

# Synthesis of poly(propylene carbonate) from highly active, inexpensive achiral (Salph)Co(III)X as initiator and bis(triphenyl phosphine) iminium as co-initiator

Shilpa Narang,<sup>1</sup> Eva Macova,<sup>2</sup> Dušan Berek,<sup>2</sup> S. N. Upadhyay,<sup>3</sup> Rajeev Mehta<sup>4</sup>

<sup>1</sup>School of Chemistry and Biochemistry, Thapar University, Patiala- 147004, Punjab, India

<sup>2</sup>Polymer Institute of the Slovak Academy of Sciences, 84541, Bratislava, Slovakia

<sup>3</sup>DAE Raja Ramanna Fellow, Department of Chemical Engineering & Technology, IIT(BHU) Varanasi, Varanasi- 221005 UP, India

<sup>4</sup>Department of Chemical Engineering, Thapar University, Patiala- 147004 Punjab, India

Correspondence to: R. Mehta (E-mail: rajeevmehta33@yahoo.com)

**ABSTRACT:** Copolymerization of carbon dioxide with racemic propylene oxide has been investigated in the presence of an inexpensive achiral (Salph)Co(III)X [Salph is *N,N'*-bis(3,5-di-*tert*-butylsalicylidene) phenylenediimine and X is pentafluorobenzoate] as initiator and [PPN]<sup>+</sup>Cl<sup>-</sup> ([PPN] is bis(triphenylphosphine) iminium) as co-initiator. Effects of monomer-to-initiator ratio, initiator/co-initiator ratio, and reaction conditions like stirring rate, temperature, and pressure of CO<sub>2</sub> on the molecular weight, yield, and selectivity of poly(propylene carbonate) over propylene carbonate have been studied. The initiator used in the study has been found to be highly active at milder conditions of pressure and temperature, giving a product with maximum  $M_w$  of  $14.8 \times 10^3$  g/mol at 25 bar and 50°C. The conversion increases with an increase in stirring rate and then becomes almost constant at 1100 rpm and above, indicating that the reaction is no longer limited by mass transfer. The molecular weight  $M_w$  of the polymer has been found to increase with increasing monomer-to-initiator ratio up to 3000:1, but it starts decreasing with a further increase in monomer-to-initiator ratio, giving a polymer of lower  $M_w$ . The activity of the initiator is considerably affected by pressure, temperature, time, and amount of co-initiator. The polymeric product has low polydispersity (near unity) with negligible formation of polypropylene oxide. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43099.

**KEYWORDS:** catalysts; copolymers; ring-opening polymerization

Received 16 August 2015; accepted 26 October 2015

DOI: 10.1002/app.43099

## INTRODUCTION

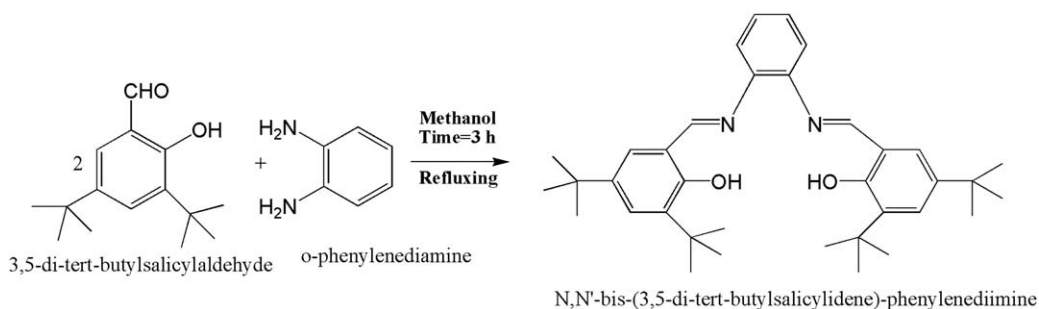
Chemical fixation of carbon dioxide (CO<sub>2</sub>) to various value-added products and a reduction in its atmospheric concentration are gaining worldwide attention.<sup>1–3</sup> CO<sub>2</sub> is thermodynamically quite stable with a bond angle of 180°, and thus it is a challenge to use it as a reagent in a chemical reaction. One of the highly interesting tasks is to couple CO<sub>2</sub> with reactive heterocyclics such as epoxides (ethylene oxide, cyclohexene oxide, styrene oxide, propylene oxide) to produce polycarbonates and cyclic carbonates.<sup>1–7</sup> Polycarbonates are environmentally benign and have several biomedical and pharmaceutical applications.<sup>4,8</sup> Among the available polycarbonates, poly(propylene carbonate) (PPC) is one of the important classes of polymers. It is used to increase the toughness of some epoxy resins and as a sacrificial binder in the ceramic industry, where it decomposes and evaporates during sintering. PPC is also highly suitable for the prepa-

