

Homogeneous Palladium Catalyst for the Oxidative Carbonylation of Bisphenol A to Polycarbonate in Propylene Carbonate

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ABSTRACT: Polycarbonates (PCs) were prepared in a propylene carbonate solvent by the oxidative carbonylation of bisphenol A with Pd/bithienyl complexes, Pd/bipyridyl complexes, and Pd—C σ -bonded complexes for comparison as homogeneous Pd catalysts. With the Pd/bipyridyl complexes, the 6,6'-disubstituted 2,2'-bipyridyl ligand showed a stronger substituent effect than the 2,2'-bipyridyl ligand, which lacked substituents at the 6,6' positions. With the Pd/bithienyl complexes, however, the substituent effect was not seen. The Pd/bithienyl complexes, which lacked substituents at the 5,5' positions, gave a PC yield

that was the same as the yield of those that had substituents at the 5,5' positions. The combination of the Pd—C σ -bonded complexes and an inorganoredox cocatalyst showed a PC polymerization behavior that was different from the other two types of complexes. When Co(OAc)₂·4H₂O was used as the inorganoredox cocatalyst, all of the Pd—C σ -bonded complexes gave a good PC yield. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 758–762, 2008

Key words: catalysts; polycarbonates; polycondensation

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. One is by the solvent method of bisphenol A (BPA) with phosgene and the other is by the melt method of BPA with diphenyl carbonate.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 thermal energy is needed. Moreover, it includes additional phenol recycling and a diphenyl carbonate reproducing processes. Therefore, a more environmentally favorable technology for PC synthesis must be developed to replace the melt process. Recently, a new PC-producing technology, a modified solution method, has been attracting interest for the preparation of PCs directly from carbon monoxide and BPA with

Pd compound/redox catalyst/onium halide systems.^{3,4} A study reported that via oxidative carbonylation, the molecular weight of PCs obtained with these catalyst systems was high, and the highest number-average molecular weight (M_n) of the PCs was $M_n = 9400$. However, dichloromethane, a halogenated solvent that negatively affects the environment, was used.

In a previous article, we reported that propylene carbonate was a peculiar solvent for the oxidative carbonylation reaction.⁵ This article describes oxidative carbonylation of BPA to PC catalyzed by a homogeneous Pd compound. As homogeneous Pd compounds, Pd/bithienyl complexes, Pd/bipyridyl complexes, or Pd—C σ -bonded complexes were used. As a halogen-free solvent, propylene carbonate was used.

EXPERIMENTAL

Materials

Pd complexes 2–13 were prepared according to previous reports.^{6–10} The structures of the complexes are shown later in Figures 1 and 2. Synthetic zeolite (A-3 powder through 75 μ m) was dried *in vacuo* at 160°C for 12 h. Carbon monoxide and oxygen gas (99.99%) were used without further purification. All other reagents were used as received.

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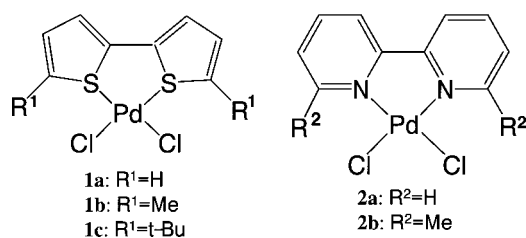


Figure 1 Structures of the Pd complexes.

Preparation of the Pd/bithienyl complex

Pd-2,2'-bithienyl complexes (**1**) were mainly synthesized by the mixture of the reagents having the corresponding bithienyl ligands¹¹ and PdCl₂(PhCN)₂ in CHCl₃ at room temperature.

Polymerization

A typical run was as follows (Run 1–7 is shown in Table I). **1b** (9.3 mg, 0.025 mmol), Co(OAc)₂·4H₂O (31.1 mg, 0.125 mmol), 1,4-benzoquinone (67.6 mg, 0.625 mmol), (*n*-Bu)₄NBr (201.5 mg, 0.625 mmol), synthetic zeolite (1 g), BPA (950 mg, 4.16 mmol), and propylene carbonate (10 mL) were charged to a 30 mL of SUS-316 autoclave followed by charging with CO (6.0 MPa) and O₂ (0.3 MPa). The autoclave was placed in an oil bath and kept at 100°C. After 24 h, the reaction was quenched by cooling of the autoclave in a water bath and by gas purging. After the reaction mixture was filtered, the product was isolated by reprecipitation from the reaction mixture

by the addition of excess methanol (200 mL) to give a PC yield of 70% (744 mg).

