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Direct Synthesis of Polycarbonate from Carbon Monoxide and Bisphenol A Catalyzed by Pd−Carbene Complex

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Aromatic polycarbonates (PCs) are one of the most useful engineering plastics because of their good heat resistance, mechanical properties, and transparency.[1] PCs are mainly prepared by the interfacial polycondensation of bisphenol A with phosgene. In recent years, there has been increasing demand for a safer and more environmentally benign process for PC synthesis. The transesterification process has the advantages of involving no solvent and no salt formation. In this process, the carbonyl carbon source is diphenyl carbonate (DPC), prepared by the reaction between phosgene and sodium phenolate or the transesterification of dimethyl carbonate with phenol.[2] The latter process, however, is thermodynamically unfavorable. Therefore, the direct preparation of PC from carbon monoxide (CO) and bisphenol A using a catalyst would appear to have considerable potential.[3] Previous reports have shown that oxidative carbonylation is possible using a $PdCl_2$ catalyst; however, the resulting PC had very low molecular weight (number-averaged molecular weight $M_n = 2800$).[3b] We have recently developed an effective catalytic system for the direct synthesis of aromatic carbonates.[4] A modest molecular weight PC ($M_n = 5600$) was successfully obtained using a palladium complex with 6,6′-disubstituted-2,2′-bipyridyl ligands.[5] Its molecular weight is still not high enough, though, for application as an engineering plastic.

Heterocyclic carbene ligands have been shown to be useful alternatives to the widely used phosphine ligands in transition metal complex-catalyzed homogeneous reactions, such as olefin metathesis,[6] the Heck reaction,[7] Suzuki coupling,[8] and copolymerizations of carbon monoxide with ethylene.[9] Stable carbene ligands can also be expected to prolong the life of catalysts, since strong coordination bonds between transition metals and heterocyclic carbene ligands prevent complexes from dissociating. This provided the impetus for our study of the utility of Pd−carbene complexes as catalysts for the oxidative carbonylation of phenol.

In a preceding paper, we reported that the Pd−carbene complexes activity was twice as high as the corresponding $PdBr_2$ catalyst that did not feature the use of ligands.[10] This finding prompted us to apply this catalyst system to the direct synthesis of PC from bisphenol A and CO. Here we report the successful direct synthesis of PC at high yield (∼80%) with close to industrially useful molecular weight ($M_n = 9400$) via oxidative carbonylation of bisphenol A using the Pd−carbene complex (Scheme 1).

Polymerization of bisphenol A with CO in the presence of the catalyst system was carried out under optimum conditions for the synthesis of DPC.[10] The catalyst system consists of the Pd−carbene complex, {1,1′-disubstituted-3,3′-methylenediimidazolin-2,2′-diylidene}palladium(II) dibromide, $PdBr_2$(c1-R) (R = Me, Et, ^{t}Bu) in Scheme 1, an inorganic redox cocatalyst (a cerium or manganese complex), an organic redox cocatalyst (hydroquinone), an organic onium salt (tributylphosphonium bromide), and a dehydrating agent (3A molecular sieves). The results are summarized in Table 1.

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Scheme 1. Oxidative Carbonylation of Bisphenol A

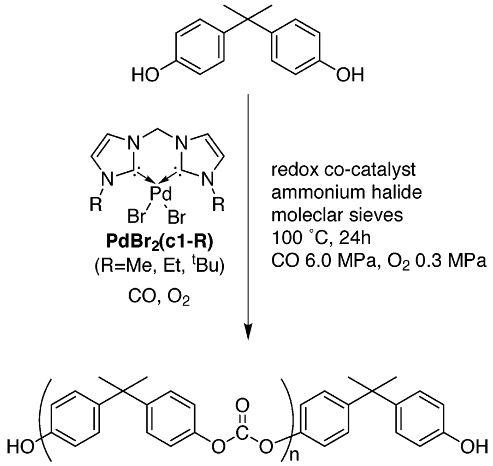

Table 1. Oxidative Carbonylation of Bisphenol A Catalyzed with Pd−Carbene Complex[a]

