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Direct synthesis of aromatic polycarbonate from polymerization of bisphenol A with CO using a Pd–Cu catalyst system

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Abstract

Direct polymerization of bisphenol A with CO was carried out using a Pd–Cu-based redox catalyst system. A base for activating the hydroxy group of bisphenol A and a dehydrating agent for removing the water produced during the reaction were other important components of the catalyst system. Synthesized polycarbonate was characterized using IR, NMR, and GPC. MALDI-TOF mass spectroscopy was used for understanding the structure of polymer chain end groups. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbonate; Bisphenol A; Pd–Cu catalyst

1. Introduction

Aromatic polycarbonate is well known as one of the most useful superengineering plastics because of its good heat distortion resistance, electrical properties, mechanical properties, and transparency [1]. However, the only major disadvantage associated with this polymer is that its synthesis involves the usage of highly toxic phosgene. Aromatic polycarbonates are generally prepared by phosgenation of bisphenol or its transesterification with carbonic acid derivatives like diphenyl carbonate which in turn are also prepared by phosgenation. In the recent years, catalyst-assisted direct synthesis of diphenyl carbonate by oxidative carbonylation of phenol has been reported in literature [2–8]. However, in most of these cases diphenyl carbonate yields obtained are extremely low. We reported recently [9,10] successful synthesis of DPC with yields as high as 76% using Pd–Cu- and Pd–Ce-based catalyst systems with overall Pd turnover number of 250.

In addition to DPC synthesis, direct synthesis of aromatic polycarbonates by this catalytic process seems to be feasible but to our knowledge there are only two patents reporting this reaction [2,11]. In both of these investigations, catalytic efficiency, polymer yield, and molecular weight obtained are extremely low and details of polymer structure are not available.

In the continuation of our studies on DPC synthesis in the present work, we investigated the use of a Pd–Cu-based catalyst system for direct synthesis of aromatic polycarbonates. Bisphenol A polycarbonate was synthesized using the catalyst system and reaction conditions, optimized during DPC synthesis. Detailed investigations of polymer structure were carried out to gain an insight of the probable side reactions and terminal group formation during the polymerization reaction.

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), $Cu(OAc)_2$ (13.6 mg; 0.075 mmol), tetrabutylammonium bromide (120 mg; 0.375 mmol), hydroquinone (41 mg; 0.375 mmol), and 1 g

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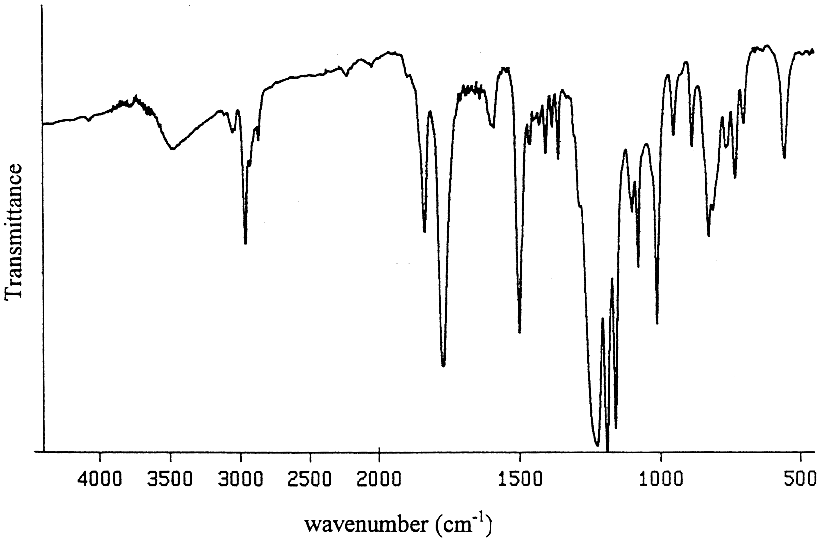


Fig. 1. IR spectrum of the polymer obtained by reaction of bisphenol A with CO in the presence of a Pd–Cu catalyst system.

of 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, 1.09 g (8.33 mol) of 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 24 h, reaction was quenched by cooling the autoclave in a water bath. Polymer was isolated by precipitation in methanol.

2.3. Polymer characterization

Molecular weight was determined by JASCO Gulliver gel permeation chromatograph (GPC) using a SHODEX K-804L column, polystyrene standards, and chloroform as solvent. IR spectrometric analysis was carried out using a Perkin–Elmer IR spectrometer. ^{1}H 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 a Shimadzu Kompact MALDI III spectrometer using 2,5-dihydroxybenzoic acid as matrix and THF as solvent.

