomers with n up to 7, although oligomers with $n = 4$–7 were not separated according to their end-group functionality. The last peak at around 34 min is a ghost peak that resulted

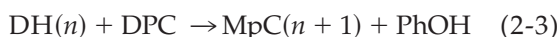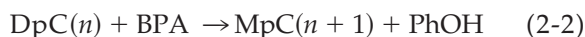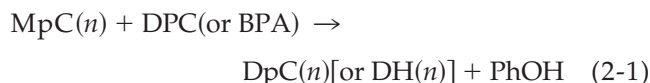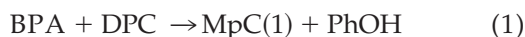from restoring the gradient composition of acetonitrile and water.

In the transesterification of BPA and DMC as another carbonylating agent, there should exist methylcarbonate-ended precursors as MmC(n) and DmC(n) instead of MpC(n) and DpC(n). However, there was no DH(1) detected in any of the experiments, except on occasion showing a trace in the HPLC spectrum. As shown in Figure 1(B), we could detect MmC(1) and methylated by-products, which were confirmed by GC/MS. We primarily used GC and GC/MS to analyze the products from the reaction of BPA and DMC, whereas we used the HPLC technique to check the formation of oligomers heavier than DH(1).

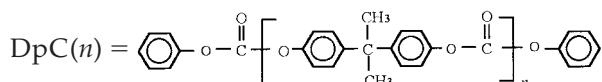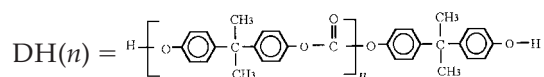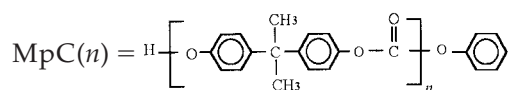Figure 1(C) shows polycarbonate precursors of DH(n) and by-products obtained from the direct oxi-

dative carbonylation of BPA and CO/O_2. DHs with n up to 3 were detected together with some by-products that were not identified by HPLC. The by-products were found to be o,p-isomers of BPA and acetate-, salicylic acid-, and o-phenylene carbonate-type–ended derivatives of bisphenols from analysis of GC/MS. The latter two by-products were also reported as major by-products by Goyal et al.[30] Furthermore, bisphenol-F and brominated and phenoxy BPA were also found in trace amounts in our analysis.

Melt-transesterification of BPA and DPC

A typical reaction scheme of the melt-transesterification of BPA and DPC is as follows. As a primary reaction between BPA and DPC, MpC(1) is produced first as in Reaction (1). The MpC(1) has two probabilities to react with another DPC or BPA like Reaction (2-1) because of the transesterification reactivity between phenylcarbonate and hydroxy functionalities.[4] Further secondary reactions (2-2) and (2-3) are also expected to occur in the melt-transesterification as suggested by kinetic studies.[2–6]

$$BPA + DPC \rightarrow MpC(1) + PhOH \qquad (1)$$

$$MpC(n) + DPC(\text{or BPA}) \rightarrow$$
$$DpC(n)[\text{or DH}(n)] + PhOH \quad (2\text{-}1)$$

$$DpC(n) + BPA \rightarrow MpC(n + 1) + PhOH \qquad (2\text{-}2)$$

$$DH(n) + DPC \rightarrow MpC(n + 1) + PhOH \quad (2\text{-}3)$$

where

The transesterification of BPA and DPC occurs readily and efficiently, even without a catalyst. About 10% of BPA was converted into MpC(1) without any catalyst in 3 days after just equimolar mixing of BPA and DPC in acetonitrile at 298 K. At 523 K without a catalyst, a 6-h reaction also produced 26.7 wt % MmC(1), 17.4 wt % DH(1) in yields, and traces of DpC(1) and oligomers of $n = 2$. Kim et al.[4] attributed

the appreciable activity in the uncatalyzed reaction to the unidentified catalysts as impurities.

Figure 1(A) is a typical HPLC spectrum of melt-transesterification of BPA and DPC with alkali metal hydroxides or carbonates as a catalyst at 433 K. The overall reaction consisted of the primary reaction of reactants (1) and the secondary reactions of MpC(1) with DPC or BPA (2-1)–(2-3). Further, the third type of reactions between oligomers probably occur as follows, although their contribution is minor under our batch reaction conditions.
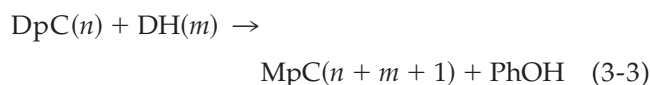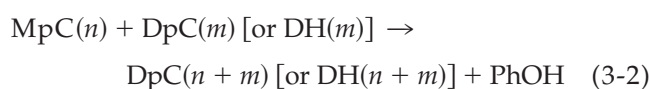
$$MpC(n) + MpC(m) \rightarrow MpC(n + m) + PhOH \qquad (3\text{-}1)$$

