

Coupled oxidative carbonylation of bisphenol-A and phenol into phenylcarbonate-ended polycarbonate precursors over a homogeneous Pd–Ce redox catalyst

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Abstract

A coupled oxidative carbonylation of bisphenol-A and phenol was investigated using a redox catalytic system of palladium acetate and cerium acetate as a novel scheme for a direct synthesis of phenylcarbonate-ended polycarbonate precursors amenable to polycondensation in a current phosgene-free polycarbonate process. Reaction variables such as solvents, bases and organic co-catalysts were examined in our novel scheme. Removal of water co-produced with desired products and adjustment of the reactants molar ratio of phenol to bisphenol-A appeared to be most critical for highly selective formation of the desired phenylcarbonate-ended precursors in one-step. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polycarbonate precursor; Phosgene-free synthesis; Coupled carbonylation; Bisphenol-A; Phenol; Pd–Ce redox catalyst

1. Introduction

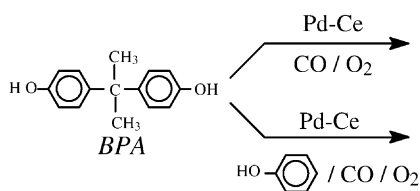
Polycarbonate has been produced by the interfacial polycondensation of bisphenol-A (BPA) and phosgene. The major drawbacks of the conventional phosgene process are environmental and safety problems involved in using highly toxic phosgene as the reagent and copious amounts of methylenechloride as the solvent [1,2]. For this reason, phosgene-free processes for polycarbonate have been proposed that employ BPA and diphenyl carbonate (DPC) with the latter synthesized also in a phosgene-free process [3–8]. Thus the current commercial phosgene-free process consists of prepolymerization of BPA and

DPC into reactive polycarbonate precursors followed by polycondensation of the precursors using melt transesterification [9–15] or solid state polymerization [2]. Although well-developed into commercialization, the phosgene-free DPC process is a complicated one involving multiple reaction steps, some of which are under severe equilibrium constraints [3,5]. Therefore, there have been some efforts to develop a phosgene-free polycarbonate process without employing the expensive DPC as an intermediate. One such a route is a direct oxidative carbonylation of BPA into polycarbonate oligomers [16–21] in a similar manner employed for an oxidative carbonylation of phenol to DPC [22–39].

The oxidative carbonylation of BPA could be a promising method of phosgene-free polycarbonate synthesis because it converts CO and BPA directly to polycarbonate oligomers as prepolymers. The direct

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insertion of carbon monoxide to the *para*-position of BPA was reported two decades ago [16,17]. Recently, the successful syntheses of polycarbonate oligomers by the direct oxidative carbonylation of BPA have been reported with homogeneous Pd catalysts [18–21] which have been found effective through the extensive works in the direct synthesis of DPC from phenol and CO [22–39]. However, the oligomers produced from the oxidative carbonylation of BPA by reaction (1) are end-uncapped oligomers and those phenolic end groups made the polymers extremely unstable [13,40]. Due to their end group functionalities, the di-hydroxy-ended prepolymer (denoted as $DH(n)$) should require a multi-step processing of pressurized carbonylation [19] in order to obtain high molecular weight polycarbonate or additional functionalization of the DHs with DPC into phenylcarbonate-ended polycarbonate precursors [21] prior to polycondensation step. In the subsequent polycondensation step of current commercial phosgene-free polycarbonate process, mono-phenylcarbonate-ended oligomers (denoted as $MpC(n)$, where n is the number of repeating unit) are precursors as prepolymer for obtaining high molecular weight polycarbonate.



We discovered that addition of phenol into the reaction system of BPA carbonylation, resulted in a successful one-step synthesis of $MpCs$ from CO [41] as shown in reaction (2). This reaction, to our best knowledge, has never been studied before and has a great practical implication in phosgene-free syntheses of polycarbonate. This coupled carbonylation of BPA and phenol involves two nucleophiles of phenoxy and bisphenoxy anions, and therefore it requires more controlled reaction conditions than the individual carbonylation of phenol or BPA. In this work, effects of catalytic reaction variables are investigated to elucidate the reaction characteristics of the novel reaction scheme with a homogeneous Pd acetate–Ce acetate redox system.

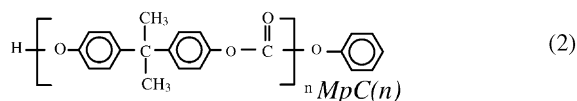
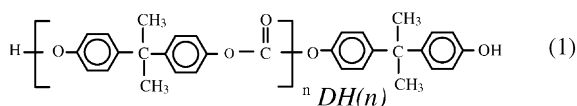
2. Experimental

2.1. Reaction procedures

For the coupled oxidative carbonylation of BPA and phenol, the reaction system and procedure were employed as those generally used for the oxidative carbonylation of phenol [39]. Charged into a 100 cm³ autoclave (Parr) were Pd acetate as a main catalyst, Ce acetate as an inorganic co-catalyst and a quinone as an organic co-catalyst to reoxidize reduced palladium and cerium, a base to activate phenols, a solvent, BPA and phenol. After purging the reactor with O₂ three times, 5 MPa of CO and 0.5 MPa of O₂ 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. All chemicals were purchased from Aldrich.