Measurement

The molecular weight and molecular weight distribution of the PCs were determined with a JASCO Gulliver gel permeation chromatograph (Hachioji, Tokyo, Japan) equipped with a SHODEX K-804L column (Minatoku, Tokyo, Japan), with polystyrene standards and chloroform as the eluent. IR spectroscopic analyses were carried out on a PerkinElmer Paragon-100 IR spectrometer (Yokohama, Kanagawa, Japan). ¹H-NMR and ¹³C-NMR spectra were obtained on a JEOL LA600 spectrometer (Showajima, Tokyo, Japan) with CDCl₃ as a solvent.

RESULTS AND DISCUSSION

The catalyst system consisted of a Pd catalyst, inorganic and organic redox cocatalysts, onium salt, and a dehydrating agent (Scheme 1). The formation of a carbonate bond by the Pd catalyst is shown in Schemes 2 and 3 with the Pd/bipyridyl or Pd/bithienyl complex and the Pd–C σ-bonded complex, respectively.¹² The redox cocatalysts were necessary to form Pd^{II} again by the oxidation of Pd⁰, which formed by the reductive elimination of the carbonate structure. The role of onium salt was to activate phenols to form palladium phenolates.

Pd/bithienyl catalyst

According to a previous article,⁶ Pd catalysts that have a nitrogen bidentate ligands such as bipyridyl,

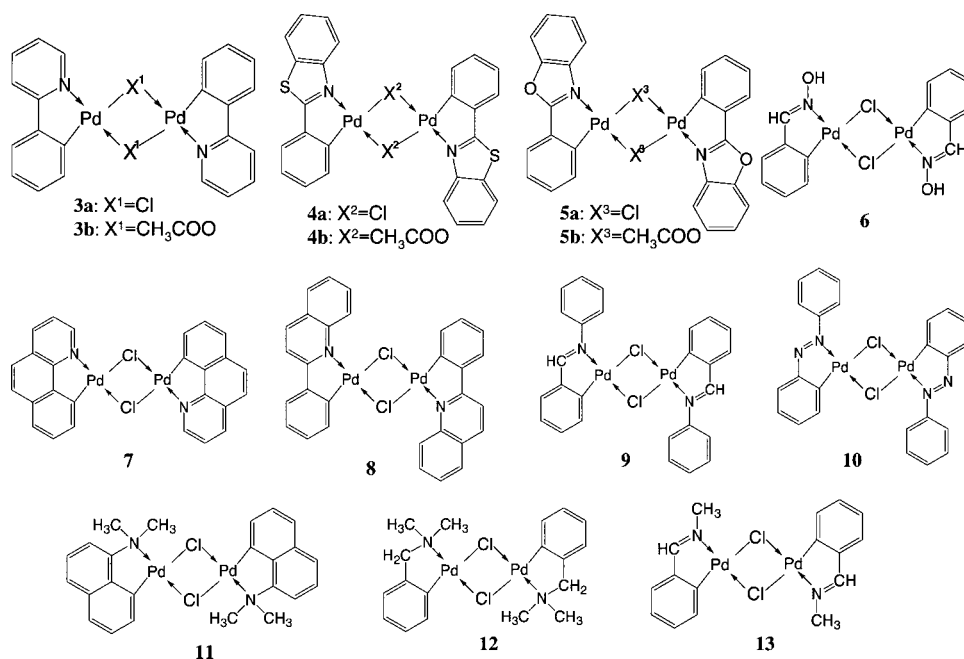


Figure 2 Structures of the Pd–C σ-bonded complexes.