$$MpC(n) + DpC(m) [\text{or DH}(m)] \rightarrow$$
$$DpC(n + m) [\text{or DH}(n + m)] + PhOH \quad (3\text{-}2)$$

$$DpC(n) + DH(m) \rightarrow$$
$$MpC(n + m + 1) + PhOH \quad (3\text{-}3)$$

Figure 2 shows the effects of the reactants' molar ratio (DPC/BPA) for a fixed ratio (10^{-4}) of catalyst mole per initial BPA mole (from 0.2 to 0.1 mol of BPA) on the conversions of BPA and DPC, distributions of oligomers, and selectivity of end-group functionality. BPA conversion increased from 64 to 91% as DPC/BPA increased from 0.5 to 2.0, in contrast to the decrease of DPC conversion. Increased DPC/BPA ratios also resulted in a drastic decrease of total DH and, instead, an increase of DpC and MpC. Thus, the ratio of DPC/BPA was the most critical variable to control the functional end groups of the oligomers produced. For DPC/BPA = 1.0 a stoichiometric relation was observed between BPA and DPC converted and phenol produced, but more BPA reacted than DPC at 0.5 and more DPC reacted at 2.0 relative to the amounts predicted by the stoichiometric relation of the primary reaction (1) between DPC and BPA. Furthermore, phenol was produced in excess amounts, indicating the presence of secondary reactions. The primary reaction of BPA and DPC was probably finished within 1 h and the secondary reactions continued even after 1 h under experimental conditions. The increase of conversions after 1 h was very slow but continuous. The oligomer distribution with n showed no significant difference up to $n = 3$, indicating that the reactivity difference among functional groups did not appear to depend significantly on the chain length, as also assumed in a kinetic analysis.[4]

The values of excess phenol in Tables I and II are obtained from the amount of phenol formed divided by consumed BPA or DPC. Excess phenol for BPA is indicative of an extra phenol formation from the reactions of MpC (or DH) and DPC and between oli-
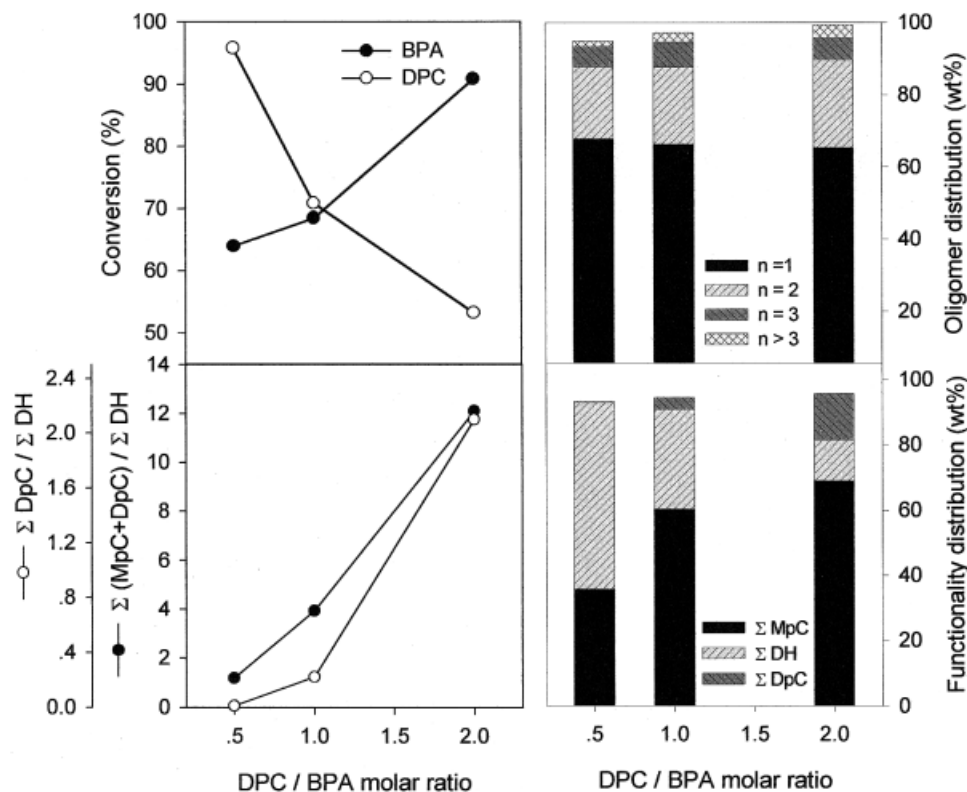
Figure 2 Effect of reactants' molar ratio on the oligomerization of BPA and DPC for a fixed catalyst amount per initial BPA: concentration of LiOH, 10^{-4} mol cat/mol BPA; reaction temperature, 433 K; initial pressure of dinitrogen, 1 MPa; stirring rate, 200 rpm; reaction time, 1 h.

gomers. Excess phenol for DPC is a sum of contributions from the secondary- and third-type reactions, except the contributions of DPC itself. These values were always positive, thus indicating that further secondary reactions of (2-1)–(2-3) and (3-1)–(3-3) had occurred. Thus, these values of excess phenol could serve as convenient indicators for the extent of secondary reactions.