2.2. Product analyses

Reaction products were analyzed by high performance liquid chromatography (HPLC), gas



chromatography (GC) and gas chromatography–mass spectrometer (GC–MS) in order to identify and quantify the polycarbonate precursors and by-products. We adopted the methods of Bailly et al. [42] and Kim et al. [13] 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 equipped with an auto-sampler. As an UV detector, 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 μ m particle size, 4.6 mm \times 250 mm). A mobile phase flow rate of 1 ml min⁻¹ was adjusted with

a gradient mode of acetonitrile and water from 65:35 to isocratic of acetonitrile. The reaction samples were diluted to 50 times with acetonitrile and 5 μl was injected by an automatic injector. The Millennium³² software was used for data reduction and integration.

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

For the characterization of carbonate linkages of the polycarbonate precursors, FT-IR was performed on a Perkin Elmer 1800. The product solution after reaction was wetted on a thin KBr wafer and scanned from 500 to 4000 cm^{-1} of infrared wavenumber.

3. Results and discussion

3.1. HPLC chromatograms and FT-IR analysis of the polycarbonate oligomers

Fig. 1 shows typical HPLC spectra of polycarbonate oligomers which could be obtained from various reactions such as a melt-transesterification of BPA with DPC (A), an oxidative carbonylation of BPA alone (B) and the coupled oxidative carbonylation of both BPA and phenol (C) proposed here. We used the HPLC spectrum of the oligomer mixture of the Fig. 1A as our reference, which was prepared from a conventional melt-transesterification of BPA and DPC with K_2CO_3 catalyst, and compared it with the spectra of products obtained from our coupled oxidative carbonylation of BPA and phenol. As shown in Fig. 1A, there exist three kinds of oligomers with respect to their end group functionality. The oligomer with mono-phenylcarbonate-ended on one side and hydroxy (of phenolic)-ended on the other side was denoted as MpC(n) with n being the number of repeating unit of BPA carbonate. Di-hydroxy-ended oligomer on both sides and di-phenylcarbonate-ended oligomers were denoted as DH(n) and DpC(n), respectively.

Fig. 1B shows polycarbonate oligomers of DH(n) and by-products obtained from the direct oxidative

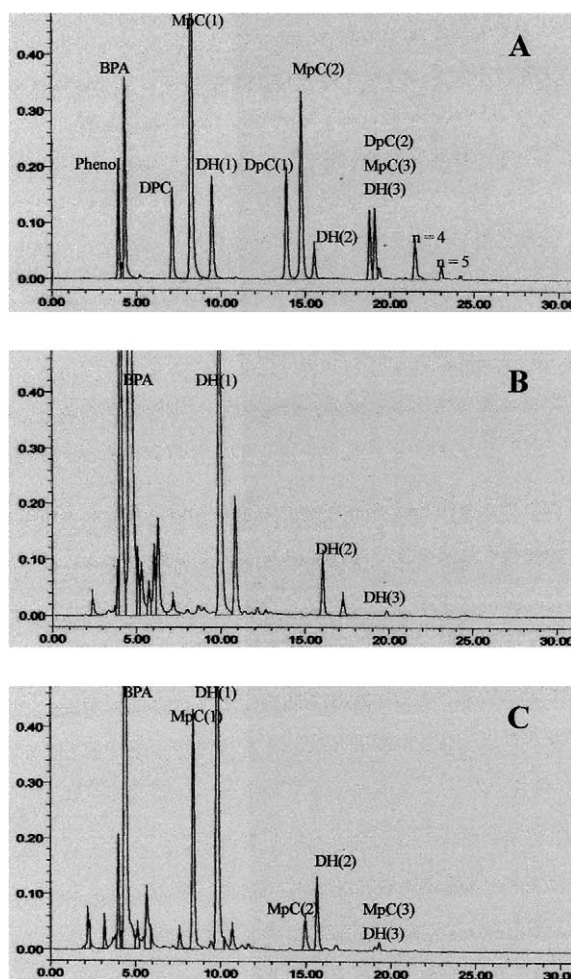


Fig. 1. Liquid chromatograms for the products obtained from the reactions of bisphenol-A with DPC (A), BPA with CO/O_2 (B) and BPA with phenol and CO/O_2 (C).

carbonylation of BPA alone. DHs were the sole type of products of polycarbonate precursors in this reaction while other types of precursors like MpCs were not produced. DHs with n up to 3 were detected together with some by-products. The by-products consisted of *o,p*-isomers of BPA and acetate-, salicylic acid- and *o*-phenylene carbonate-type ended derivatives of bisphenols as determined from analysis of GC–MS. The latter two were also reported as major by-products in the oxidative carbonylation of BPA alone [18,19]. Furthermore, bisphenol-F, brominated and phenoxy BPA were also found in trace amounts