ration of electroceramics like dielectric materials and piezoelectric ceramics.<sup>9</sup>

Most of the earlier research in this area was focused on the identification of active initiators for copolymerization of cyclohexene oxide with CO<sub>2</sub>. The search for efficient initiators for copolymerization of propylene oxide with CO<sub>2</sub> to synthesize PPC came into the limelight in the last decade mainly because of the commercial benefits that can be gained from it. Many different inorganic, salen-based ligand metal complexes and organometallic initiators have been used in this copolymerization reaction.<sup>10–22</sup> Although all classes have been found to be active, better polydispersity has been achieved with organometallic and ligand metal complexes as initiators. On the other hand, higher molecular weights have been obtained using inexpensive inorganic initiators, but the polymerization was rather slow.<sup>4,6</sup> Thus both groups of initiators have their own benefits

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**Figure 1.** Reaction scheme for preparation of *N,N'*-bis-(3,5-di-*tert*-butylsalicylidene)-phenylenediamine (Salph).

and limitations. In recent years, a variety of catalysts such as salen-based ligand metal complexes coordinated with cobalt,<sup>14–17,20,21</sup> chromium,<sup>8,18</sup> zinc,<sup>19</sup> and tetravalent metal complexes with a 1,9-bis(2-oxidophenyl)dipyrrinate ligand<sup>12</sup> have been investigated. Double metal cyanide complexes,<sup>10,11,23</sup>  $Y(\text{CCl}_3\text{OO})_3/\text{glycerin}/\text{ZnEt}_2$  complex anchored to different supports,<sup>13</sup> lanthanide complexes<sup>24</sup> and so on, have also been found to be active for copolymerization of propylene oxide and  $\text{CO}_2$ . Lu *et al.*<sup>25</sup> and Nguyen *et al.*<sup>26</sup> reported that Lewis base initiators are effective at low and even at atmospheric pressures. Most of the available studies in this area deal with the copolymerization in the presence of chiral initiator systems, which are quite expensive. Although a few achiral initiators have also been explored for polycarbonate production, the yield has been low.<sup>14,27</sup> The present study deals with the synthesis of an economical and simple achiral (Salph)Co(III)OBzF<sub>5</sub> initiator and its use in the synthesis of polycarbonate. Polymer conversion using the catalyst has been achieved under milder conditions of temperature and pressure. The effect of stirring rate has been studied. It has rendered the interesting results that the cyclic product was formed below 800 rpm, and increasing the impeller speed to 1100 rpm leads to PPC as the major product. It is shown that at an impeller speed of 1100 rpm or more, mass transfer is no longer the limiting parameter. The effect of changing the monomer-to-initiator ratio on the conversion and molecular weight of the formed polymer has been critically analyzed for the first time on such systems. A comprehensive study involving the effect of parameters such as reaction time, pressure, temperature, and initiator/co-initiator ratio on the yield and molecular weight has also been done.

## MATERIALS AND METHODS

### Materials

Laboratory reagent grade *o*-phenylenediamine was obtained from Loba Chemicals Pvt. Ltd (Mumbai, Maharashtra, India). Propylene oxide,  $[\text{PPN}]^+\text{Cl}^-$  ( $[\text{PPN}]^+$  i.e., bis(triphenylphosphine)iminium), and 3,5-di-*tert*-butylsalicylaldehyde were purchased from Aldrich (Saint Louis, USA). Absolute alcohol was obtained from E. Merck (Darmstadt, Germany). Analytical reagent grade cobaltous acetate and molecular sieves (4A) were obtained from Sd-Fine Chemicals (Mumbai, Maharashtra, India). Calcium hydride and pentafluorobenzoic acid were purchased from High Media (Mumbai, Maharashtra, India). High-purity  $\text{CO}_2$  (99.99%) was obtained from Sigma Gases (Delhi, India).