Figure 3 shows the effects of catalyst (LiOH–H$_2$O) concentration on the melt-transesterification of BPA and DPC. The activity depended on the concentration directly below 1.0×10^{-4} mol cat/mol BPA, corresponding to 33 ppm in reactants. Conversions of BPA and DPC increased as the catalyst concentration increased and then reached a plateau. The functional

group mole ratio of the total DpC/total DH showed the same trend with conversions but the mole ratio of total (MpC + DpC)/total DH initially decreased rapidly and then remained constant at around 14 above 0.5×10^{-4} mol cat/mol BPA. This behavior could be explained by the fact that the formation of monomeric carbonates ($n = 1$), especially MpC(1), is dominant at low catalyst concentrations. Therefore the primary reaction occurred initially and then the produced MpC(1) was converted into DpC(1) and DH(1). It is interesting that total (MpC + DpC)/total DH remained constant above the catalyst concentration of the 0.5×10^{-4} mol cat/mol BPA, although the conversions and total DpC/total DH were increased fur-

TABLE I
**Quantification of Phenol Excesses in Figure 2**

DPC/BPA	Conversion (%) of		Phenol excess (%) for	
	BPA	DPC	BPA	DPC
0.5	64.0	95.8	Stoi[a]	+29.3
1.0	68.5	70.9	+74.1	+63.2
2.0	90.8	53.3	+75.4	+29.4

[a] Stoichiometric amount with BPA.

TABLE II
Quantification of Phenol Excesses in Figure 3

10^{-4} mol cat/ mol BPA	Conversion (%) of		Phenol excess (%) for	
	BPA	DPC	BPA	DPC
0.1	10.4	5.0	Stoi[a]	Stoi[a]
0.5	59.2	36.0	+55.8	+11.1
1.0	90.8	53.3	+75.4	+29.4
10	89.6	55.0	+60.7	+9.1

[a] Stoichiometric amount with BPA and DPC, respectively.
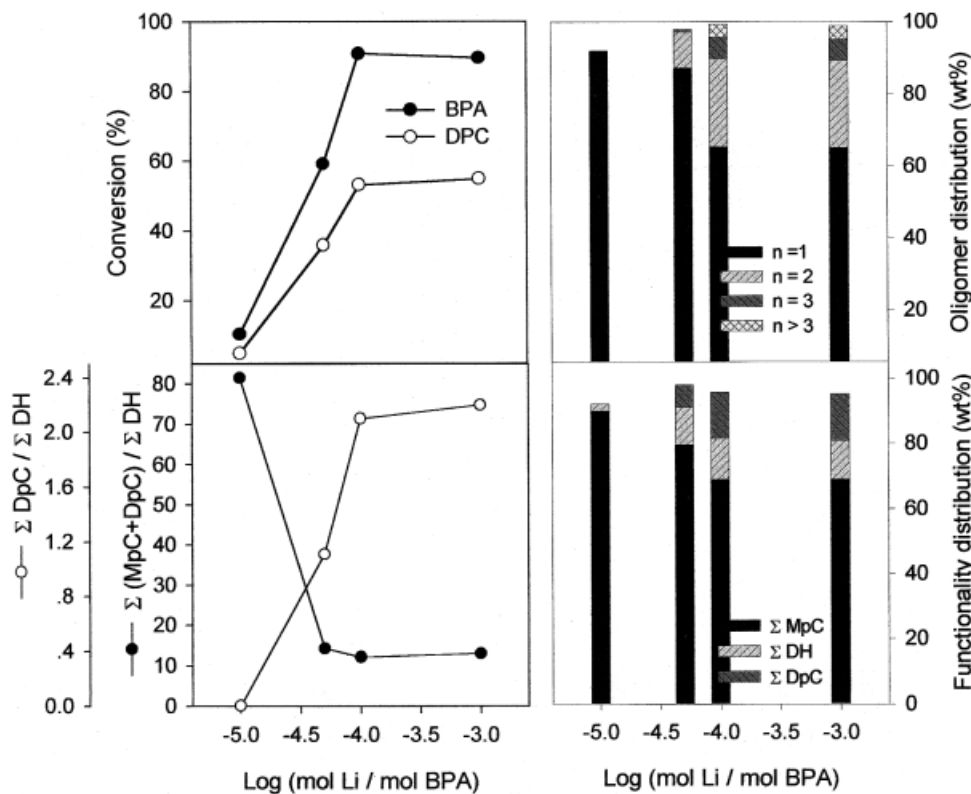
Figure 3 Effects of LiOH catalyst concentration on the oligomerization of BPA and DPC: Reactants molar ratio DPC/BPA, 2; reaction temperature, 433 K; initial pressure of dinitrogen, 1 MPa; stirring rate, 200 rpm; reaction time, 1 h.

ther with increasing catalyst concentration up to 10^{-4} mol cat/mol BPA. This indicates that, in reaction (2-1), the reaction of MpC(n) with DPC to form DpC(n) prevails over the reaction with BPA to DH(n) because DPC was employed in excess.