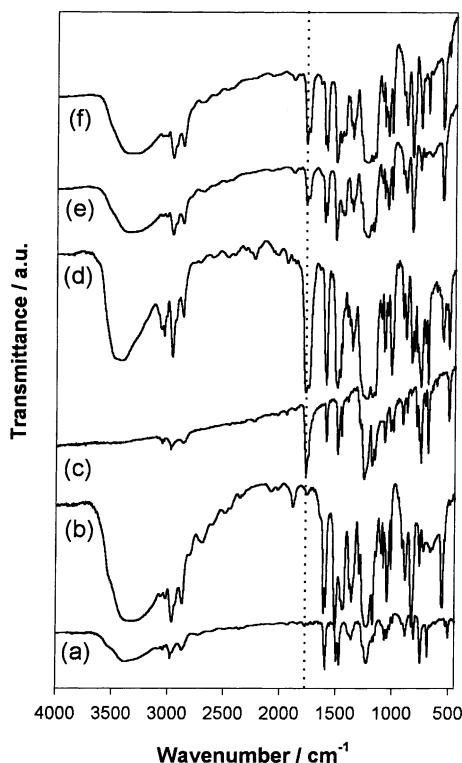


Fig. 2. Typical FT-IR spectra for the reactants and products. Authentic phenol (a), authentic BPA (b), authentic DPC (c), a typical product mixture of the reaction between BPA and DPC (d), that of the oxidative carbonylation of BPA alone (e), and that of the coupled oxidative carbonylation of BPA and phenol (f).

in some analyses. When additional phenol was introduced in the system of the oxidative carbonylation of BPA, the desired products of MpCs were synthesized successfully as presented in Fig. 1C. The DH type products were also present as in the case of the carbonylation of BPA alone, but the by-products were less in most cases as shown by the smaller HPLC peaks at ca. 11 and 5–7 min of eluant times.

In Fig. 2, the polycarbonate precursors were analyzed by FT-IR including the authentic reactants. The spectrum (f) for the products of our coupled carbonylation of BPA and phenol showed a stronger stretching band at ca. 1774 cm^{-1} attributed to the carbonyl of a linear carbonate which was also found in authentic DPC (c) than that for the carbonylation of BPA alone (e) under the same reaction condition except the presence of phenol. It could be attributed to additional

existence of linear carbonate linkages in MpCs, compared with the reaction mixture of (e) which did not produce the MpCs. Under our optimized $\text{Pd}(\text{OAc})_2\text{-Ce}(\text{OAc})_3$ system, we rarely detected the band at the frequency of ca. 1836 cm^{-1} due to cyclic carbonyl stretching in *o*-phenylene carbonate type BPA as reported in [18].

3.2. The coupled oxidative carbonylation of BPA and phenol as a novel reaction scheme for polycarbonate oligomers

The $\text{Pd}(\text{OAc})_2\text{-Ce}(\text{OAc})_3$ was found to be the best homogeneous redox catalytic system by us in synthesizing the DPC [39]. Therefore, we carried out some preliminary experiments for our new reaction (2) using $\text{Pd}(\text{OAc})_2\text{-Ce}(\text{OAc})_3$ as the catalytic redox system. In oxidative carbonylation of BPA alone, only DH type oligomers were formed with DH(1) dominating. Oxidative carbonylation of phenol itself gave DPC as expected. The reaction of BPA and DPC under our carbonylation condition resulted in the formation of MpCs while the formation of DHs was not seemingly influenced. In the coupled oxidative carbonylation of both BPA and phenol, a substantially greater amount of MpCs was formed for the same initial amount of BPA. 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 [41].

Compared to the oxidative carbonylation of BPA alone (reaction (1)), the conversion of BPA was not changed but the by-products were reduced significantly when phenol was introduced into the coupled oxidative carbonylation system with BPA. More importantly, $\text{MpC}(n)$ was produced in an amount corresponding to a half the weight-selectivity of $\text{DH}(n)$. The amounts of two products are similar in moles when equimolar amount of BPA and phenol are used. Thus the reaction (2) could be employed as a novel reaction scheme to produce reactive polycarbonate precursors although the DHs are produced as well in a large amount [41]. Our new catalytic system of the coupled oxidative carbonylation gives a few positive synergetic effects on the activities of BPA and phenol. It increases the turnover rates of both BPA and phenol conversions comparing to the individual oxidative

Table 1

The effect of solvent on the coupled oxidative carbonylation of BPA and phenol^a

Run	Solvent	Conversion of BPA (%)	Product distribution (wt.%)					MpC/DH ^b	
			MpC(1)	MpC(2)	DH(1)	DH(2)	$n \geq 3$		By-products
1	3-Pentanone	25.5	4.9	0	8.3	0	0	86.8	1.18
2	Methylene chloride	38.3	21.2	Trace	47.0	2.8	0	29.0	0.87
3	THF	45.2	22.3	3.1	53.6	6.9	0.9	13.2	0.82
4	Chlorobenzene	29.2	17.1	Trace	38.1	Trace	0	44.8	0.90
5	Anisole	24.6	21.0	Trace	52.7	Trace	0	26.3	0.80
6	Toluene	37.9	19.3	Trace	42.1	Trace	0	38.6	0.92
7	Benzene	26.8	15.5	Trace	43.0	Trace	0	41.5	0.72
8	Cyclohexane ^c	67.0	16.6	3.1	35.0	6.3	1.4	37.6	0.93

