

## A One-Step Synthesis of Reactive Polycarbonate Precursors by the Coupled Oxidative Carbonylation of Bisphenol-A and Phenol with Carbon Monoxide

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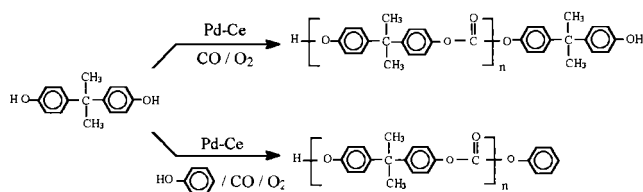
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The reactive polycarbonate precursors of phenyl carbonate-ended oligomers amenable to polycondensation in the phosgene-free polycarbonate process were catalytically synthesized via a novel one-step reaction of the coupled oxidative carbonylation of bisphenol-A and phenol with carbon monoxide.

Polycarbonate (PC) has been produced by the interfacial polycondensation of bisphenol-A (BPA) 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 methylenechloride as the solvent.<sup>1</sup> For this reason, phosgene-free processes for polycarbonate have been proposed, in which melt transesterification<sup>2,3</sup> or solid state polymerization is employed by using BPA and diphenyl carbonate (DPC), the latter being synthesized in a phosgene-free process.<sup>4-6</sup> The process consists of prepolymerization of BPA and DPC into reactive polycarbonate precursors followed by polycondensation of the precursors. However, it is not easy to obtain DPC efficiently from a phosgene-free process. In a recently commercialized phosgene-free polycarbonate process, DPC is produced from transesterification between dimethyl carbonate (DMC) and phenol, and DMC is, in turn, synthesized via oxidative carbonylation of methanol. The conversion from DMC to DPC proceeds in two steps and both steps are subject to severe equilibrium constraint. Thus, reactive distillation is usually employed in order to obtain high yields of DPC. Because of these difficulties involved in DPC synthesis, there have been extensive efforts to develop a phosgene-free polycarbonate process without employing expensive DPC as an intermediate. One such a route is direct oxidative carbonylation of BPA into polycarbonate oligomers<sup>7-11</sup> in a similar manner employed for an oxidative carbonylation of phenol to DPC.<sup>12,13</sup> However, the oligomers produced from the carbonylation of BPA alone have dihydroxy-ended (DH) functionality which requires multi-step processing of pressurized carbonylation<sup>9</sup> or subsequent transesterification of DH with DPC<sup>11</sup> in order to high molecular weight polycarbonate due to its limited reactivity. Furthermore, the dihydroxy-ended groups weaken the physical and chemical properties of final polycarbonate.<sup>14</sup>

We have studied various probable routes for the phosgene-free polycarbonate synthesis such as the transesterifications of BPA with DPC or DMC, and a direct carbonylation of BPA with CO. Each route produced polycarbonate precursors with different end groups. In terms of the reactivity in the subsequent polycondensation step, monophenyl carbonate-ended oligomers (MpC(n), n = number of repeating unit) were the most desired precursors for obtaining high molecular weight polymers. We found that addition of phenol in the reaction of BPA carbonylation, resulted in successful synthesis of MpCs in

one-step from CO.



In contrast, by obtaining MpC directly from CO-O<sub>2</sub>, the proposed new catalytic reaction of coupled carbonylation of BPA and phenol achieves a one-step synthesis of reactive polycarbonate precursors and saves at least two reaction steps from the commercial process. This reaction, to our best knowledge, has never been studied before and has a great practical implication in phosgene-free syntheses of polycarbonate.

For the coupled oxidative carbonylations of BPA and phenol, the reaction system and procedure were employed which were similar to those generally used for the oxidative carbonylation of phenol.<sup>13</sup> Thus, Pd(II) acetate (0.06 mmol), Ce(III) acetate monohydrate (0.30 mmol; inorganic cocatalyst), tetrabutylammonium bromide (1.50 mmol; base), benzoquinone (1.50 mmol; organic cocatalyst), tetrahydrofuran (30 mL; solvent), BPA (30 mmol) and the equimolar phenol were charged in the 100 cm<sup>3</sup> autoclave (Parr). All chemicals were purchased from Aldrich. After purging the reactor three times with O<sub>2</sub>, 5 MPa of CO and 0.5 MPa of O<sub>2</sub> were successively charged 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. Identification and quantification of products were performed by high performance liquid chromatography (HPLC) and gas chromatography (GC) as well as GC-MS.

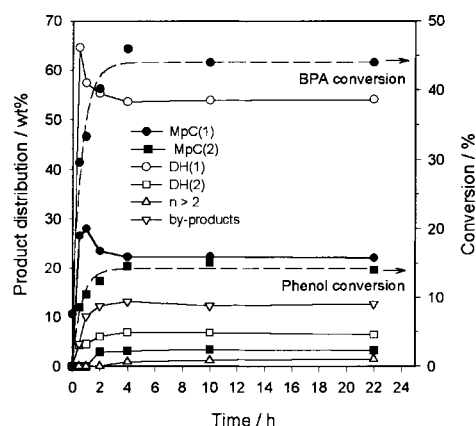
A typical reaction profile of the coupled carbonylations of BPA and phenol with time is shown in Figure 1. The conversions of reactants and concentrations of products ceased to change within 4 h. This saturation of BPA and phenol conversions after 4-h reaction was caused by the equilibrium limits, not by deactivation of catalysts because the conversions were increased to 65% for BPA and to 25% for phenol, when coproduced water was removed with 4 g of dehydrated molecular sieve 3 A. The desired MpC was formed as weight-selectivity of 25.4% and the selectivities of DH and by-products were respectively 60.5% and 13.2%. The oligomers up to n = 5 were formed. The by-products were composed of phenyl salicylate and o-phenylene carbonate-type bisphenols. The concentration profile of DH(1) shows a sharp maximum. Hence, although DH(1) has no reactivity in the subsequent polycondensation, it is a potential reactant to be converted into the reactive precursor MpC(n) by further coupled carbonylation with CO and phenol in the system. The concentraon of