entry	Pd complex	inorganic redox catalyst	$10^{-3}M_w$[b]	$10^{-3}M_n$[b]	yield,[c] %
1	PdBr$_2$(c1-Me)	Ce(TMHD)$_4$	9.7	5.4	21
2	PdBr$_2$(c1-Me)	Mn(OAc)$_2$4H$_2$O	5.4	3.8	25
3	PdBr$_2$(c1-Et)	Ce(TMHD)$_4$	8.7	5.1	28
4	PdBr$_2$(c1-Et)	Mn(OAc)$_2$4H$_2$O	8.1	4.7	18
5	PdBr$_2$(c1-^{t}Bu)	Ce(TMHD)$_4$	24.0	9.4	80
6	PdBr$_2$(c1-^{t}Bu)	Mn(OAc)$_2$4H$_2$O	14.4	7.2	77

[a] Reaction conditions: bisphenol A, 2.08 mmol; PdBr$_2$(c1-R), 0.0125 mmol; inorganic redox cocatalyst, 0.075 mmol; ^{n}Bu$_4$PBr, 0.375 mmol; hydroquinone, 0.375 mmol; CH$_2$Cl$_2$, 5 mL; 3A molecular sieves, 1 g; CO, 6.0 MPa; O$_2$, 0.3 MPa; 100 °C, 24 h. [b] Molecular weight (g/mol) determined by GPC using polystyrene standards. [c] Precipitated from methanol. TMHD = 2,2,6,6-tetramethyl-3,5-heptanedionate.

PdBr$_2$(c1-Me) and PdBr$_2$(c1-Et) both having short alkyl substituents on the ligand gave low-molecular-weight PCs at low yields, plus a substance insoluble in methylene chloride. This can be explained by a cross-linking reaction due to the formation of a salicylate structure in PC.[5] The molecular weights and yields of PCs increased with increasing bulkiness of the substituents in the 1,1′-position of the carbene complex. By using PdBr$_2$(c1-^{t}Bu), the M_n and weight-average molecular weight M_w of PC reached 9400 and 24 000, respectively, estimated by GPC on a polystyrene standard. In the same evaluation method, commercially available PC (Idemitsu Petrochemical, TARFLON A1500) showed that M_n and M_w are 14 400 and 31 200. The molecular weight obtained from entry 5 in Table 1 is the highest reported for the direct synthesis of PC via oxidative carbonylation of bisphenol A and is almost comparable to that of commercially available PCs which is required that M_n is greater than 10 000. Furthermore, no insoluble polymers were formed. This result indicates the minimal formation of the undesirable salicylate structure formed by cross-linking. To identify the soluble part in methanol, liquid chromatographic analysis of the filtrate was carried out, and the bisphenol A and the low-molecular-weight oligomers (dimer to pentamer) were detected in the filtrate. On the other hand, the cyclic PC was not detected. These low-molecular-weight oligomers remained soluble in methanol, thereby decreasing the isolated polymer yield.

The steric hindrance of substituents R at the 1,1′-position of PdBr$_2$(c1-R) greatly influences the activity and selectivity of the catalyst: that is, the bulky substituents of ligands may accelerate the reductive elimination rate by steric repulsion on the crowded palladium center of the intermediates[4d,10] and also prevent the formation of salicylate structures by the rearrangement of carbonate moieties.

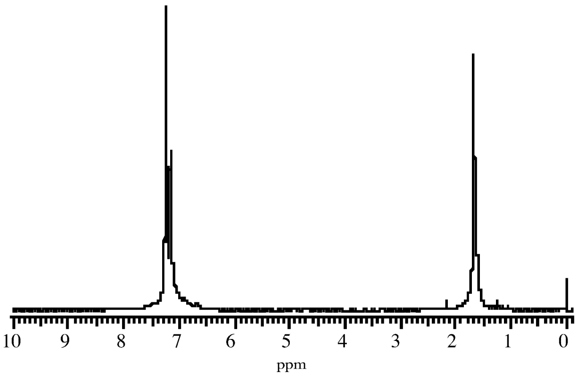

Figure 1. 600 MHz ^{1}H NMR spectrum of the polymer obtained by reaction of bisphenol A with CO in CDCl$_3$.