^a Pd(OAc)₂, 0.06 mmol; Ce(OAc)₃·H₂O, 0.30 mmol; benzoquinone, 1.50 mmol; Bu₄NBr, 1.50 mmol; solvent, 30 ml; BPA, 30 mmol; phenol, 30 mmol; CO pressure, 5 MPa; O₂ pressure, 0.5 MPa; temperature, 373 K; time, 4 h.

^b The molar ratio of total MpC to total DH.

^c The values of products-rich phase from phase-separated products with solvent-rich phase after 4 h reaction.

carbonylation of BPA or phenol under the same reaction condition. Furthermore, a reduced amount of by-products is formed [41].

3.3. Effect of solvent on the coupled oxidative carbonylation

Methylene chloride is frequently used as a solvent in old phosgene-based and new phosgene-free polycarbonate synthesis processes. It is desired to replace it with other environmentally benign and more efficient solvents because it causes a serious environmental pollution as a volatile organic compound. Table 1 shows effect of various solvents on the coupled carbonylation of BPA and phenol. The solvents are sorted in descending order of their 'dielectric constants' which are compatible with their polarities.

The solvent properties play an important role in solubility of reactants, products and catalyst systems. Also it changes the charge distribution in reactant molecules at the transition state by its polarity. The Table 1 did not show any consistent trend in activity and selectivity on our coupled carbonylation of BPA and phenol with respect to the magnitude of dielectric constants of the solvents tested. However, it is expected that solubility of reactants, CO, O₂ and catalytic system in the solvents has contributed to the observed effect. There were significant differences in catalytic efficiency and product distribution in different solvents. Phenyl salicylate-ended BPA was a major by-product when tetrahydrofuran (THF) was

used as solvent, but *o*-phenylene carbonate-ended and phenyl acetate-ended BPA were also included in the other solvents. The BPA conversion was highest with the least amount of by-products in THF except cyclohexane system which showed the highest BPA conversion, but mediocre MpC selectivity and phase-separation. THF showed the better activity and selectivity than the methylene chloride. Thus, hereafter THF is the solvent of our choice for the coupled oxidative carbonylation of BPA and phenol over Pd–Ce redox catalysts. Reactivity of THF itself under the catalytic system was not observed from GC–MS analysis of the reaction mixture after reaction. Also it dissolved the reactants and catalytic system completely, to make a homogeneous reaction system.

3.4. Effect of base on the coupled oxidative carbonylation

For the individual oxidative carbonylation of phenol or BPA, a base is essential to produce phenoxy anions which could attack Pd complex as nucleophiles. Frequently-used bases are tertiary amines, pyridines, mineral bases, and quaternary ammonium halides. Quaternary ammonium halides were efficient for this system even with a small amount because they had a sufficient basicity to ionize the phenols and a low nucleophilicity to Pd complex. Also they might play a role of a 'phase transfer catalyst' in the system although this effect has not been fully established [22]. Reactivity of the carbonylation with these

Table 2

The effect of base (halide salt and mineral) on the coupled oxidative carbonylation of BPA and phenol^a

Run	Base	Conversion of BPA (%)	Product distribution (wt.%)						MpC/DH ^b
			MpC(1)	MpC(2)	DH(1)	DH(2)	$n \geq 3$	By-products	
1	TBAB	45.2	22.3	3.1	53.6	6.9	0.9	13.2	0.82
2	TBAC	24.2	18.9	Trace	51.2	Trace	0	29.9	0.74
3	TBAI	46.0	4.4	0	4.0	0	0	91.9	2.20
4	TBPB	36.7	22.6	2.7	58.6	5.6	Trace	10.5	0.77
5	NaOAc·3H ₂ O	36.1	4.1	0	10.0	0	0	85.9	0.82
6	K ₂ CO ₃	25.8	4.2	0	5.7	0	0	90.1	1.47

^a Pd(OAc)₂, 0.06 mmol; Ce(OAc)₃·H₂O, 0.30 mmol; benzoquinone, 1.50 mmol; base, 1.50 mmol; THF, 30 ml; BPA, 30 mmol; phenol, 30 mmol; CO pressure, 5 MPa; O₂ pressure, 0.5 MPa; temperature, 373 K; time, 4 h. TBAB, tetrabutylammonium bromide; TBAC, tetrabutylammonium chloride; TBAI, tetrabutylammonium iodide; TBPB, tetrabutylphosphonium bromide.

^b The molar ratio of total MpC to total DH.

quaternary ammonium halides depended on the kinds of alkyl and halide [22,23].