TABLE I
Oxidative Carbonylation of BPA-Catalyzed Pd/Bithienyl Complexes

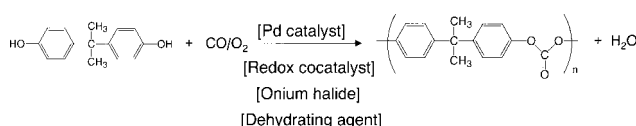
Run	Pd complex	Redox catalyst	PC yield (%)	GPC ^a		
				M_n	M_w	M_w/M_n
1-1	1a	Ce(OAc) ₃ ·H ₂ O	27	1790	2530	1.41
1-2	1a	Mn(OAc) ₂ ·4H ₂ O	39	1930	3110	1.61
1-3	1a	Co(OAc) ₂ ·4H ₂ O	66	3010	4960	1.65
1-4	1a	Mn(TMHD) ₃	43	2340	4200	1.79
1-5	1b	Ce(OAc) ₃ ·H ₂ O	26	1880	2600	1.38
1-6	1b	Mn(OAc) ₂ ·4H ₂ O	57	2190	3600	1.64
1-7	1b	Co(OAc) ₂ ·4H ₂ O	70	2710	4750	1.75
1-8	1b	Mn(TMHD) ₃	65	2650	5220	1.97
1-9	1c	Ce(OAc) ₃ ·H ₂ O	36	1940	2910	1.50
1-10	1c	Mn(OAc) ₂ ·4H ₂ O	59	2280	3770	1.65
1-11	1c	Co(OAc) ₂ ·4H ₂ O	63	2840	4650	1.64
1-12	1c	Mn(TMHD) ₃	30	2150	3670	1.71

GPC = gel permeation chromatography; M_w = weight-average molecular weight; TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate. The reaction conditions were as follows: BPA (4.16 mmol), Pd complex (0.025 mmol), redox catalyst (0.125 mmol), 1,4-benzoquinone (0.625 mmol), (*n*-Bu)₄NBr (0.625 mmol), synthetic zeolite (1 g), propylene carbonate (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol.

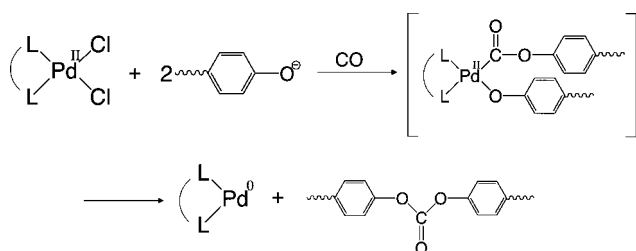
^a Calculated with a calibration curve for polystyrene.

biquinoline, and phenanthroline are effective in the oxidative carbonylation of BPA to PC, so a Pd catalyst that had the sulfur bidentate ligand, 2,2'-bithienyl (Fig. 1), was used. The results are summarized in Table I. For comparison, Pd/bipyridyl catalysts were used as well (Table II). An earlier article⁴ stated that when Pd/bipyridyl complexes as catalysts and dichloromethane as a solvent are used, the 6,6'-disubstituted 2,2'-bipyridyl ligand is more effective than the 2,2'-bipyridyl ligand, which lacks the substituents at the 6,6' positions. In our study, the Pd/bipyridyl complexes that had methyl groups at the 6,6' positions gave good PC yields when propyl-

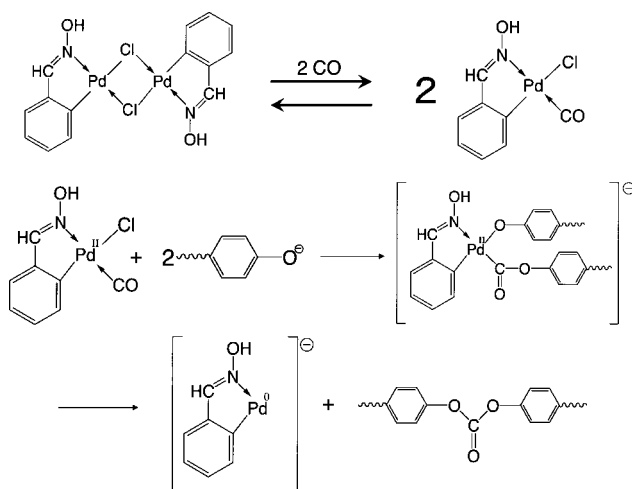
ene carbonate was used as a solvent (Table II). On the other hand, with the Pd/bithienyl complexes, the substituent effect was not found. The Pd/bithienyl complexes, which lacked the substituents at the 5,5' positions, gave a PC yield the same as the yield of those that had the substituents at the 5,5' positions. In the Pd/bipyridyl complex, nitrogen formed a coordinate bond with palladium with a 2sp² hybrid orbital. On the other hand, in the Pd/bithienyl complex, sulfur had a coordinate bond with palladium with a 3sp² hybrid orbital. So the bond length of S—Pd was longer than that of N—Pd. Because, in the Pd/bithienyl complex, the



Scheme 1 Oxidative carbonylation of BPA.



Scheme 2 Formation of a carbonate bond by a Pd/bipyridyl or Pd/bithienyl complex.