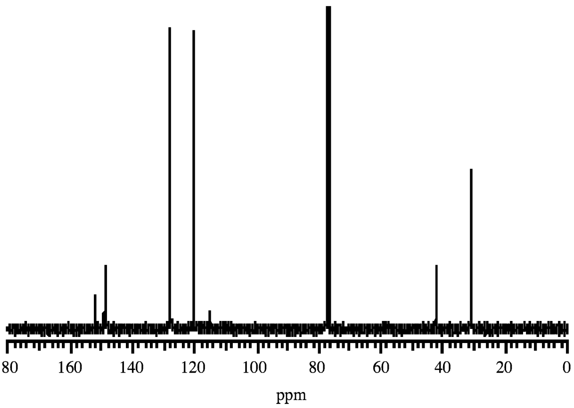

Figure 2. 600 MHz ^{13}C NMR spectrum of the polymer obtained by reaction of bisphenol A with CO in CDCl$_3$.

The structure of PCs obtained was confirmed by IR, ^{1}H NMR, and ^{13}C NMR analyses. The IR spectrum of PC (entry 5) exhibited strong absorption at 1776 cm^{-1} due to the carbonyl stretching of carbonate groups, with no peaks at 1770 or 1836 cm^{-1} assigned to the salicylate cross-linking structure or the *o*-phenylene carbonate terminal,[3b] respectively. A peak due to the polymer terminal OH stretching absorption was observed at 3476 cm^{-1}. Figure 1 shows the ^{1}H NMR spectrum of PC (entry 5). A singlet at 1.67 ppm due to methyl protons and a multiplet in the range 7.0−7.3 ppm due to aromatic protons can be seen. The terminal aromatic protons located in the ortho position of the terminal hydroxyl group are found at 6.69 ppm. In the ^{13}C NMR spectrum of PC (Figure 2) (entry 5), the characteristic signal of carbon nuclei in carbonate bonds appears at 152.1 ppm. The signals of the carbon nuclei of substituted phenyl groups are observed at 149.0 and 148.3 ppm, and those of unsubstituted phenyl groups in the ortho position of the carbonate or isopropylidene structure are found at 127.9 and 120.3 ppm, respectively. A peak due to the terminal unsubstituted aromatic carbon atoms ortho to the terminal hydroxyl group appears at 114.8 ppm. Peaks at 42.5 and 30.9 ppm can be assigned to quaternary and methyl carbon atoms, respectively. These findings clearly indicate the formation of the desired PC.

In summary, we have developed a direct oxidative carbonylation procedure of bisphenol A to PC catalyzed with an efficient Pd complex system. $PdBr_2(c1\text{-}^tBu)$ produced the highest molecular weight ($M_n = 9600$, $M_w = 24\,000$) and yield (80%). This method will open up the potential for direct synthesis of PCs from bisphenols and CO. More detailed optimization studies are in progress to further improve molecular weights.

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(11) A typical procedure was as follows. $PdBr_2(c1\text{-}^tBu)$ (6.6 mg, 0.0125 mmol), $Ce(TMHD)_4$ (65.5 mg, 0.075 mmol), hydroquinone (41.3 mg, 0.375 mmol), tetrabutylphosphonium bromide (63.8 mg, 0.188 mmol), and activated 3A molecular sieves (1 g) were charged in a 50 mL stainless steel autoclave and dried at 70 °C for 2 h under vacuum before reaction. After drying, bisphenol A (0.47 g, 2.08 mmol) and dichloromethane (5 mL) were added, followed by charging 6.0 MPa of CO and 0.3 MPa of O_2. The reactor was heated at 100 °C for 24 h, after which the reaction was quenched by cooling the autoclave in a water bath and by degassing. After filtering the reaction mixture, the product was isolated by precipitation from the condensed reaction mixture (5 mL) by adding excess methanol to give light brown PC at 80% yield (0.41 g).

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