ELSEVIER

Polymer 41 (2000) 2289–2293

polymer

Polymer Communication

# Pd catalyzed polycarbonate synthesis from bisphenol A and CO: control of polymer chain—end structure

M. Goyal[a,b,c], R. Nagahata[a,b], J. Sugiyama[a,b], M. Asai[a,b], M. Ueda[a,b,d], K. Takeuchi[a,b,*]

[a]*Joint Research Centre for Precision Polymerization-Tsukuba, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*
[b]*National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*
[c]*New Energy and Industrial Technology Development Organization, Sunshine 60, 3-1-1 Higashi-Ikebukuro, Toshima-Ku, Tokyo 170-6028, Japan*
[d]*Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

Received 2 June 1999; received in revised form 16 July 1999; accepted 2 August 1999

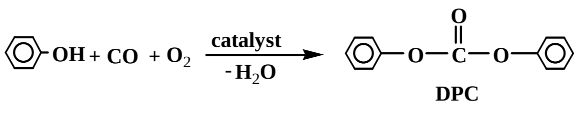
## Abstract

Direct polymerization of bisphenol A with CO was carried out using a catalyst system constituted of a Pd carbonylation catalyst, an inorganic redox catalyst, an organic redox cocatalyst, a base and a dehydrating agent. Usage of $Cu(OAc)_2$ as inorganic redox cocatalyst led to the synthesis of polycarbonate of $M_w$ 3600 but the formation of *o*-phenylene carbonate (*o*-PC) and salicylic acid type groups at the chain ends was observed. In an attempt to eliminate end group formation and explore the possibility of higher molecular weight polymer synthesis, various modifications were made in the catalyst system. On replacing Cu with Ce, *o*-PC formation could be eliminated completely. In addition, the usage of bis(triphenylphosphoranylidene) ammonium bromide (PPNBr) instead of tetrabutylammonium bromide [$n(Bu)_4NBr$] resulted in elimination of acid group formation leading to the synthesis of polymer of $M_w$ $3.8 \times 10^3$ (determined by GPC), with hydroxy group at both chain terminii. Polymer structure was investigated in detail by IR, NMR, and MALDI-TOF-MS studies. © 1999 Elsevier Science Ltd. All rights reserved.

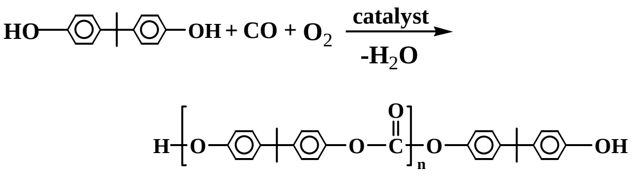
*Keywords*: Polymerization; Bisphenol A; Polycarbonate

## 1. Introduction

For the synthesis of highly useful aromatic polycarbonates, melt transesterification method is gaining more popularity in recent years than the currently used interfacial polycondensation method because of environmental reasons [1]. However, the diphenyl carbonate (DPC), a starting material of the former method involves the usage of extremely toxic phosgene. Therefore, it has been of great interest to find a non-phosgenated method for DPC synthesis and in recent years patented literature reported catalyst assisted oxidative carbonylation of phenol to diphenyl carbonate [2–7].



This reaction can be applied to direct synthesis of polycarbonates by polymerizing the diphenol with CO as shown below:



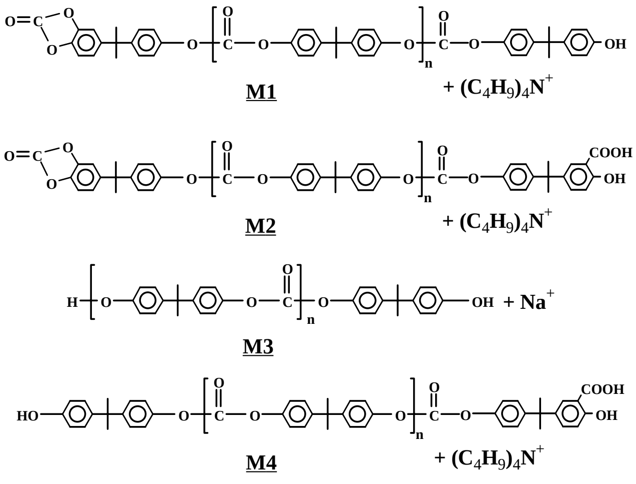
However, to our knowledge there are only two patents [2,7] reporting the synthesis of aromatic polycarbonates by this catalytic process and in both of these investigations catalytic efficiency, yield, and molecular weight obtained are very low.