We observed the same trend shown in Figure 3 when the melt-transesterification was carried out with different reaction times with a catalyst concentration of 5×10^{-5} mol cat/mol BPA (not shown). Conversions of BPA and DPC increased as the reaction proceeded. The wt % of oligomers with n = 2, 3, or 4 increased with reaction time, whereas that of monomer (n = 1) decreased. Total MpC decreased and total DpC increased while total DH remained unchanged. It could be concluded that as the reaction time increased, the formation of the heavier oligomers became favorable and MpC(1) formed initially was converted to DpC(1), whereas DH(1) apparently did not change once it was formed.
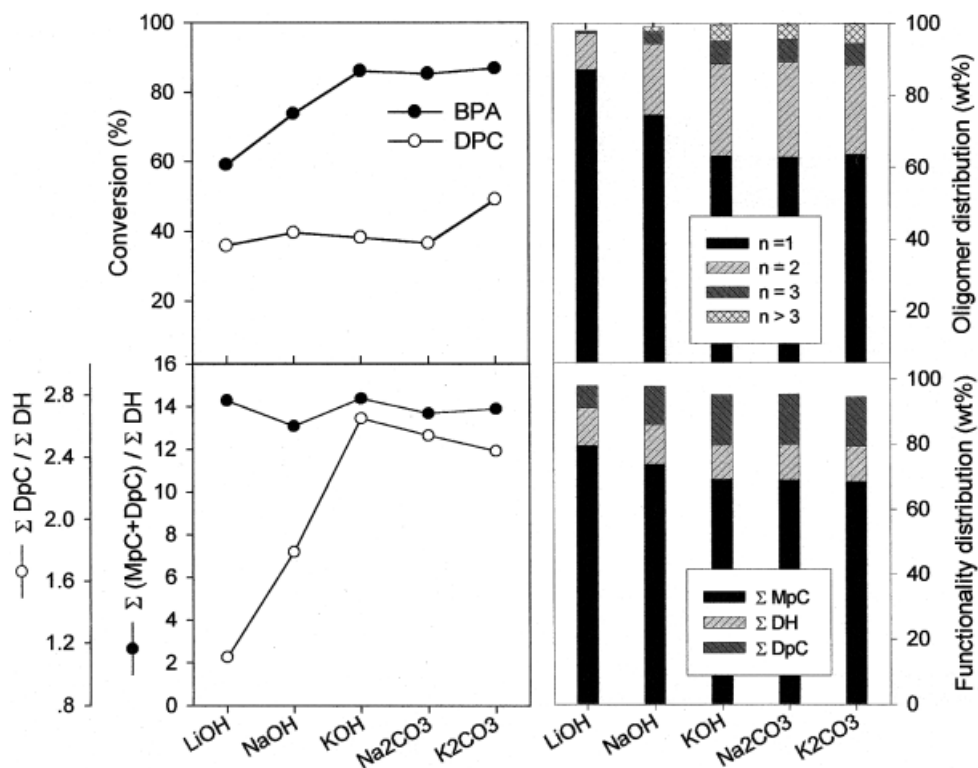
Several alkali-metal hydroxides and carbonates were tested as catalysts. As shown in Figure 4, all the catalysts tested were superior to LiOH in the aspects of reaction rates and fractions of carbonate-ended oligomers. A pseudoequilibrium state was reached within 1 h, except LiOH, which showed a slower rate. However, the secondary reactions continued. The phenol excess values for BPA in Table III in NaOH and

K_2CO_3 were greater than those for DPC, suggesting that more oligomers reacted with DPC than with BPA. Furthermore, the difference of phenol excesses for BPA and DPC may also be attributed to reactions between oligomers as in (3-1)–(3-3). However, the phenol excess in KOH and Na_2CO_3 showed almost the same value for both BPA and DPC, indicating the similar extent of the secondary reactions of the oligomers with BPA and DPC *or* between oligomers.

The melt-transesterification of bisphenol-A and diphenyl carbonate occurred readily to reactive precursors of phenylcarbonate-ended oligomers without a serious equilibrium constraint. Alkali carbonates were more efficient catalysts than were other alkali and transition metal compounds, especially at the low temperatures. High yields and selective formation of reactive phenylcarbonate-ended oligomers were achieved with a proper DPC/BPA molar ratio, which was found to be a critical variable to control the functional end groups of oligomers produced.
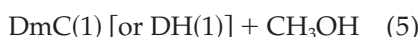
Transesterification of BPA and DMC