Scheme 3 Formation of a carbonate bond by a Pd—C σ -bonded complex.

TABLE II
Oxidative Carbonylation of BPA-Catalyzed Pd/Bipyridyl Complexes

Run	Pd complex	Redox catalyst	PC yield (%)	GPC ^a		
				M_n	M_w	M_w/M_n
2-1	2a	Ce(OAc) ₃ ·H ₂ O	20	—	—	—
2-2	2a	Mn(TMHD) ₃	14	—	—	—
2-3	2b	Ce(OAc) ₃ ·H ₂ O	86	4110	7500	1.82
2-4	2b	Mn(OAc) ₂ ·4H ₂ O	49	2050	3170	1.55
2-5	2b	Co(OAc) ₂ ·4H ₂ O	55	1910	5230	2.74
2-6	2b	Mn(TMHD) ₃	83	2480	5880	2.37

GPC = gel permeation chromatography; M_w = weight-average molecular weight; TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate. The reaction conditions were as follows: BPA (4.16 mmol), Pd complex (0.025 mmol), redox catalyst (0.125 mmol), 1,4-benzoquinone (0.625 mmol), (*n*-Bu)4NBr (0.625 mmol), synthetic zeolite (1 g), propylene carbonate (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol.

^a Calculated with a calibration curve for polystyrene.

TABLE III
Oxidative Carbonylation of BPA-Catalyzed Pd—C σ -Bonded Complexes

Run	Pd complex	Redox catalyst	PC yield (%)	GPC ^a		
				M_n	M_w	M_w/M_n
3-1	3a	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-2	3a	Mn(OAc) ₂ ·4H ₂ O	70	3040	5860	1.93
3-3	3a	Co(OAc) ₂ ·4H ₂ O	61	2680	5150	1.92
3-4	3a	Mn(TMHD) ₃	3	—	—	—
3-5	4a	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-6	4a	Mn(OAc) ₂ ·4H ₂ O	0	—	—	—
3-7	4a	Co(OAc) ₂ ·4H ₂ O	63	2300	3950	1.72
3-8	4a	Mn(TMHD) ₃	61	2300	5200	2.26
3-9	5a	Ce(OAc) ₃ ·H ₂ O	5	—	—	—
3-10	5a	Mn(OAc) ₂ ·4H ₂ O	67	2910	5330	1.83
3-11	5a	Co(OAc) ₂ ·4H ₂ O	48	2300	3200	1.39
3-12	5a	Mn(TMHD) ₃	48	2800	5330	1.90
3-13	6	Ce(OAc) ₃ ·H ₂ O	56	2230	3630	1.63
3-14	6	Mn(OAc) ₂ ·4H ₂ O	53	1970	3100	1.57
3-15	6	Co(OAc) ₂ ·4H ₂ O	73	2330	3860	1.66
3-16	6	Mn(TMHD) ₃	58	2100	4040	1.92
3-17	7	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-18	7	Co(OAc) ₂ ·4H ₂ O	55	3040	5530	1.82
3-19	8	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-20	8	Co(OAc) ₂ ·4H ₂ O	60	3170	6330	2.00
3-21	9	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-22	9	Co(OAc) ₂ ·4H ₂ O	62	3240	6030	1.86
3-23	10	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-24	10	Co(OAc) ₂ ·4H ₂ O	59	3060	5330	1.74
3-25	11	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-26	11	Co(OAc) ₂ ·4H ₂ O	46	2580	3750	1.45
3-27	12	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-28	12	Co(OAc) ₂ ·4H ₂ O	65	3040	5410	1.78
3-29	13	Ce(OAc) ₃ ·H ₂ O	0	—	—	—
3-30	13	Co(OAc) ₂ ·4H ₂ O	61	3050	5360	1.76
3-31	3b	Ce(OAc) ₃ ·H ₂ O	74	3060	4950	1.62
3-32	3b	Mn(OAc) ₂ ·4H ₂ O	0	—	—	—
3-33	3b	Co(OAc) ₂ ·4H ₂ O	62	2900	4930	1.70
3-34	3b	Mn(TMHD) ₃	20	2780	5030	1.81
3-35	4b	Ce(OAc) ₃ ·H ₂ O	79	2550	4330	1.70
3-36	4b	Mn(OAc) ₂ ·4H ₂ O	67	2190	4210	1.92
3-37	4b	Co(OAc) ₂ ·4H ₂ O	31	1640	2180	1.33
3-38	4b	Mn(TMHD) ₃	52	2380	5030	2.11
3-39	5b	Ce(OAc) ₃ ·H ₂ O	77	3440	6140	1.78
3-40	5b	Mn(OAc) ₂ ·4H ₂ O	65	2740	5040	1.84
3-41	5b	Co(OAc) ₂ ·4H ₂ O	58	2760	4460	1.62
3-42	5b	Mn(TMHD) ₃	0	—	—	—

