

NOTE

Halogen-Free Solvent for Oxidative Carbonylation of Bisphenol A to Polycarbonate

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ABSTRACT: Halogen-free solvents for oxidative carbonylation of bisphenol A to polycarbonate using carbon monoxide were investigated. Tetrahydrofuran, γ -butyrolacton, and acetophenone, which dissolve both bisphenol A and polycarbonate, gave a polycarbonate yield that was lower than using a halogenated solvent of dichloromethane. On the other hand,

propylene carbonate that has a carbonate bond gave a polycarbonate yield the same as using dichloromethane. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2840–2842, 2007

Key words: polycarbonate; oxidative carbonylation; propylene carbonate; halogen-free solvent

INTRODUCTION

Polycarbonates (PCs) are excellent engineering thermoplastics because of their good impact strength, thermal resistance, and transparency.¹ They can be prepared mainly in two ways by the solution method of bisphenol A (BPA) with phosgene and the melt method of BPA with diphenyl carbonate (DPC).² However, there is a problem with the solution method that uses halogenated solvents, which negatively affect the environment. The melt method includes a melt process that can be an environmentally favorable technology from the point of not using a solvent, but a large amount of heat is needed. Moreover, it includes additional phenol recycling process and DPC reproducing process. Therefore, more environmentally favorable technology for PC synthesis must be developed other than the melt method. Recently, a new PC producing technology, a modified solution method, has been attracting interest to prepare PC directly from carbon monoxide and BPA using Pd complex/redox cocatalyst/onium halide systems.^{3,4} A study reported that, via oxidative carbonylation, the molecular weight of PC obtained with these catalyst systems was high, and the highest number-average molecular weight (M_n) of PC was $M_n = 9400$. However, dichloromethane (MC), a halogenated solvent that negatively affects the environment, was used in it.

This article describes halogen-free solvents for oxidative carbonylation of BPA to PC catalyzed by conventional Pd complexes.

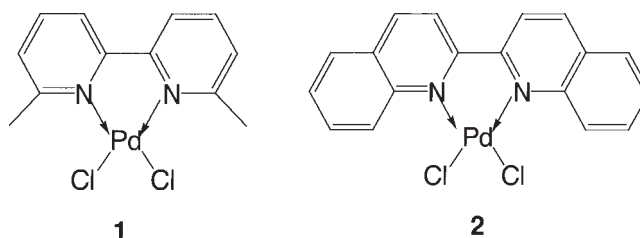
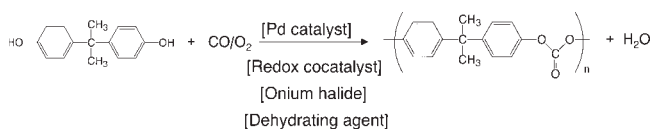
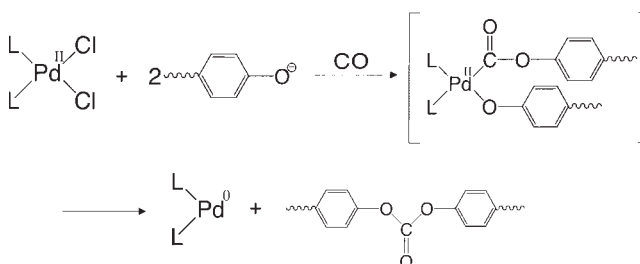


Figure 1 Structures of Pd complexes.



Scheme 1 Oxidative carbonylation of BPA.



Scheme 2 Formation of carbonate bond by Pd catalyst.