Recently, in a separate publication we reported successful synthesis of aromatic polycarbonates of $M_w$ $3.6 \times 10^3$ in as high yield as 50%, using Pd–Cu based catalyst system [8] with Pd:bisphenol A ratio as 1:332. Structural analysis of this polymer revealed that the polymer chains were end capped by the formation of *o*-phenylene carbonate (*o*-PC) and salicylic acid type end groups. Assuming that these end caps might be responsible for low molecular weight, in the present work an attempt was made to prevent the formation

---

[*] Corresponding author. Tel.: +81-298-54-6348; fax: +81-298-54-6327.
*E-mail address:* takeuchi@nimc.go.jp (K. Takeuchi)

PII: S0032-3861(99)00583-2



Scheme 1.

of such end groups and synthesize bishydroxy ended polycarbonate. Hydroxy terminated polymer has an additional advantage that it can be used as a prepolymer for further reactions such as multi-step oxidative carbonylation to obtain high molecular weight polymer.

During detailed investigations of diphenyl carbonate synthesis as model reaction, we found that Cu component of the redox catalyst system is mainly responsible for *o*-PC group formation. Replacement of Cu with other metals such as Ce or Mn could help in complete elimination of *o*-PC formation without altering the efficiency of catalyst system [9,10]. In continuation of this study, here we wish to report end cap free bisphenol A polycarbonate synthesis using Pd–Ce–PPNBr based catalyst system. The polymer obtained in one step was once again subjected to oxidative carbonylation under the same conditions as used in first step, to obtain higher molecular weight polymer.

## 2. Experimental

### 2.1. Materials

Bisphenol A was recrystallized from chlorobenzene. Dichloromethane was distilled prior to use and stored over molecular sieves. Molecular sieves were activated at 350°C for 10 h under $N_2$ before use. All other chemicals were used as received.

### 2.2. Polymer synthesis

$PdCl_2$ 2.2 mg (0.012 mmol), $Ce(OAc)_3$ 25.0 mg (0.075 mmol), tetrabutylammonium bromide 120 mg (0.375 mmol), hydroquinone 41 mg (0.375 mmol), and 1 g activated 3A molecular sieves were charged to a 50 ml stainless steel autoclave and dried at 70°C for 2 h under vacuum before the reaction. After the drying, 0.945 g (4.16 mol) bisphenol A and 5 ml dichloromethane were added followed by charging 60 kg/cm$^2$ CO and 3 kg/cm$^2$ $O_2$, and the autoclave was placed in an oil bath preheated to 100°C. After specified time, reaction was quenched by cooling the autoclave in water bath. Polymer was isolated by precipitation in methanol.