Table 2 shows the effect of quaternary halide salts as bases on our system of the coupled oxidative carbonylation of BPA and phenol. The bases tested here are ionic compounds with ion-pair. We observed tetrabutylammonium bromide (TBAB) and tetrabutylphosphonium bromide (TBPB) gave the best result in BPA conversion and selectivity for oxidative carbonylation to MpC as well as DH with the least by-products formation in agreement with the oxidative carbonylation of phenol into DPC [36,37]. Tetrabutylammonium chloride (TBAC) showed a comparable selectivity to carbonylated products, but resulted in

higher by-products formation and lower BPA conversions than TBAB and TBPB. However, mineral bases showed poor selectivity for MpC and DH because they produced enormous amounts of by-products consisting of *o,p*-isomers of BPA from isomerization of BPA. It might be attributed to their weaker basicity to activate bisphenol but that is still strong enough to isomerize BPA itself in our reaction conditions.

A base with high basicity and low nucleophilicity is required for facile ionization of phenol to phenoxide ion while itself is not competing with phenoxide ion for nucleophilic attack toward the Pd complex [37]. Because of the presence of a non-bonding electron pair on nitrogen, amines are Lewis bases. Table 3 shows

Table 3

The effect of base (amine compound as Lewis base) on the coupled oxidative carbonylation of BPA and phenol^a

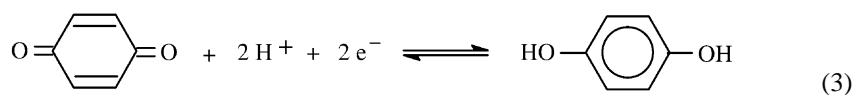
Run	Base	pK _a ^b	Conversion of BPA (%)	Product distribution (wt.%)						MpC/DH ^c
				MpC(1)	MpC(2)	DH(1)	DH(2)	$n \geq 3$	By-products	
1	BEMP	>15	55.0	5.1	0	5.8	Trace	0	89.1	1.75
2	DBU	11.9	2.0	0	0	Trace	0	0	99+	–
3	TBA	10.9	11.9	12.4	0	28.2	Trace	0	59.4	0.88
4	TEA	10.75	21.6	15.2	Trace	39.5	Trace	0	45.3	0.77
5	TMED	9.15	25.7	9.8	0	20.2	Trace	0	70.0	0.97
6	DABCO	8.2	34.7	4.2	0	13.3	0	0	82.5	0.63
7	2,6-Lutidine	6.6	21.0	0	0	Trace	0	0	99+	–
8	Pyridine	5.2	21.2	0	0	Trace	0	0	99+	–

^a Pd(OAc)₂, 0.06 mmol; Ce(OAc)₃·H₂O, 0.30 mmol; benzoquinone, 1.50 mmol; base, 1.50 mmol; THF, 30 ml; BPA, 30 mmol; phenol, 30 mmol; CO pressure, 5 MPa; O₂ pressure, 0.5 MPa; temperature, 373 K; time, 4 h. BEMP, 2-*t*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine; DBU, 1,8-diazabicyclo[5,4,0] undec-7-ene; TBA, tributyl amine; TEA, triethyl amine; TMED, *N,N,N',N'*-tetramethylethylene diamine; DABCO, 1,4-diazabicyclo[2,2,2] octane.

^b The pK_a values were taken from [43].

^c The molar ratio of total MpC to total DH.

some Lewis bases of amine compounds with their basicity. Only the tertiary amines in the range of pK_a 9–11 gave fairly good MpC selectivities. Note that phenols have a pK_a value of ca. 10. The low and extremely high basicity showed poor selectivity to coupled carbonylation products. This could be explained by two factors. One is basicity of an appropriate strength to activate BPA and phenol



simultaneously. The other is a geometric effect such that the bases should not hinder the electrostatic attraction between phenols and bases. Most non-selective bases produced enormous amounts of by-products including *o,p*-isomer of BPA as well as phenyl salicylate-, *o*-phenylene carbonate- and phenyl acetate-ended BPA. The different activity of bases having similar structure could be attributed to the difference in their basic strength, nucleophilicity toward Pd, steric hindrance, and stability under the reaction condition [37].

In our coupled carbonylation of BPA and phenol, TBAB or TBPB are effective to activate phenol and BPA simultaneously in agreement with results obtained in the oxidative carbonylation of phenol alone. The mineral bases and Lewis bases of amine compounds are not effective in the coupled oxidative carbonylation of BPA and phenol in spite of their basic strengths.

3.5. Effect of organic co-catalyst on the coupled oxidative carbonylation

Quinones, which are readily produced by oxidation of dihydroxybenzenes, are easily reduced, forming again the dihydroxy derivatives. For example, the redox reaction between 1,4-benzoquinone (BQ) and 1,4-hydroquinone (HQ) is reversible as follows [44].

The electrical potential of this cell reaction is given by the Nernst equation at 25 °C and depends on acidity of reaction media and molar concentrations of BQ and HQ [44].