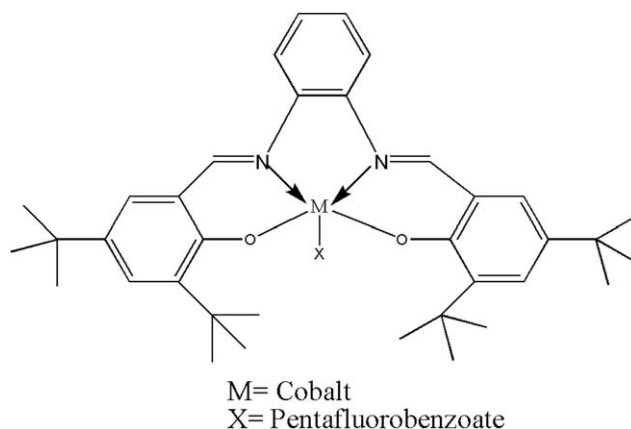
The racemic propylene oxide was distilled over  $\text{CaH}_2$  before the reaction, and  $\text{CO}_2$  was passed over 4A molecular sieves to

remove moisture. The reactions were carried out in a 100 ml autoclave reactor.

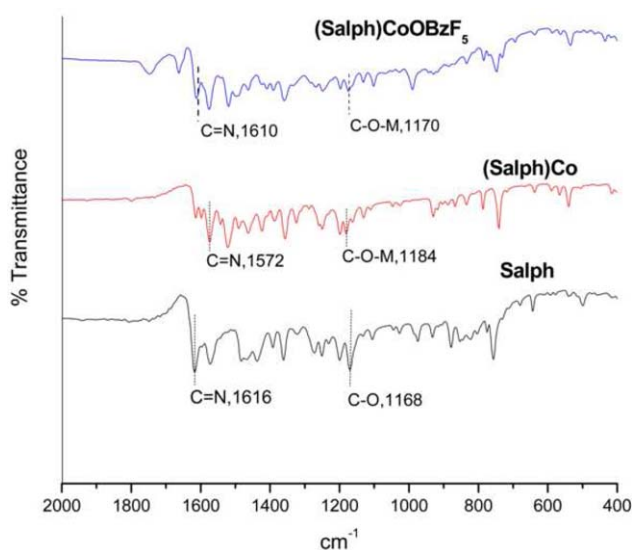
### Preparation of Initiator

The ligand [*N,N'*-bis-(3,5-di-*tert*-butylsalicylidene)-phenylenediamine, or Salph] was prepared by refluxing *o*-phenylenediamine with 3,5-di-*tert*-butylsalicylaldehyde under continuous stirring in a 1:2 molar ratio using ethanol as solvent.<sup>28,29</sup> The reaction was carried out for 3 h. At the end of the reaction, the ligand (Salph) was obtained after filtration in the form of bright yellow crystals. The reaction scheme is given in Figure 1. The estimated confirmation for reaction completion was done with the help of thin layer chromatography (TLC, with  $\text{SiO}_2$  as stationary phase and eluent with chloroform:methanol as 9:1), which gave only a single spot. Further, characterization of the crystalline product was done with Fourier transform infrared spectroscopy (FTIR),  $^1\text{H-NMR}$ , and Carbon, Hydrogen, Nitrogen, Sulphur (CHNS) analysis.

The complexation of Salph was carried out with cobaltous acetate tetrahydrate employing a 1:1 molar mixture of components in methanol by refluxing for 3 h with continuous stirring. The solid product thus obtained was vacuum filtered. In order to bind pentafluorobenzoate (OBzF<sub>5</sub>) to the axial position, one equivalent of Salph cobalt complex was stirred with one equivalent of pentafluorobenzoic acid for about 18 h in air using toluene as solvent.<sup>22</sup> The synthesized initiator (Figure 2) along with the co-initiator  $[\text{PPN}]^+\text{Cl}^-$  was used to catalyze the reaction between propylene oxide and  $\text{CO}_2$ .