### 2.3. Polymer characterization

Molecular weight was determined by JASCO Gulliver gel

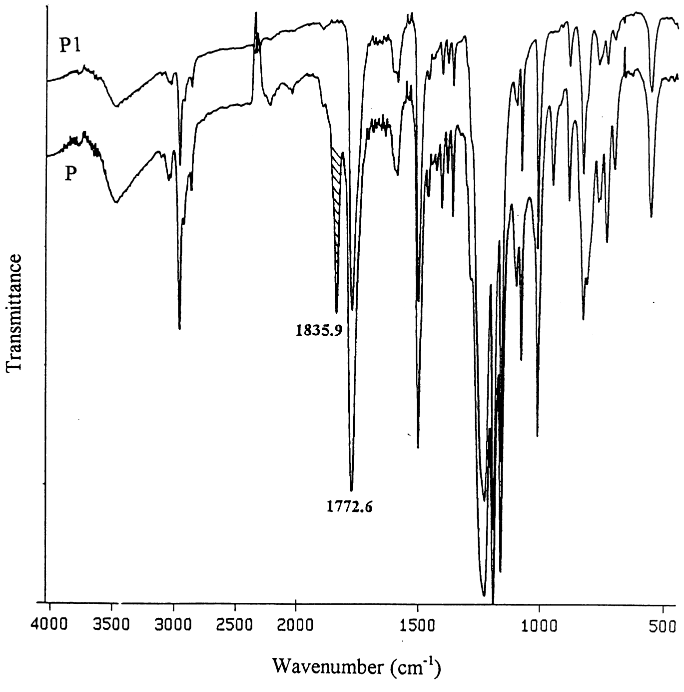


Fig. 1. IR spectra of polymer P and P1.

Table 1
Results of bisphenol A polymerization

| Polymer | Inorganic redox catalyst | Ammonium halide | Reaction time (h) | $M_n$ /$10^3$[a] | $M_w$ /$10^3$[a] | Yield[b] (%) | End group type[c] |
|---|---|---|---|---|---|---|---|
| P | $Cu(OAc)_2$ | $(n\mathrm{Bu})_4NBr$ | 24 | 2.8 | 3.6 | 50 | –OH *o*-PC SA |
| P1 | $Ce(OAc)_3\cdot H_2O$ | $(n\mathrm{Bu})_4NBr$ | 24 | 1.7 | 2.1 | 50 | –OH |
| P2 | $Ce(OAc)_3\cdot H_2O$ | $(n\mathrm{Bu})_4NBr$ | 48 | 2.3 | 3.0 | 50 | –OH SA |
| P3 | $Ce(OAc)_3\cdot H_2O$ | PPNBr | 24 | 1.9 | 3.5 | 55 | –OH |
| P4 | $Ce(OAc)_3\cdot H_2O$ | PPNBr | 48 | 2.0 | 3.8 | 80 | –OH |

[a] Molecular weight determined by GPC using polystyrene standards.

[b] Isolated yield.

[c] Refer to Scheme 1, *o*-PC: *o*-phenylene carbonate end group, SA: salicylic acid type end group.