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TABLE I
Effect of Solvent for Oxidative Carbonylation of BPA^a

Run	Pd catalyst	Onium halide	Redox catalyst ^b	Solvent ^c	PC yield (%)			
					GPC ^d			
					M_n	M_w	M_w/M_n	
1-1	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	BQ	MC	43	2220	3210	1.45
1-2	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	BQ	THF	20	1010	2720	2.69
1-3	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	BQ	BL	12	2020	2780	1.38
1-4	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	BQ	AP	1	–	–	–
1-5	Pd(OAc) ₂	Ph ₄ NBr	BQ	MC	63	2990	4440	1.48
1-6	Pd(OAc) ₂	Ph ₄ NBr	BQ	THF	6	1610	2010	1.25
1-7	Pd(OAc) ₂	Ph ₄ NBr	BQ	BL	18	1970	2670	1.36
1-8	Pd(OAc) ₂	Ph ₄ NBr	BQ	AP	1	–	–	–
1-9	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ PBr	BQ	MC	40	2190	3030	1.38
1-10	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ PBr	BQ	THF	0	–	–	–
1-11	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ PBr	BQ	BL	23	2080	2680	1.29
1-12	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ PBr	BQ	AP	2	–	–	–
1-13	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	HQ	MC	56	2750	4050	1.47
1-14	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	HQ	THF	1	–	–	–
1-15	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	HQ	BL	15	1950	2430	1.25
1-16	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	HQ	AP	2	–	–	–
1-17	1	(<i>n</i> -Bu) ₄ NBr	BQ	MC	53	3170	4590	1.45
1-18	1	(<i>n</i> -Bu) ₄ NBr	BQ	THF	0	–	–	–
1-19	1	(<i>n</i> -Bu) ₄ NBr	BQ	BL	8	1580	2020	1.28
1-20	1	(<i>n</i> -Bu) ₄ NBr	BQ	AP	3	–	–	–
1-21	2	(<i>n</i> -Bu) ₄ NBr	BQ	MC	54	2600	3870	1.49
1-22	2	(<i>n</i> -Bu) ₄ NBr	BQ	THF	0	–	–	–
1-23	2	(<i>n</i> -Bu) ₄ NBr	BQ	BL	4	970	1650	1.70
1-24	2	(<i>n</i> -Bu) ₄ NBr	BQ	AP	2	–	–	–

^a Reaction conditions: BPA (4.16 mmol), Pd catalyst (0.025 mmol), Ce(OAc)₃·H₂O (0.125 mmol), redox catalyst (0.625 mmol), onium halide (0.625 mmol), molecular sieves 3 Å (1 g), solvent (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, 24 h. The PC produced was isolated by reprecipitation from the each solution by adding excess methanol.

^b BQ, 1,4-benzoquinone; HQ, hydroquinone.

^c MC, dichloromethane; THF, tetrahydrofuran; BL, γ -butyrolactone; AP, acetophenone.

^d Calculated by using calibration curve for polystyrene.

EXPERIMENTS

Materials

Pd complexes **1** and **2** (Fig. 1) were prepared according to previous report.⁵ Molecular sieve 3 Å was dried *in vacuo* at 160°C for 12 h. Carbon monoxide and oxygen gases (99.99%) were used without further purification. All other reagents were used as received.

Polymerization

A typical run was as follows (Run 3-5 in Table III): **1** (9.0 mg, 0.025 mmol), Co(AcO)₂·4H₂O (31.1 mg, 0.125 mmol), benzoquinone (67.6 mg, 0.625 mmol), (*n*-Bu)₄NBr (201.5 mg, 0.625 mmol), molecular sieve 3 Å (1 g), bisphenol A (BPA) (950 mg, 4.16 mmol), and propylene carbonate (10 mL) were charged to a 30 mL SUS-316 autoclave followed by charging with CO (6.0 MPa) and O₂ (0.3 MPa). The auto-

TABLE II
Effect of Solvent for Oxidative Carbonylation of BPA^a

Run	Solvent	PC yield (%)	GPC ^b		
			M_n	M_w	M_w/M_n
2-1	Dimethyl carbonate	0	–	–	–
2-2	Diethyl carbonate	0	–	–	–
2-3	Diphenyl carbonate	0	–	–	–
2-4	Ethylene carbonate	3	–	–	–
2-5	Propylene carbonate	44	2630	3590	1.37
2-6	Dichloromethane	43	2220	3210	1.45

^a Reaction conditions: BPA (4.16 mmol), Pd(OAc)₂ (0.025 mmol), Ce(OAc)₃·H₂O (0.125 mmol), 1,4-benzoquinone (0.625 mmol), (*n*-Bu)₄NBr (0.625 mmol), molecular sieves 3 Å (1 g), solvent (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by adding excess methanol.