**Table 1.** Oxidative carbonylation at 373 K with 5.0 MPa CO and 0.5 MPa O<sub>2</sub><sup>a</sup>

Run	Initial reactant / mmol			TON <sub>BPA</sub> <sup>b</sup>	TON <sub>PhOH</sub> <sup>c</sup>	Products / mmol					MpC/DH <sup>d</sup>
	BPA	Phenol	DPC			DPC	MpC(1)	MpC(2)	DH(1)	DH(2)	
1	30	-	-	210	-	0	0	0	4.55	0.50	-
2	-	30	-	-	40	0.85	0	0	0	0	-
3	30	-	4.5	288	-	1.40 <sup>e</sup>	2.4	0.35	4.50	0.83	0.51
4	30	30	-	226	75	0.30	3.0	0.20	3.65	0.30	0.81

<sup>a</sup>Pd(II) acetate, 0.06 mmol; Ce(III) acetate, 0.30 mmol; benzoquinone, 1.50 mmol; tetrabutylammonium bromide, 1.50 mmol; tetrahydrofuran, 30 mL.

<sup>b</sup>BPA moles converted and <sup>c</sup>Phenol moles converted per Pd mole for 4 h. <sup>d</sup>The mole ratio of total MpC to total DH. <sup>e</sup>Unreacted DPC.

**Figure 1.** A typical reaction profile with time of the coupled oxidative carbonylation of bisphenol-A (BPA) and phenol.

MpC(1) also showed a maximum, indicating its further oligomerization with time. It was also observed that as the equilibrium was shifted to the forward reaction by adding dehydrating agents, the mole ratio of MpC/DH increased and the absolute amount of DH(1) decreased, resulting in the increases of MpC and oligomers of  $n \geq 2$ .

A critical question in understanding this reaction system is how MpC is formed, which is totally absent in oxidative carbonylation of BPA alone without phenol under our reaction conditions. There are two possibilities; direct phenoxy-carbonylation of BPA-CO-phenol and via series reaction steps of carbonylation of phenol to DPC followed by the transesterification of BPA and DPC produced in situ in the reactor. To elucidate the reaction scheme for the production of MpC in our BPA-phenol-CO system, we performed several controlled reactions under otherwise the same reaction conditions as illustrated in Table 1. In oxidative carbonylation of BPA alone, only DH type oligomers were formed with DH(1) dominating (Run 1). Oxidative carbonylation of phenol itself gave DPC as expected (Run 2). The reaction of BPA and DPC (Run 3) resulted in the formation of MpC while the formation of DHs was not seemingly influenced compared to Run 1. Note that this reaction has usually been studied at 453–523 K in the presence of a base catalyst.<sup>2,3</sup> In the coupled oxidative carbonylation of both BPA and phenol (Run 4), a substantially greater amount of MpCs was formed. The formation of DHs, however, was reduced. These results suggest that the in situ formation of DPC and subsequent transesterification of this DPC with BPA take place in the coupled oxidative carbonylation of BPA and phenol. Overall, there seems to be three types of reactions taking place in our reaction system. DHs are produced by the direct oxidative carbonylation of two BPA molecules and DPC

are produced by the carbonylation of two phenol molecules with the same catalytic system. The third type is the reaction between BPA and DPC produced in situ to produce desired MpCs. The transesterification of BPA and DPC is catalyzed by a base<sup>3</sup> and quaternary ammonium halide salt contained as a catalyst component of oxidative carbonylation appears responsible for the transesterification as well.

Considering that dual nucleophilic attacks of bisphenoxy and phenoxy ions are possible in a single catalytic cycle of Pd, some contribution from the phenoxy-carbonylation of BPA with phenol and CO might be included in the formation of total MpCs. The increased molar ratio of MpC/DH in Run 4 relative to Run 3 indicates the conversion of DH to MpC as also indicated in the concentration profile in Figure 1. It is interesting to note that turnover numbers (TON) with respect to BPA and phenol during 4 h of coupled oxidative carbonylation are higher than individual carbonylations of BPA and phenol. This apparent synergistic effect also indicates the presence of a kinetic coupling between two oxidative carbonylation reactions. Furthermore, the formation of by-products is reduced from weight-selectivity of 18% in individual carbonylation of BPA to 13% in the coupled carbonylation.

The proposed reaction scheme of coupled oxidative carbonylation of BPA and phenol makes possible one-step synthesis of reactive precursors in a phosgene-free polycarbonate process. The synthesis of expensive intermediates such as DMC and DPC could be avoided. It also has advantages in reaction rates, MpC selectivity and by-product formation.

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