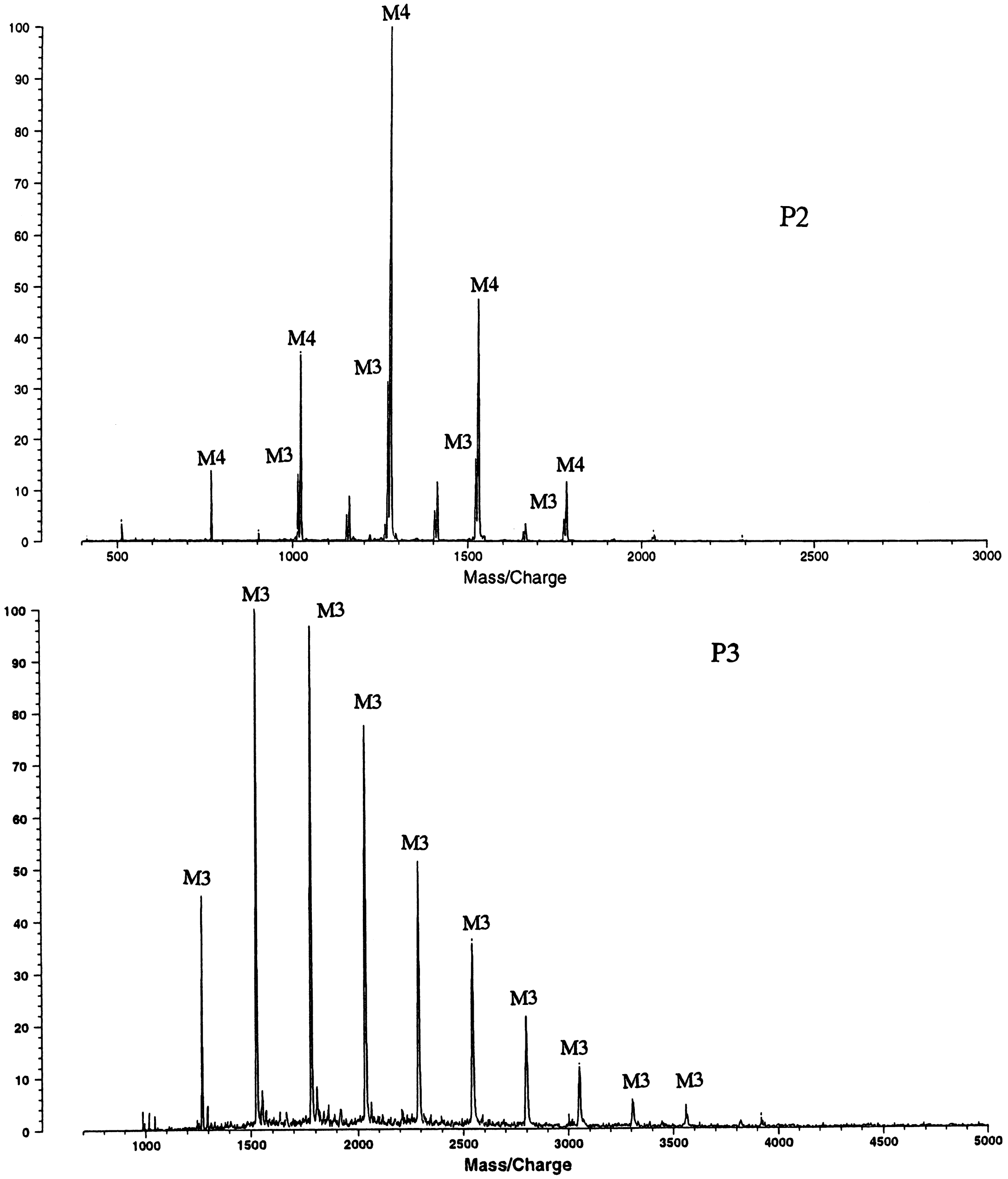


Fig. 2. MALDI mass spectra of the Polymer P2 and P3 (matrix; 2,5 dihydroxybenzoic acid, solvent; THF).

permeation chromatograph (GPC) using SHODEX K-804L column, polystyrene as standards, and chloroform as solvent. IR spectrometric analysis was carried out using Perkin–Elmer Paragon-1000 IR spectrometer. $^1H$ and $^{13}C$ NMR spectra were obtained on a JEOL LA600 spectrometer using $CDCl_3$ (containing 1% TMS as an internal reference) solvent. Matrix assisted laser desorption ionization—time of flight (MALDI-TOF) mass analysis was carried out on Shimadzu Kompact MALDI III spectrometer using 2,5-dihydroxy benzoic acid as matrix and THF as solvent.

## 3. Results and discussion

Bisphenol A polymerization in the presence of Pd–Cu based redox catalyst system resulted in polycarbonate (P) of $M_w$ 3600 with *o*-PC and salicylic acid end group formation (Scheme 1, M1 and M2). Details of this investigation are presented elsewhere [8]. In the current work, $Cu(OAc)_2$ component of the catalyst system was replaced with cerium acetate and reaction of bisphenol A was carried out under the same conditions as employed during previous work and detailed in Section 2. After 24 h of reaction, a light brown colored product (P1) was obtained on precipitation in methanol. IR spectra of the product P1 and that of polymer P are given in Fig. 1. Both P and P1 display a strong peak at 1774 $cm^{-1}$ attributable to linear carbonate carbonyl stretching, thereby confirming polycarbonate formation. However, polymer P1 did not display any peak at 1836 $cm^{-1}$ which was attributed to carbonyl stretching of *o*-PC cyclic carbonate end groups of polymer P. Absence of this peak in the spectrum of polymer P1 suggests that replacement of Cu with Ce resulted in *o*-PC end group free polycarbonate. $M_n$ and $M_w$ of polymer P1 determined from GPC using polystyrene standards were found to be 1700 and 2100, respectively (Table 1).