**Figure 2.** [*N,N'*-bis-(3,5-di-*tert*-butylsalicylidene)-phenylenediamine]-Co(III)OBzF<sub>5</sub> complex.



**Figure 3.** FTIR spectra of Salph, (Salph)Co, and (Salph)Co(III)OBzF<sub>5</sub> used as initiator. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Characterization of Initiator

The synthesized ligand was analysed using CHNS, <sup>1</sup>H-NMR, and FTIR techniques. The CHNS analysis was used for the determination of carbon, hydrogen, and nitrogen content in the given ligand to confirm the successful synthesis of the Salph ligand. The various elements observed were C, 80.6%; H, 9.07%; and N, 5.35%; which was in agreement with the theoretical values of C, 79.95%; H, 8.95%; and N, 5.18%.

In the <sup>1</sup>H-NMR spectra of the ligand, the presence of a sharp singlet for the —C(H)=N proton at 8.6 ppm clearly indicates a similar environment for all such protons and hence a planar structure. The signal for OH protons in the ligand is observed at 13.4 ppm, and a multiplet due to aromatic protons appears within the range of 7.2–7.4 ppm, thereby clearly indicating the synthesis of the initiator.

The FTIR spectrum of the initiator is shown in Figure 3. The band at 1168 cm<sup>-1</sup> in Salph attributed to C—O is shifted to a higher frequency in the complex by about 30–40 cm<sup>-1</sup> (1184 cm<sup>-1</sup>), which confirms the participation of oxygen in the C—O—M bond. The band again is shifted to lower frequency (around 1170 cm<sup>-1</sup>) when pentafluorobenzoate was bound to the axial position. The band for the ligand around 1610 cm<sup>-1</sup> due to C=N stretching shifted to a lower frequency (around 1572 cm<sup>-1</sup>). This band again shifted to higher frequency (around 1610 cm<sup>-1</sup>) when electron-withdrawing pentafluorobenzoate was attached to the complex. The band due to C—N at 1480 cm<sup>-1</sup> in the ligand shifted to a lower frequency by about 20 cm<sup>-1</sup> (around 1460 cm<sup>-1</sup>), further confirming the coordination of nitrogen with the metal.

### Copolymerization of Propylene Oxide with CO<sub>2</sub>

The autoclave reactor was heated to about 80°C under vacuum for 3 h and then cooled to room temperature while maintaining the vacuum. A mixture of (Salph)Co(III)OBzF<sub>5</sub>/[PPN]<sup>+</sup>Cl<sup>-</sup> dispersed in distilled propylene oxide was added to the reactor. Dry CO<sub>2</sub> was then introduced at the desired pressure and tem-

perature. The mixture was stirred with a mechanical stirrer for a required period of time after which it was cooled down to room temperature, and the remaining CO<sub>2</sub> was vented out into a fume hood. After opening the reactor, the reaction product was dissolved in a small amount of dichloromethane, and the reaction was terminated using 5% acidified methanol. At this stage, a small aliquot of the reaction mixture was taken for <sup>1</sup>H-NMR analysis in order to find the conversion of monomer to poly(propylene carbonate) and cyclic carbonate. Finally, PPC was precipitated by adding an excess of methanol, and the resultant polymer thus obtained was dried under vacuum overnight at 50°C.