3. Results and discussion

Before the polymer synthesis, diphenyl carbonate synthesis was studied and used as a model reaction to determine the suitable components of the catalyst system and optimum reaction conditions. Details of this study are published elsewhere [9]. The catalyst system comprised a carbonylation catalyst, a combination of inorganic and organic redox cocatalyst for in situ regeneration of active Pd species, a base and a dehydrating agent. Among the various group VIIIb metal complexes, only Pd complexes were found to be effective as a carbonylation catalyst. A combination of $Cu(OAc)_2$ and hydroquinone was found to be the best as redox cocatalyst and tetrabutylammonium bromide worked efficiently as a base for converting phenol into active phenoxide ion. 3A molecular sieves were found to give the best results as desiccating agent. When the reaction was carried out at a temperature of 100°C for 24 h using CO and O_2 pressure of 60 and 3 kg/cm^2, respectively, a high DPC yield of 76%, with Pd turnover number as 250, could be achieved. Besides DPC, *o*-phenylene carbonate (*o*-PC) was obtained as a major side product (5% yield under optimum conditions) along with small amounts of phenyl acetate and phenyl salicylate.

Polymerization of bisphenol A was carried out under these optimum reaction conditions with Pd:bisphenol A ratio of 1:332, for 24 h. On adding the reaction mixture to methanol a light-brown coloured polymer was obtained in 50% yield. M_n and M_w of this polymer determined from GPC, were found to be 2.8×10^3 and 3.6×10^3, respectively. In order to check the amount of residual bisphenol A, liquid chromatographic analysis of the filtrate was carried out and it was found that only 0.08% bisphenol A was remaining in the filtrate. These results suggest almost complete conversion of bisphenol A, but the polymer was obtained only in 50% yield. This anomaly could be explained by the appearance of low molecular weight oligomer peaks (dimer to pentamer) in LC analysis. These low molecular weight oligomers remained soluble in the methanol thereby decreasing the isolated polymer yield.

The IR spectrum of the the isolated polymer shown in Fig. 1 displays a strong peak at 1774 cm^{-1} attributable to carbonyl stretching of a linear carbonate linkage thus confirming polycarbonate formation. However, an additional peak at 1836 cm^{-1}, which does not belong to linear polycarbonate, was also observed. On comparison with the authentic sample of *o*-PC it was found that the 1836 cm^{-1} peak belongs to carbonyl stretching of this cyclic carbonate.

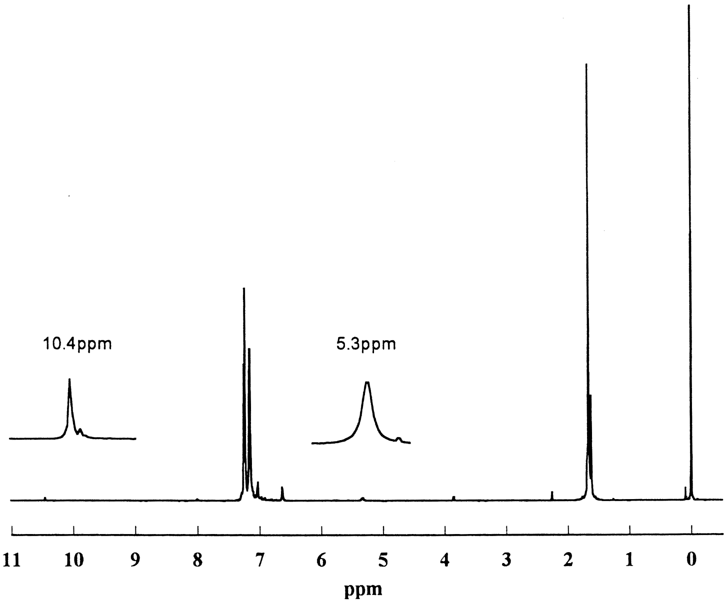


Fig. 2. ^{1}H NMR spectrum of the polymer obtained by reaction of bisphenol A with CO in the presence of a Pd–Cu catalyst system.

Thus it can be assumed that *o*-PC is present as a terminal group in the polycarbonate obtained. Formation of *o*-phenylene carbonate in as high a yield as 5% during diphenyl carbonate synthesis also supports this observation.

The ^{1}H NMR spectrum (Fig. 2) exhibited a singlet between 1.64 and 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. Besides these characteristic peaks and a few small peaks due to residual catalyst components, a very small peak was observed at 10.45 ppm which is exchangeable with D_2O and may be attributed to hydrogen-bonded phenolic protons of a salicylic acid-type group. This observation suggests the formation of a COOH group in the *ortho* position to the terminal hydroxyl groups of the polymer chains.