A role of quinones in our system is to assist the oxidation of reduced Pd and/or Ce during the catalytic cycle through electron transfer like the reaction (3). Of course Ce acetate is also able to oxidize the Pd, but Ce alone without organic cocatalysts such as benzoquinone is not sufficient to oxidize the reduced Pd fast enough into active Pd species to sustain redox cycle of Pd without deactivation. Table 4 showed the effects of quinones as electron transfer agents to accelerate the redox cycle of Pd–Ce in our reaction condition. We observed that benzoquinone was the best organic cocatalyst with the highest activity and the least formation of by-products. Hydroquinone also showed a good selectivity but a lower BPA conversion than benzoquinone. The quinones having a heterocyclic structure seemed to promote the side reactions

Table 4
The effect of organic co-catalysts on the coupled oxidative carbonylation of BPA and phenol^a

Run	Organic co-catalyst (E° , in V) ^b	Conversion of BPA (%)	Product distribution (wt.%)					By-products	MpC/DH ^c
			MpC(1)	MpC(2)	DH(1)	DH(2)	$n \geq 3$		
1	1,4-Hydroquinone	34.6	22.2	2.3	56.8	5.2	Trace	13.5	0.77
2	1,4-Benzoquinone (0.699)	45.2	22.3	3.1	53.6	6.9	0.9	13.2	0.82
3	1,2-Naphthoquinone (0.56)	51.2	13.2	3.5	35.0	3.4	Trace	44.9	0.80
4	9,10-Anthraquinone (0.13)	44.7	13.4	1.7	40.1	3.5	Trace	41.3	0.67
5	Quinoline	27.3	12.2	Trace	29.4	Trace	0	58.4	0.83

^a Pd(OAc)₂, 0.06 mmol; Ce(OAc)₃·H₂O, 0.30 mmol; organic cocatalyst, 1.50 mmol; TBAB, 1.50 mmol; THF, 30 ml; BPA, 30 mmol; phenol, 30 mmol; CO pressure, 5 MPa; O₂ pressure, 0.5 MPa; temperature, 373 K; time, 4 h.

^b Reduction potential of quinones at 198 K [44].

^c The molar ratio of total MpC to total DH.

although BPA conversions were not significantly different from that with BQ.

Goyal et al. [37] suggested that the organic co-catalyst helped mostly the reoxidation of reduced Cu that was formed during the reoxidation of reduced Pd. They reported that hydroquinone and benzoquinone were best among other quinones due to their strong oxidation potential and less steric hindrance in the oxidative carbonylation of phenol alone. As a mechanism of Pd reoxidation by an organic co-catalyst, Vavasori and Toniolo [36] and Grennberg et al. [45] suggested a direct oxidation of Pd⁰ by combining with benzoquinone as a ligand to form a Pd⁰-benzoquinone complex, which was subject to a redox scheme to form Pd⁺² and hydroquinone.

3.6. Effect of dehydration on the coupled oxidative carbonylation

A dehydrating agent such as molecular sieves could shift the chemical equilibrium of BPA and phenol conversions in the forward reaction by removing water co-produced with the oxidative carbonylation products. We investigated how removal of the water from the reaction mixture would affect our coupled oxidative carbonylation, especially with respect to the selective formation of the desired MpCs. The molecular sieve 3A was activated with a flow of air at 400 °C for 4 h and stored in an oven at 120 °C. We added the molecular sieve into the reactor without exposure to the atmosphere. When up to 4 g of an activated 3A molecular sieve was introduced into the reaction system, the conversions were linearly increased by 20% more for BPA and 10% more for phenol compared to the case without the molecular sieve as shown in Fig. 3A. The mole ratio of total MpC to total DH was also increased from 0.81 to 1.10, indicating the forward shifting of equilibrium by removing water molecules from the reaction system promoted more the formation of MpC than that of DH. However insignificant increases of the reaction rates and a small change of the products distribution was observed with more than 4 g of the dehydrating agent. This might be caused by a kinetic limitation, because the conversion of BPA and the ratio of MpC/DH increased up to 72% and 1.20, respectively, after an extended reaction time of 10 h. The selectivity of MpC(1) remained almost invariant with the molecular sieve loadings, but the

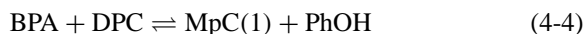
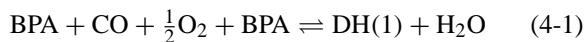
DH(1) selectivity was decreased. The formation of heavier oligomers of $n \geq 2$ was slightly increased. Also, the amount of by-products was reduced significantly from 13 to 7%. The amount of by-products derived from phenol reaction was also reduced or remained invariant compared to the case without the molecular sieves.

From the pattern of products profile in Fig. 3C, it could be observed that the increase in phenol conversion results in increased formation of MpC(1). Removing co-produced H₂O demonstrated the positive effects on our coupled oxidative carbonylation; BPA conversion and selectivity for the desired MpCs increased while selectivities for undesired DHs and by-products decreased.