### Characterization of Polymer

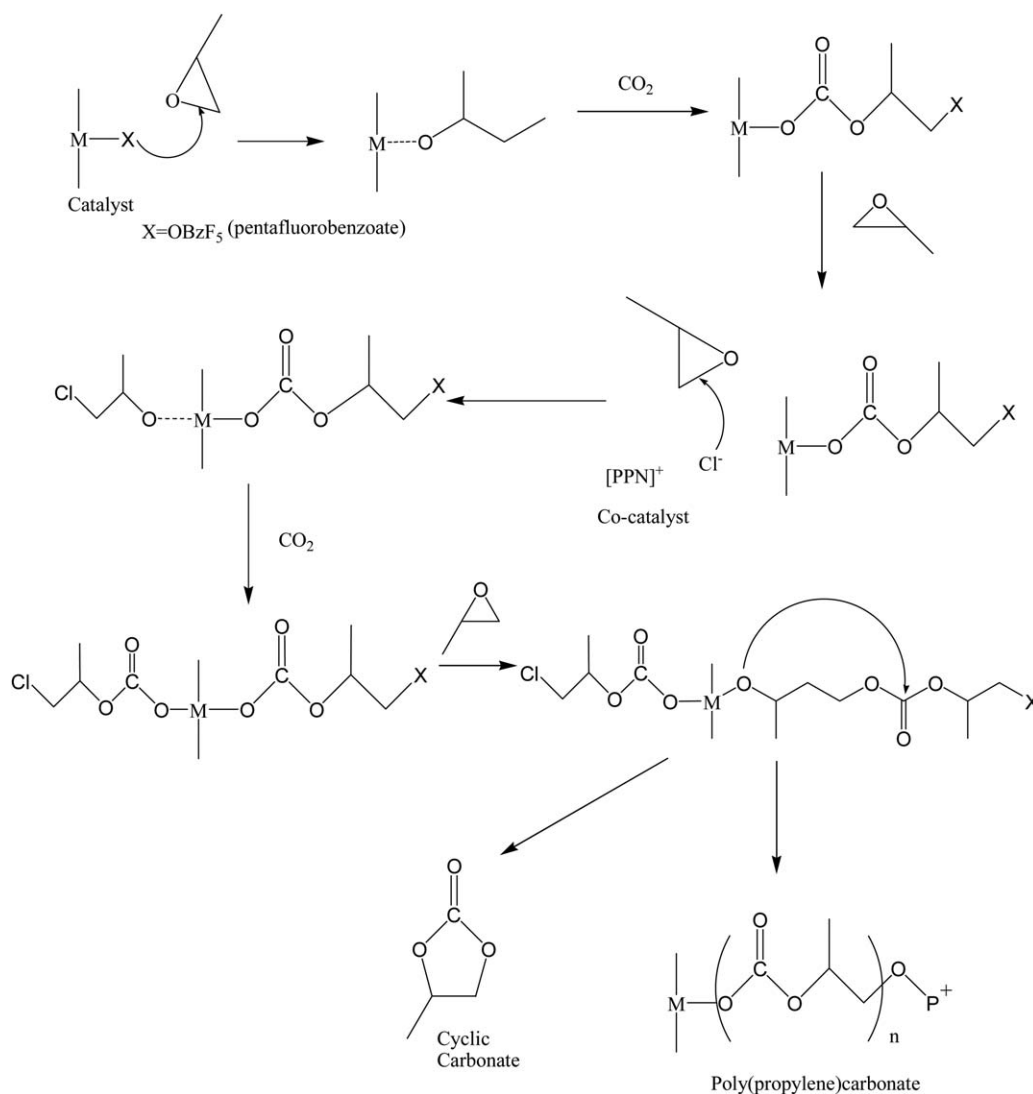
Gel permeation chromatography (GPC) measurements were carried out using a common instrument that consisted of a pump (Watrex, Praque, Czech Republic, flow rate 1 mL min<sup>-1</sup> eluted with Tetrahydrofuran (THF)), an injection valve (Rheodyne, Rohnert Park, USA, Model 7105 with the sample loop 50 μL), a column (linear SHODEX GPC KF 806L, Tokyo, Japan) and an evaporative light scattering detector (ELSD; PL-Agilent, Model 1000, Santa Clara, USA). The <sup>1</sup>H- and <sup>13</sup>C-NMR techniques were used for the characterization of polymer structure, and <sup>1</sup>H-NMR was also used for the quantification of the product. The correlation of <sup>1</sup>H-NMR and <sup>13</sup>C-NMR was carried out from 450 to 4000 cm<sup>-1</sup> using heteronuclear single quantum coherence (HSQC) spectroscopy in order to confirm the structure of the polymeric product. The spectra were recorded using CDCl<sub>3</sub> as a solvent and tetramethylsilane as an internal standard on a Jeol ECS-400 Spectrophotometer (Akishima, Tokyo, Japan). FTIR measurements were carried out using an Agilent Cary-660 spectrophotometer (Santa Clara, USA) from 450 to 4000 cm<sup>-1</sup>. The attenuated total reflectance (ATR) mode was used for all of the measurements. The CHNS analysis was carried on a Thermo Scientific Flash 2000 (Milan, Italy) Organic Elemental Analyser equipped with a thermal conductivity detector.