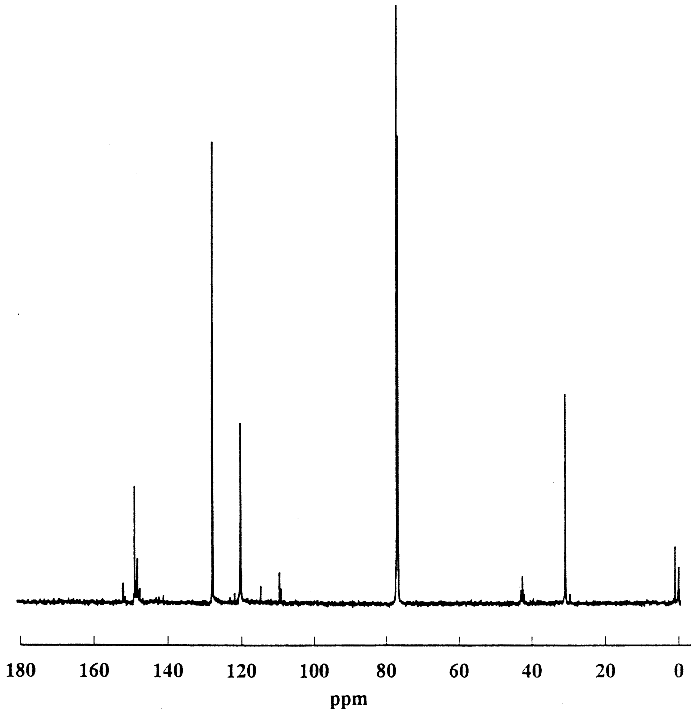


Fig. 3. ^{13}C NMR spectrum of the polymer obtained by reaction of bisphenol A with CO in the presence of a Pd–Cu catalyst system.

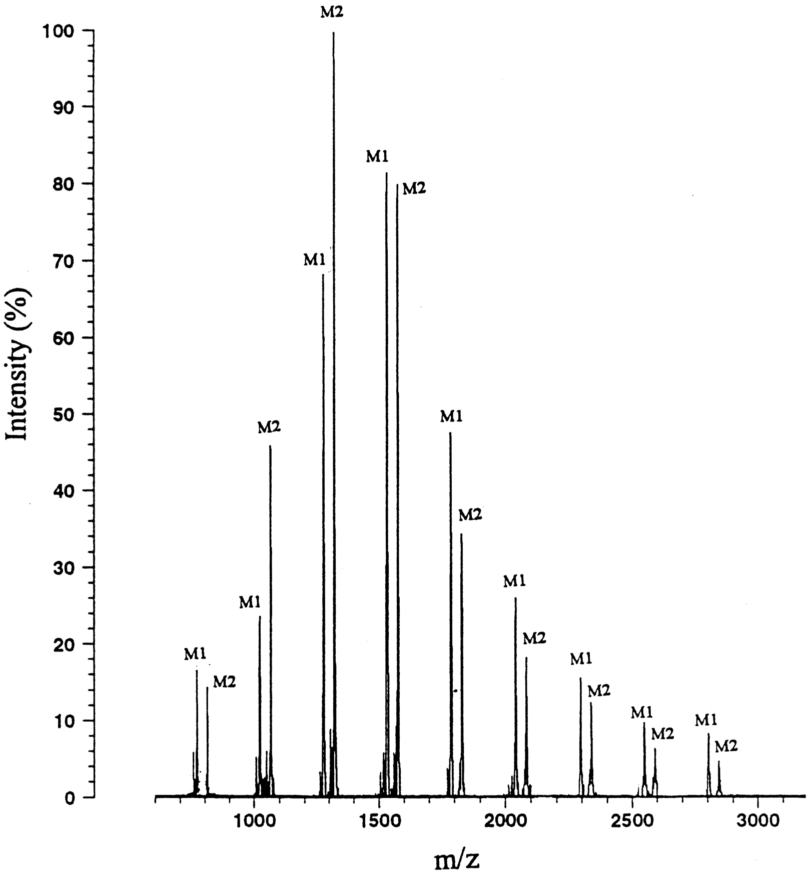
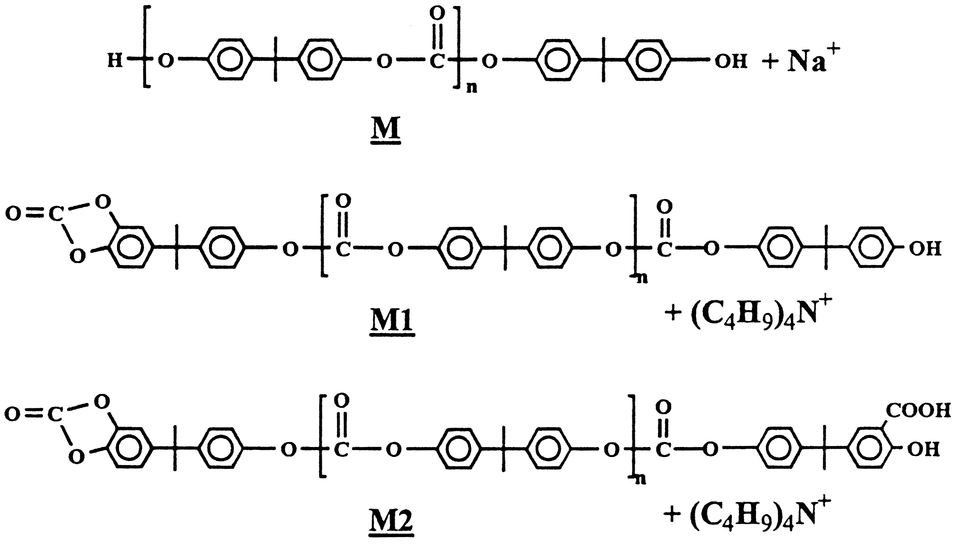