3.7. Effect of molar ratio of phenol to bisphenol-A

The reactant molar ratio of phenol to BPA (PhOH/BPA) is a critical variable to control the selective formation of MpCs. The effect of PhOH/BPA was investigated in a range of 0.01–2.0 for a fixed amount of BPA (30 mmol) on our coupled oxidative carbonylation with the chosen system of Pd acetate–Ce acetate–benzoquinone–Bu₄NBr–THF. As shown in Fig. 4, conversion of BPA increased for PhOH/BPA values of up to 1.0 and then decreased for higher ratios. The decrease might be caused by competition of phenol with BPA for the fixed amount of catalyst sites in the system. However, note that the value of MpC/DH increased almost linearly up to 1.8 as PhOH/BPA increased. Thus, as more phenol is introduced, formation of MpCs is more favored over the formation of DHs and by-products as shown in Fig. 4B.

In the coupled oxidative carbonylation of BPA and phenol, there are four kinds reactions occurring simultaneously [41].



Reactions (4-1) and (4-2) are the individual oxidative carbonylations of BPA and phenol respectively

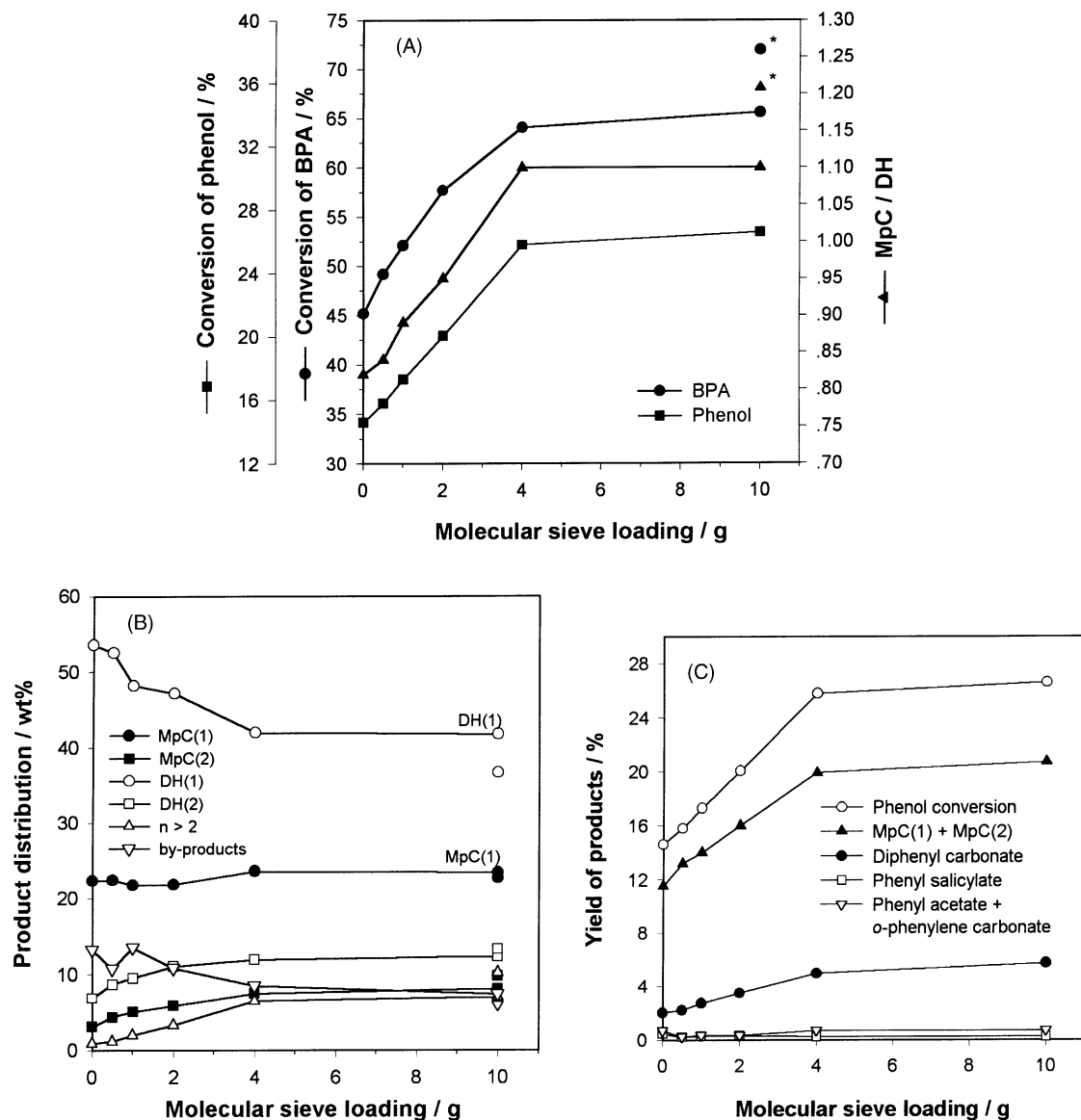


Fig. 3. Dehydration effects on the coupled oxidative carbonylation of BPA and phenol. Pd(OAc)₂, 0.06 mmol; Ce(OAc)₃H₂O, 0.30 mmol; benzoquinone, 1.50 mmol; TBAB, 1.50 mmol; THF, 30 ml; BPA, 30 mmol; phenol, 30 mmol; CO pressure, 5 MPa; O₂ pressure, 0.5 MPa; temperature, 373 K; time, 4 h; 3A molecular sieve used. Point alone denotes after 10 h reaction.