Structure of the polymer was confirmed by $^1H$ and $^{13}C$ NMR analysis also. $^1H$ NMR spectrum exhibited a singlet between 1.64–1.68 ppm due to methyl protons, a multiplet in the range of 7.0–7.3 ppm due to aromatic protons, and a very small broad peak at 5.33 ppm (exchangeable with $D_2O$) assigned to terminal –OH protons. A small peak at 6.9 ppm could be assigned to terminal aromatic protons.

In $^{13}C$ NMR spectrum, appearance of a peak at 152.1 ppm confirmed the carbonate bond formation. Peaks observed at 149.0 and 148.3 ppm were assigned to substituted aromatic carbons whereas those at 127.9, 120.1, and 114.7 ppm represented unsubstituted aromatic carbons. Peaks at 42.5 and 30.9 ppm were due to quaternary carbon and methyl carbons, respectively.

In order to investigate the terminal functionalities of the polymer chains, MALDI-TOF mass analysis was carried out using 2,5-dihydroxybenzoic acid as matrix. MALDI spectrum exhibited a single series of ion peaks at $m/z$ $254.28n + 251.2$ where 254.28 is the mass of repeat unit, $n$ is the number of repeat units, and 251.2 represents the mass of end group and sodium cation. These mass values were consistent with those of sodium cationized polycarbonate oligomeric species containing –OH group at both the ends (Scheme 1, M3). Ions were seen for the oligomeric species from tetramer to 12mer. These results show that Pd–Ce catalyst system could effectively lead to synthesis of polycarbonate with both chain termini as –OH groups.

In an effort to increase the molecular weight of the polymer, reaction time was increased from 24 to 48 h. However, resulting polymer P2 did not show any substantial increase in the molecular weight. In addition, its $^1H$ NMR spectrum besides exhibiting peaks assignable to polycarbonate protons displayed an additional small peak at 10.45 ppm (exchangeable with $D_2O$). On comparison with authentic sample of salicylic acid it was found that 10.45 ppm peak indicates the presence of salicylic acid type structures in the polymer. This salicylic acid type groups may be present at the chain ends and arise due to the formation of –COOH group in *ortho* position to terminal hydroxy groups of the polymer chains.

MALDI-MS spectrum of polymer P2 provided further evidence for the presence of salicylic acid type end groups. Spectrum shown in Fig. 2 displayed two series of intact ion peaks suggesting that the polymer is a mixture of two types of oligomeric chains (M3 and M4). As IR exhibited carbonate as single functional group, these two oligomeric series may differ only in the structure of their terminal groups. Calculations revealed that series M3 was similar to the one obtained in polymer P1 as it had a mass consistent with bishydroxy-ended polycarbonte which was observed at $m/z$ $254.28n + 251.2$, where 254.28 is the mass of repeat unit, $n$ is the number of repeat units, and 251.2 represents the mass of bishydroxy end group and $Na^+$ cation. Whereas, the second series (M4) appears to be tetrabutylammonium adduct of polycarbonate chains with hydroxyl group at one end and salicylic acid type structure at the other end (Scheme 1). Appearance of an intense peak of ion mass 242.2 in MALDI spectrum supports the assumption of cationization of M4 by tetrabutylammonium ion. In order to confirm further the tetrabutylammonium cationization of oligomeric series M4, polymerization was conducted with tetrabutylphosphonium bromide instead of tetrabutylammonium bromide. Peaks in the MALDI mass spectrum of resulting polymer showed a shift of 17 suggesting that oligomeric chains in this case were cationized by tetrabutylphosphonium ion, thereby confirming tetrabutylammonium cationization.