Fig. 4. MALDI mass spectrum of the polymer obtained by reaction of bisphenol A with CO in the presence of a Pd–Cu catalyst system.

In the ^{13}C NMR spectrum (Fig. 3), 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. Besides these peaks assignable to linear polycarbonate, the ^{13}C NMR spectrum exhibited an additional peak at 109.7 ppm. On comparison with the ^{13}C NMR spectra of salicylic acid and *o*-phenylene carbonate it was found that both of them exhibited a peak at almost the same position. Thus it can be assumed that the



Scheme 1.

peak at 109.7 ppm is indicative of formation of either or both of these groups at the polymer chain terminus.

To gain further understanding of the terminal groups, MALDI-TOF mass spectroscopy was carried out. The mass spectrum of the polymer (Fig. 4) showed two series of ion peaks (M1 and M2). In the MALDI mass spectrum generally, the ion peaks are observed as $[M + H]^+$ or $[M + Na]^+$ ions. Thus H^+ cationized polycarbonate chains with a hydroxyl group at both the chain termini should exhibit intact ion peaks at m/z 254.28n + 229.2 and those cationized by Na^+ should appear at m/z 254.28n + 251.2 (Scheme 1,M) where 254.28 is the mass of the repeat unit, n is the number of repeat units and 229.2/251.2 represent the mass of the bishydroxy end group and corresponding cation. However, the mass of the oligomeric series M1 and M2 did not resemble any of these series. This observation reveals that neither oligomeric chains have the hydroxyl group in both end groups nor are they ionized by Na^+ or H^+ cations.

Further investigations revealed that the MALDI mass spectrum of the polymer exhibited a very intense peak due to the tetrabutylammonium ion at m/z 242.2 indicating that oligomeric chains might be cationized by the tetrabutylammonium ion. Regarding end groups, IR and NMR studies indicated the presence of *o*-PC and salicylic acid-type terminal groups in the polymer. Thus mass calculations were made by taking the presence of *o*-PC and salicylic acid-type terminal groups as well as the tetrabutylammonium ion into consideration. These calculations showed that the mass of oligomeric series M1 was in agreement with that containing an *o*-PC group at one end and –OH group at the other (Scheme 1). The tetrabutylammonium ion cationized M1 series was observed at m/z 254.28n + 270.2 + 242.4, where 254.28 is the mass of the repeat unit, n is the number of repeat unit, 270.2 is the mass of the *o*-PC-ended terminal group and 242.4 is the mass of the tetrabutylammonium ion. Similarly, M2 was found to be a series of tetrabutylammonium-cationized oligomeric chains containing *o*-PC at one end and a salicylic acid-type group at the other end (Scheme 1). This series was observed at m/z 254.28n + 313.2 + 242.4, where 313.2 represents the mass of the *o*-PC and acid-ended terminal groups together. Ions were seen for the oligomeric species from trimer to nonomer.

In order to confirm that oligomeric series M1 and M2 were cationized by the tetrabutylammonium ion, polymerization was conducted with tetrabutylphosphonium bromide instead of tetrabutylammonium bromide. Peaks in the MALDI mass spectrum of the resulting polymer showed a shift of 17 suggesting that oligomeric chains in this case were cationized by tetrabutylphosphonium ion, thereby confirming tetrabutylammonium cationization in the polymer under investigation.

To summarize, we have successfully synthesized aromatic polycarbonate of M_w 3.6×10^3 by direct oxidative carbonylation of bisphenol A using a Pd–Cu-based redox catalyst system. Detailed structural investigations revealed the formation of *o*-phenylene carbonate and salicylic acid-type terminal groups. Further investigations to synthesize end-cap free polycarbonate are currently in progress.

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