^b Calculated by using calibration curve for polystyrene.

TABLE III
Comparison Between ProC and MC for Oxidative Carbonylation of BPA^a

Run	Pd catalyst	Onium halide	Solvent ^b	PC yield (%)	GPC ^c		
					M_n	M_w	M_w/M_n
3-1	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	ProC	44	2630	3590	1.37
3-2	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ NBr	MC	43	2220	3210	1.45
3-3	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ PBr	ProC	42	2590	3600	1.39
3-4	Pd(OAc) ₂	(<i>n</i> -Bu) ₄ PBr	MC	40	2190	3030	1.38
3-5	1	(<i>n</i> -Bu) ₄ NBr	ProC	55	2760	4040	1.46
3-6	1	(<i>n</i> -Bu) ₄ NBr	MC	53	3170	4590	1.45
3-7	2	(<i>n</i> -Bu) ₄ NBr	ProC	55	2530	4230	1.67
3-8	2	(<i>n</i> -Bu) ₄ NBr	MC	54	2600	3870	1.49

^a Reaction conditions: BPA (4.16 mmol), Pd catalyst (0.025 mmol), Ce(OAc)₃·H₂O (0.125 mmol), 1,4-benzoquinone (0.625 mmol). The PC produced was isolated by reprecipitation from the each solution by adding excess methanol.

^b ProC, propylene carbonate; MC, dichloromethane.

^c Calculated by using calibration curve for polystyrene.

clave was placed in an oil bath and kept at 100°C. After 24 h, the reaction was quenched by cooling the autoclave in a water bath and by gas purging. After filtering the reaction mixture, the product was isolated by reprecipitation from the reaction mixture by adding excess methanol (200 mL) to give a polycarbonate yield of 55% (581 mg).

Measurement

The molecular weight and molecular weight distribution of polycarbonate (PCs) were determined using a JASCO Gulliver GPC system equipped with a SHODEX K-804L column, using polystyrene as standard and chloroform as an eluent.

RESULTS AND DISCUSSION

The catalyst system consists of a Pd catalyst, inorganic and organic redox cocatalysts, onium salts, and a dehydrating agent (Scheme 1). The formation of a carbonate bond by the Pd catalyst is shown in Scheme 2. The redox cocatalysts are necessary in the reduction of Pd^{II} to Pd⁰ when the carbonate bond is formed. It is considered that the working of onium salt is by activation of phenols.

Tetrahydrofuran (THF), γ -butyrolacton (BL), or acetophenone (AP) were used as solvents that dissolved both BPA and polycarbonate. The results are summarized in Table I. Several types of Pd complexes, onium salts, and organo-redox catalysts were examined. However, a reaction condition that gave a polycarbonate yield and molecular weight same as using dichloromethane (MC) could not be found. These solvents have the oxygen that has unshared electron pairs, so there is a possibility that the oxygen forms a coordination bond with Pd. Consequently, it is considered that the approach of BPA

to Pd is obstructed, thus the reaction does not progress easily.

Because of using MC as the solvent, a reaction to form the carbonate bond progresses, and the oxidative carbonylation reaction is not obstructed by the carbonate compound although the carbonate bond has unshared electron pairs. Solvents that have a carbonate bond were examined. The results are summarized in Table II. When dimethyl carbonate, diethyl carbonate, or diphenyl carbonate was used, PCs were not obtained at all. However, when using propylene carbonate (ProC), PC was obtained with a yield same as using MC. ProC is a peculiar solvent for the oxidative carbonylation reaction. When several different catalyst systems were used with ProC, each of them gave a PC yield the same as using MC (Table III).

CONCLUSIONS

With propylene carbonate as a halogen-free solvent, oxidative carbonylation of BPA to polycarbonate using carbon monoxide was advanced. More detailed optimization studies are in progress to improve the activity of the oxidative carbonylation catalysts using propylene carbonate.

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