These results suggest that increase in the reaction time leads to new end group formation, which may restrict further chain propagation.

Formation of acid end-capped polymer is highly undesirable if it is to be used in further reactions for obtaining high molecular weight polycarbonate.

In further investigations, $(nBu)_4NBr$ was replaced with more stable bis(triphenylphosphoranylidene) ammonium bromide (PPNBr) and the polymerization was carried out.

Results of the 24 and 48 h reactions are given in Table 1. MALDI mass analysis of 24 h reaction product P3 revealed that the polymer had only one type of oligomers chains with hydroxyl group at both the ends (Fig. 2). On increasing the reaction time from 24 to 48 h, an increase in isolated yield from 55 to 80% was observed. MALDI mass analysis of the polymer P4 also revealed a series of oligomeric chains, mass of which was consistent to that of M3 and there was no peak corresponding to acid ended series M4.

These results show that unlike Pd–Ce– ($n$Bu$_4$)NBr system where acid-ended polymer formation took place on increasing the reaction time from 24 to 48 h, Pd–Ce–PPNBr did not lead to any end cap formation and the bishydroxy ended polymer could be obtained in high yield which is suitable for use in any further reactions. However, the $^1$H NMR spectra of polymer P3 and P4 still displayed a small peak at 10.45 ppm indicative of presence of acidic proton. This observation suggested that replacement of ($n$Bu)$_4$NBr with PPNBr reduced the formation of acid group to a great extent and the concentration of small amount of acid formed was not sufficient enough to display itself in MALDI mass spectrum.

In further investigations, the possibility of achieving high molecular weight polymer by two step oxidative carbonylation was explored. In the second step, 0.5 g of nearly bishydroxy ended polymer P4 ($M_w$ 4000) was used as starting material instead of bisphenol A and the reaction was carried out according to the typical procedure described in Section 2 using Pd–Ce–PPNBr based catalyst system. GPC analysis of the resulting reaction mixture confirmed that the second step of oxidative carbonylation resulted in high molecular weight polymer with $M_w$ 33,000.

To summarize, we have successfully carried out direct synthesis of bisphenol-A polycarbonate of $M_w$ up to 4000, by oxidative carbonylation reaction, using Pd based redox catalyst system. Replacement of Cu catalyst with Ce led to complete elimination of *o*-PC end group formation and that of ($n$Bu)$_4$NBr with PPNBr reduced the acid group formation to traces. Two step oxidative carbonylation, where almost completely bishydroxy ended polymer obtained in first step was used as a starting material in the second step led to synthesis of polymer of $M_w$ 33,000. Further investigations to optimize the reaction conditions of the second step to achieve higher molecular weight polycarbonate synthesis are currently under progress.

## References

[1] Freitag D, Grigo U, Muller PR, Nouvertne W. Encyclopedia of polymer science and engineering, vol. 11. New York: Wiley, 1988. p. 648.

[2] Hallgren JE. US Patent, 4,201,721 1980.

[3] Chin-The CT. Eur. Patent, 0,350,697 A2 1990.

[4] Kezuka H, Okuda F. Eur. Patent, 0,508,340 A2 1992.

[5] Joyce RP, King JA, Pressman EJ. US Patent, 5,231,210 1993.

[6] Iwane H, Miyagi H, Imada S, Seo S, Yoneyama T. Eur. Patent, 0,614,876 A1 1994.

[7] Hallgren JE, Lucas GM. J Organometal Chem 1981;212:135.

[8] Goyal M, Nagahata R, Sugiyama J, Asai M, Ueda M, Takeuchi K. Polymer 1999;40:3237.

[9] Goyal M, Nagahata R, Sugiyama J, Asai M, Ueda M, Takeuchi K. J Mol Catalysis 1999;147:137.

[10] Goyal M, Nagahata R, Sugiyama J, Asai M, Ueda M, Takeuchi K. Catalysis Lett 1998;54:29.