A typical reaction scheme of the transesterification of BPA and DMC followed a pattern similar to that of the melt-transesterification of BPA and DPC. It was also similar to the transesterification of phenol and DMC to
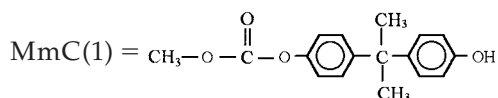
Figure 4 Alkali metal hydroxides and carbonates as catalysts for the oligomerization of BPA and DPC: Concentration of catalyst, 5×10^{-5} mol cat/mol BPA; DPC/BPA molar ratio, 2; reaction temperature, 433 K; initial pressure of dinitrogen, 1 MPa; stirring rate, 200 rpm; reaction time, 1 h.

make DPC(15–24) and was expected to be subject to a severe equilibrium limitation in the liquid-phase reaction.
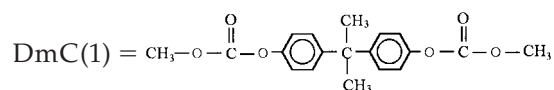
$$BPA + DMC \rightarrow MmC(1) + CH_3OH \quad (4)$$

$$MmC(1) + DMC \text{ (or BPA)} \rightarrow$$
$$DmC(1) \text{ [or DH(1)]} + CH_3OH \quad (5)$$

where

$$MmC(1) = CH_3-O-\overset{O}{\underset{\|}{C}}-O-\langle\bigcirc\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle\bigcirc\rangle-OH$$

TABLE III
Quantification of Phenol Excesses in Figure 4

Catalyst	Conversion (%) of		Phenol excess (%) for	
	BPA	DPC	BPA	DPC
LiOH	59.2	36.0	+55.8	+11.1
NaOH	73.9	39.7	+110.4	+69.8
KOH	86.2	38.3	+129.5	+123.5
Na$_2$CO$_3$	85.4	36.7	+161.3	+163.6
K$_2$CO$_3$	86.9	49.3	+112.4	+62.2

$$DmC(1) = CH_3-O-\overset{O}{\underset{\|}{C}}-O-\langle\bigcirc\rangle-\overset{CH_3}{\underset{CH_3}{C}}-\langle\bigcirc\rangle-O-\overset{O}{\underset{\|}{C}}-O-CH_3$$

Recently, Haba et al.[29] reported the synthesis of DmC(1) from the transesterification of BPA with a large excess of DMC (68 times the mole of initial BPA). DmC(1) could be produced with 22% yield with respect to BPA converted after 48 h under a catalyst system of dibutyltinchlorooxide and dimethylaminopyridine. Also, they used a substantial amount of a 4-Å molecular sieve (3.5 times the weight of initial BPA) to remove the methanol coproduced to alleviate the equilibrium limitation of the transesterification of BPA and DMC.[29]

Lewis acids such as titanium alkoxides are well-known transesterifiaction catalyts and it was found that solid catalysts of titania supported on silica or activated carbon could efficiently catalyze the transesterification of phenol and DMC.[15–17] Thus, we compared the activities of homogeneous versus heterogeneous Ti catalysts. To prepare heterogeneous Ti catalysts, silica was impregnated with a solution of toluene and 10 wt % (as Ti) of titanium alkoxides such as tetrabutoxy titanium (TBOT, Aldrich) and tetraisopropoxy titanium (TIPOT, Aldrich), and dried in an oven at 383 K for 12 h to remove toluene.
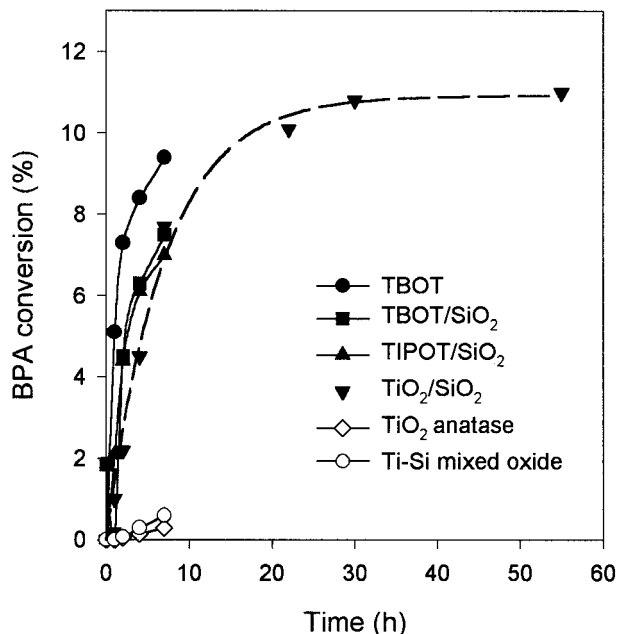
Figure 5 Various Ti catalysts on the transesterification of BPA and DMC: catalyst loading, 6×10^{-2} mmol for homogeneous TBOT and 0.5 g (1 mmol Ti) for heterogeneous solid catalysts; charge of BPA, 120 mmol; DMC/BPA molar ratio, 5; reaction temperature, 433 K; initial pressure of dinitrogen, 1 MPa; stirring rate, 400 rpm.