GPC = gel permeation chromatography; M_w = weight-average molecular weight; TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate. The reaction conditions were as follows: BPA (4.16 mmol), Pd complex (0.0125 mmol), redox catalyst (0.125 mmol), 1,4-benzoquinone (0.625 mmol), (*n*-Bu)4NBr (0.625 mmol), synthetic zeolite (1 g), propylene carbonate (10 mL), CO (6.0 MPa), O₂ (0.3 MPa), 100°C, and 24 h. The PC produced was isolated by reprecipitation from the propylene carbonate solution by the addition of excess methanol.

^a Calculated with a calibration curve for polystyrene.

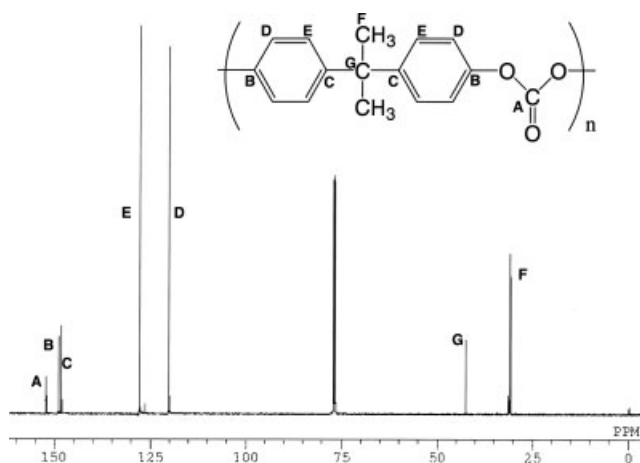


Figure 3 ^{13}C -NMR spectrum of the polymer (Run 1–7 in Table I).

distance between Pd as the active site and the 5,5' positions of the ligand was very long, the substituent effect was not generated. The Pd/bithienyl complex gave a good PC yield when $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was used in propylene carbonate.

Pd—C σ -bonded complex

The Pd—C σ -bonded complex forms carbonyl complexes under carbon monoxide (Scheme 3),¹² so it has the possibility of improving its activity. Several Pd—C σ -bonded complexes were investigated (Fig. 2). The results are summarized in Table III. The combination of the Pd—C σ -bonded complexes and the inorganoredox cocatalyst showed a PC polymerization behavior that was different from two other types of complexes. For example, when $\text{Ce}(\text{OAc})_3 \cdot \text{H}_2\text{O}$ was used as the inorganoredox cocatalyst, the Pd—C σ -bonded complexes bridged by chlorine had little activity except for **6**, but those bridged by acetate gave high PC formation (yield = 74–79%). When a manganese compound was used as the inorganoredox cocatalyst, some of the Pd—C σ -bonded complexes had activity, but many of them did not. On the other hand, when $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was used as the inorganoredox cocatalyst, all of the Pd—C σ -bonded complexes

gave a good PC yield. This result is the same as that when Pd/bithienyl catalysts were used.

Polymer characterization

The structures of the PCs were characterized by IR, ^1H -NMR, and ^{13}C -NMR spectroscopies. The IR spectra of the PCs indicated characteristic carbonate bonds at 1770 and 1230–1260 cm^{-1} . The ^1H -NMR spectra of the PCs indicated characteristic methyl protons at 1.7 ppm and aromatic protons at 7.0–7.3 ppm. The ^{13}C -NMR spectrum and the structure of the PC (Run 1–7 in Table I) are shown in Figure 3.

CONCLUSIONS

PCs were prepared in a propylene carbonate solvent by the oxidative carbonylation of BPA with Pd/bithienyl complexes and Pd—C σ -bonded complexes for comparison as homogeneous Pd catalysts. With the Pd/bithienyl complexes, the substituent effect was not seen. The Pd/bithienyl complexes, which lacked the substituents at the 5,5' positions, gave a PC yield that was the same as the yield of those that had the substituents at the 5,5' positions. When $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was used as the inorganoredox cocatalyst, all of the Pd complexes gave a good PC yield.

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