that are well known to occur with Pd redox catalytic systems. However, in our coupled oxidative carbonylation of BPA and phenol, the dual nucleophilic attacks of bisphenoxy and phenoxy ions are probable in a single catalytic cycle of Pd, that leads to the phenoxy-carbonylation of BPA with phenol and CO

as presented in the reaction (4-3). The reaction (4-4) is the transesterification of BPA and DPC produced in situ in the reaction (4-2) and is the main source of MpCs in our reaction system [41]. Increased amounts of phenol would drive the reactions (4-2)–(4-4) in the forward direction although the effect is partly

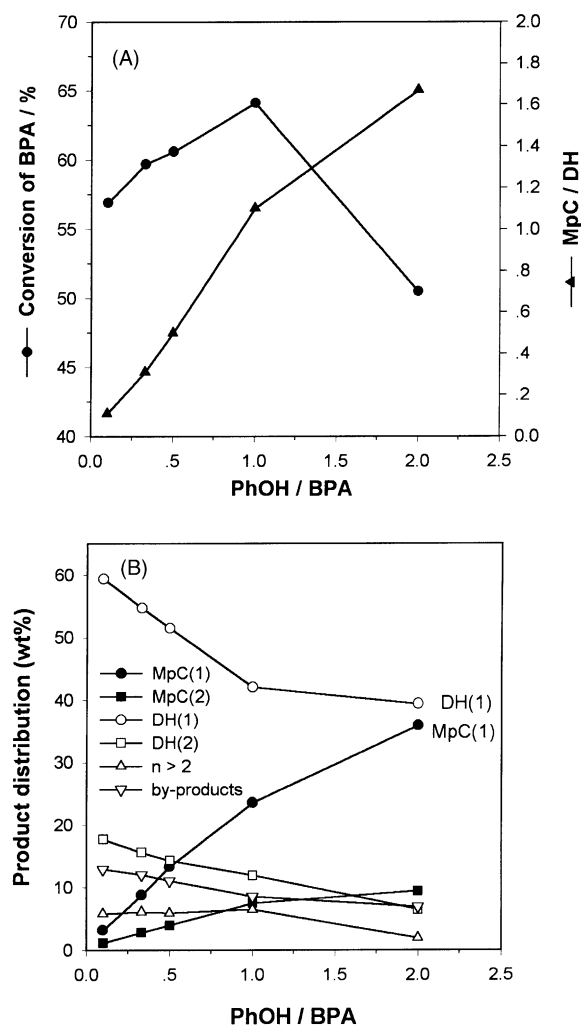


Fig. 4. Effects of the amount of phenol on the coupled oxidative carbonylation of BPA and phenol. Pd(OAc)₂, 0.06 mmol; Ce(OAc)₃·H₂O, 0.30 mmol; benzoquinone, 1.50 mmol; TBAB, 1.50 mmol; THF, 30 ml; BPA, 30 mmol; CO pressure, 5 MPa; O₂ pressure, 0.5 MPa; temperature, 373 K; time, 4 h; 3A molecular sieve, 4 g.

neutralized for reaction (4-4) because its reverse reaction is also promoted by excess phenol.

Oxidative carbonylation of phenol should be more difficult than that of BPA in terms of their equilibrium conversions. Therefore an excess amount of phenol is essential to obtain the desired MpCs selectively with least formation of DHs under our coupled oxidative carbonylation condition. However, in the reaction

stoichiometry, only one mole of phenol would be sufficient for *n* moles of initial BPA, with *n* being repeating unit of MpC type oligomers, if the complete conversion of BPA is achieved.

4. Conclusions

A novel coupled oxidative carbonylation of bisphenol-A and phenol was proposed as a one-step reaction to synthesize the polycarbonate precursors of phenylcarbonate-ended bisphenol-A oligomers. The catalytic activity and selectivity to the desired precursors were significantly affected by reaction variables such as solvent, base, organic cocatalyst under the homogeneous catalytic redox system of palladium acetate and cerium acetate. The most efficient catalytic reaction system consisted of THF as a solvent, TBAB as a base, and benzoquinone as an organic cocatalyst. In our coupled oxidative carbonylation of bisphenol-A and phenol, the phenylcarbonate-ended precursors were synthesized via a transesterification of bisphenol-A and DPC produced in situ from the oxidative carbonylation of phenol. Removal of co-produced water and adjusting the molar feed ratio of phenol to bisphenol-A appeared to be most critical variables to increase the conversion of bisphenol-A as well as to achieve the highly selective formation of the desired polycarbonate precursors.

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