TiO_2 supported on silica was prepared from calcination of the TBOT-impregnated silica, $TBOT/SiO_2$, with an air stream at 773 K.[15] As shown in Figure 5, heterogeneous Ti catalysts showed activities comparable to those of homogeneous TBOT or TIPOT. As previously observed in the transesterification between phenol and DMC, major active species in heterogeneous catalysts seemed to be isolated Ti^{+4} ions coordinated with 4 or 5 oxygens on silica surface.[16,17] Crystalline TiO_2 appeared inactive in the transesterification of BPA and DMC because a pure anatase TiO_2 powder showed negligible activity. Considering its stability and facile recovery and regeneration after reaction, silica-supported titania was chosen as the best catalyst in the transesterification of BPA and DMC in the liquid phase.

A further study was carried out to investigate the equilibrium conversion of BPA over 10 wt % Ti-loaded TiO_2/SiO_2 catalyst with an extended reaction time of 55 h. As shown in Figure 5, the conversion of BPA approached about 11% during the 55-h reaction time, which is believed to be the equilibrium conversion. The first product of the transesterification of BPA and DMC was MmC(1), produced in an amount of 10% of initial BPA. The transesterification of MmC(1) and DMC produced DmC(1) in less than 10% of MmC(1) produced, indicating a similar degree of equilibrium limitation

for both reactions (4) and (5). The further transesterifications of MmC(1) and DmC(1) to heavier products seemed not so feasible, unlike in the case of BPA and DPC, although these reactions also involve transesterification between the hydroxyl and carbonate functional groups. There were no heavier oligomers or by-product through side reactions in a level detectable by GC and GC/MS. DH(1) was not detected either, as shown in Figure 1(B).

The liquid-phase transesterification of BPA and DMC was carried out at reaction temperatures of 393–503 K over 1 wt % Ti-loaded TiO_2/SiO_2 catalyst. As shown in Figure 6, it showed no activity for 7 h when temperature was 393 K and less than 2% of BPA conversion at 413 K. A drastic increase in the initial rate was achieved at reaction temperatures higher than 473 K. These relatively high temperatures made the time versus activity profile bend at around 1–2 h and increase slowly thereafter. This behavior could be explained by the two negative effects on the reaction rates at longer reaction times: (1) approaching the chemical equilibrium and (2) occurrences of side reactions such as O-methylation and side-ring methylation of BPA with DMC. It is well known that DMC is capable of methylation as well as carbonylation (transesterification) of aromatic compounds.[17,18,21] Below the reaction temperature of 433 K, no by-product was detected by GC and GC/MS analyses even after 55 h. There were
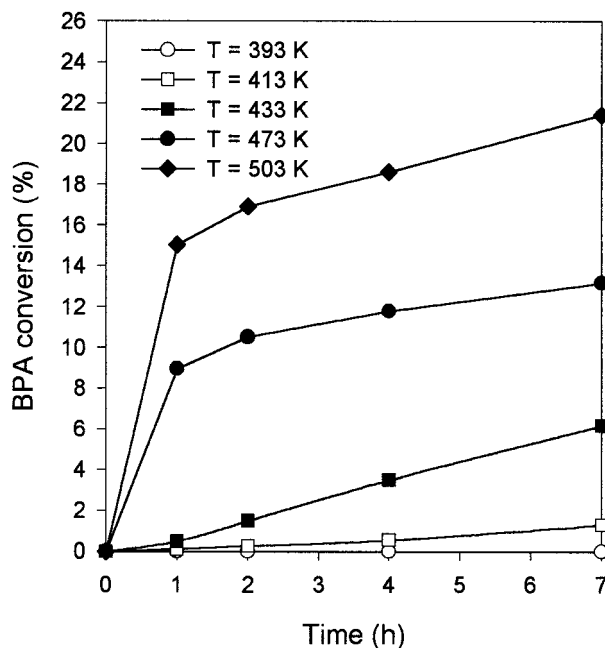
Figure 6 Effects of reaction temperature on the transesterification of BPA and DMC: 1 wt % Ti loaded TiO_2/SiO_2 catalyst loading, 0.5 g; charge of BPA, 120 mmol; DMC/BPA molar ratio, 5; reaction temperature, 433 K; initial pressure of dinitrogen, 1 MPa; stirring rate, 400 rpm.

TABLE IV
Product Distribution of Transesterification Between BPA and DMC at the Reaction Temperatures of 473 and 503 K

At 473 K (h)	BPA conv. (%)	Selectivity[a] (%)					mC(1) Yield[b] (%)
		A	B	C	MmC(1)	DmC(1)	
1	8.9	—	—	—	95.6	4.4	8.9
2	10.5	—	—	—	95.8	4.2	10.5
4	11.8	1.4	1.6	—	92.1	4.9	11.4
7	13.2	2.9	1.4	—	90.5	5.4	12.6
At 503 K (h)							
1	15.1	3.3	1.5	—	89.5	5.7	14.4
2	16.9	8.7	1.3	—	84.8	5.2	15.2
4	18.6	19.9	1.1	1.7	72.9	4.4	14.4
7	21.4	36.8	0.7	2.8	56.6	3.1	12.8

[a] A, B, and C are by-products described in the text.
[b] mC(1) yield is a sum of MmC(1) yield and DmC(1) yield.
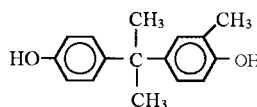
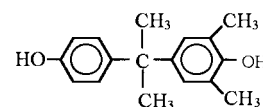three kinds of by-products formed from methylations of bisphenol by DMC in the same manner as in the reaction of the transesterifiaction of phenol and DMC.[15,17]
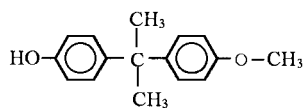
(A)   **(B)**   **(C)**

A is produced from O-methylation of BPA with DMC-like anisole formation from phenol and DMC. **B** and **C** are formed from *ortho*-methylation of BPA with DMC equivalent to cresol and dimethyl phenol, respectively, in the phenol–DMC reaction. These molecules are unreactive in the postpolymerization step because they have no carbonate functional end groups to react further. Therefore, minimization of the by-products is indispensably required to obtain high molecular weight polycarbonate from the BPA and DMC route.

Table IV shows product distributions of transesterification between BPA and DMC at 473 and 503 K under the same conditions as those in Figure 6. The by-products were observed after 4-h reaction time at 473 K but they were produced for whole reaction time in much greater quantities at 503 K. The formation of **A** showed an almost linear increase with time, whereas the mC(1) yield [the sum of MmC(1) and DmC(1)] decreased after 2-h reaction time as the result of extensive side reactions of BPA. The products' profile with reaction time was exactly the same as that observed in the previous work for liquid-phase transesterification of phenol and DMC,[15] indicating a similar reaction mechanism prevailed in both transesterification reactions. There was no indication of the formation of heavier oligomers in HPLC analyses.

Activity of the transesterification of BPA and DMC was investigated with different reactant molar ratios of DMC/BPA over 1 wt % Ti-loaded TiO_2/SiO_2 catalyst, as shown in Table V. To understand the DMC concentration effect on the activity, total Ti loading per initial charge of BPA was fixed at 8.76×10^{-4} mol Ti/mol BPA. The formation of heavier oligomers with $n \geq 2$ were not detected as DMC concentration was increased, but the BPA conversion at 7 h increased because of the shift in equilibrium. However, its increase was not linear because the reaction time of 7 h was insufficient to reach a complete equilibrium state. The **A**-type by-product was produced in large amounts at DMC/BPA = 2, suggesting that the lower DMC concentration has a negative effect on the transesterification. Above DMC/BPA = 5, the products distribution remained invariant except for a slight increase of DmC(1) and the selectivity of mC(1) stayed around 95%.

The beneficial usage of DMC is well established as an environmentally benign material for carbonylation as well as methylation reactions. The transesterification of bisphenol-A and dimethyl carbonate is subject to a serious equilibrium limitation in obtaining reactive polycarbonate precursors and coproduces a significant amount of methylated bisphenol-A. Recycling and reflux of excess DMC could be employed to im-

TABLE V
Reactants' Molar Ratio Effect on the Transesterification of BPA and DMC[a]

DMC/BPA	BPA conv. (%)	Selectivity[b] (%)					mC(1) yield[c] (%)	TON[d]
		A	B	C	MmC(1)	DmC(1)		
2	7.4	10.3	1.1	0.4	83.3	4.8	6.5	84
5	13.2	2.9	1.4	—	90.5	5.4	12.6	151
10	16.0	3.3	1.4	0.3	87.4	7.8	15.2	183
20	21.2	4.1	1.5	0.6	86.2	7.6	19.9	242

[a] Reaction conditions: total Ti loading per initial charge of BPA, 8.76×10^{-4} mol Ti/mol BPA; reactants' molar ratio DMC/BPA, 5; reaction temperature, 473 K; initial pressure of dinitrogen, 1 MPa; stirring rate, 400 rpm; time, 7 h.
[b] A, B, and C are by-products as discussed in the text.
[c] mC(1) yield is a sum of MmC(1) yield and DmC(1) yield.
[d] BPA moles converted per total Ti for 7-h reaction.

prove the yield by shifting equilibrium toward the forward reaction. However, any recycling scheme involving fractionation should be difficult because of the small difference of boiling points between DMC and methanol.

Direct oxidative carbonylation of BPA with CO/O₂

$$2BPA + CO + \tfrac{1}{2}O_2 \rightarrow DH(1) + H_2O \qquad (6)$$
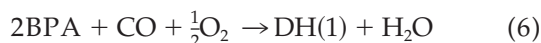
The direct synthesis of polycarbonate precursors from BPA and CO using a Pd–Cu redox catalytic system was reported recently.[30,31] The number of studies on this subject is highly limited in contrast to the extensive works on direct insertion of CO into phenol[32–39] for phosgene-free synthesis of diphenyl carbonate. It was claimed that DHs having an average molecular weight of about 3600 could be synthesized with the PdCl₂–Cu(OAc)₂–hydroquinone catalyst system and a substantial amount of a 3-Å molecular sieve to remove coproduced water. The catalyst system was also found, by the same investigators, to be the best in the direct oxidative carbonylation of phenol to DPC. In principle, the direct insertion of a CO molecule into BPA is the most direct method to the synthesis of

polycarbonte precursors without involving DMC or DPC as intermediates. However, the obtained hydroxy (or phenolic)-ended oligomers are also the least reactive in the polycondensation step. They are also known to weaken the physical and chemical properties of the final polycarbonate.[4,40]

The direct oxidative carbonylation of BPA with CO/O₂ was investigated, as shown in Table VI. We tried the same catalyst system of Goyal et al.[30] in the direct oxidative carbonylation of BPA in Run 1. BPA conversion of 67% was obtained, even without the dehydrating agent of a molecular sieve. However, we observed large amounts of side-reaction products, as reported by Goyal et al.[30] When phenol was introduced in the same reaction system,[42] the BPA conversion was not significantly changed, although the by-products were reduced dramatically. Instead, MpC(n) was produced in an amount of half the weight-selectivity of DH(n), but a similar amount in moles as indicated from the ratio of MpC/DH. Thus the following overall reaction seems to take place:

$$BPA + CO + \tfrac{1}{2}O_2 + Phenol \rightarrow MpC(1) + H_2O \qquad (7)$$

The same effect was observed in the Pd(OAc)₂–Ce(OAc)₃ system, which showed a little lower BPA

TABLE VI
The Direct Oxidative Carbonylation of BPA With and Without Phenol[a]

Run	System	BPA conv. (%)	Product distribution (wt %)						MpC/DH[c]
			MpC (1)	MpC (2)	DH (1)	DH (2)	$n \geq 3$	By-products[b]	
1	Pd–Cu w/o phenol	67.0	0	0	34.8	10.1	3.3	51.8	0
2	Pd–Cu with phenol	59.2	19.4	4.6	33.8	6.9	1.2	34.1	1.13
3	Pd–Ce w/o phenol	39.6	0	0	53.2	5.1	trace	41.7	0
4	Pd–Ce with phenol	38.3	21.2	trace	47.0	2.8	0	29.0	0.87

[a] Reaction conditions: Pd(II) chloride (Runs 1 and 2) or Pd(II) acetate (Runs 3 and 4), 0.06 mmol; Cu(II) chloride or Ce(III) acetate, 0.30 mmol; hydroquinone (Runs 1 and 2) or benzoquinone (Runs 3 and 4), 1.50 mmol; Bu₄NBr, 1.50 mmol; dichloromethane, 30 mL; BPA, 30 mmol; phenol, 30 mmol; CO pressure, 5 MPa; O₂ pressure, 0.5 MPa; temperature, 373 K; time, 4 h.
[b] Major by-products are phenyl salicylate and o-phenylene carbonate-ended bisphenol-A.
[c] The ratio of total MpC moles to total DH moles.

conversion than that of the PdCl$_2$–Cu(OAc)$_2$ system. However, by-product formation was reduced significantly. The Pd(OAc)$_2$–Ce(OAc)$_3$–benzoquinone system was found to be the best homogeneous catalytic system in synthesizing the diphenyl carbonate.[37]

Oxidative carbonylation of BPA alone provides the shortest path from BPA to polycarbonate precursors. However, dihydroxy-ended oligo-carbonates (DH) were produced as the sole *para*-insertion product of CO and phenyl salicylate and *o*-phenylene carbonate–ended BPA were formed as major by-products.[29,30] DH is the least reactive polycarbonate precursor in the polycondensation step of the phosgene-free polycarbonate process compared to phenyl or methylcarbonate-ended precursors. The new catalytic reaction of the coupled carbonylations of BPA and phenol with CO alleviates this problem by producing comparable amounts of both MpC- and DH-type polycarbonate precursors.[42]

CONCLUSIONS

Among three routes to synthesis of polycarbonate precursors from bisphenol-A without using phosgene, the melt-transesterification of bisphenol-A and diphenyl carbonate proceeded easily, to produce reactive precursors without a significant equilibrium constraint. On the other hand, the transesterification of bisphenol-A and dimethyl carbonate showed a serious equilibrium limitation in obtaining polycarbonate precursors with high yields. Furthermore, a significant amount of methylated bisphenol-A was also produced as a by-product. The direct oxidative carbonylation of bisphenol-A with CO is the most direct method, although it produced diphenolic-ended oligomers and a significant amount of by-products, which are the least reactive in the subsequent polycondensation step of the phosgene-free polycarbonate process. A novel method to synthesize the reactive polycarbonate precursors of phenylcarbonate-ended oligomers was successfully carried out from the coupled oxidative carbonylation of bisphenol-A and phenol.

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