## RESULTS AND DISCUSSION

Copolymerization of propylene oxide with carbon dioxide to form poly(propylene carbonate) and cyclic carbonates has been studied. The proposed mechanism for the reaction is shown in Figure 4, and it is in close agreement with the similar mechanisms presented in the literature.<sup>30,33</sup> The effect of various parameters such as stirring, initiator/co-initiator ratio, monomer-to-initiator ratio, pressure, and temperature on the percentage of conversion, molecular weight, and polydispersity of polymeric products have been investigated, and the results are given in Table I. The effects of individual parameters are discussed below.

### Effect of Reaction Time

It has been found that PPC conversion increases with reaction time. But, keeping the reaction time constant and increasing the temperature leads to a decrease in poly(propylene carbonate) conversion and an increase in cyclic carbonate conversion. However, at the same temperature, the percentage conversion increases monotonically with an increase in reaction time. This is quite significant for ring-opening polymerization, where the reproducibility of results is lower because the reaction can easily



**Figure 4.** Proposed mechanism of the copolymerization of propylene oxide with CO<sub>2</sub>.

be terminated even with the presence of a small amount (ppm level) of impurities or water. It has further been observed that with an increase in reaction time the process becomes more selective for the PPC formation. With regard to average molecular weights, except for the initial part of the reaction at 0.5 hour, the  $M_n$  and  $M_w$  values do not change significantly. The molecular weight distribution as given by the value of polydispersity, the ratio  $M_w/M_n$ , is remarkably narrow.

#### Effect of Agitation

The polymerization reactions were carried out at different impeller speeds. The results are shown in Table I. At 25°C and 700 rpm no product was obtained. Further, at 700 rpm and 50°C, the conversion of propylene oxide to cyclic carbonate took place with no detectable PPC conversion. To further augment the contact surface among the monomers, propylene oxide and CO<sub>2</sub>, only a small amount of propylene oxide was initially employed, which enabled the impeller blades to create a whirl at the interface of propylene oxide and CO<sub>2</sub> and thus break the upper surface of propylene oxide. It was observed

that, with an increase in stirring speed, the conversion of propylene oxide to PPC increased, and the best combination of conversion and molecular weight was achieved at 1100 rpm. Therefore, to exclude that the slower mass transfer rate controls the polymerization kinetics, all further reactions were carried out at 1100 rpm.

The Clausius-Clapeyron relation was used to know the physical state of the system. Though the relation is strictly applicable only to single-constituent systems, we have employed it for polycarbonate synthesis with two constituents (CO<sub>2</sub> and propylene oxide) that mutually reacted. It is estimated that at 15 bar the boiling point of propylene oxide is around 160°C, which is nearly three times higher than the reaction temperature. This clearly indicates that propylene oxide must exist in a liquid state during the reaction. It is expected that at higher agitation speeds the interfacial area for contact between propylene oxide and carbon dioxide will increase, thereby resulting in the availability of more and more propylene oxide for polymerization to provide higher PPC conversion. The extremely narrow molar

**Table I.** Effect of Various Operating Parameters on Percent Conversion

Operating parameter	Percent conversion		$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	PD
	PPC	Cyclic carbonate			
Effect of reaction time: $P = 15$ bar, $T = 50^\circ\text{C}$ , $M_o/I_o = 2000:1$					
Time, $h = 0.5$	17.0	12.0	6.0	7.0	1.13
Time, $h = 1.0$	29.0	27.0	11.0	15.0	1.29
Time, $h = 1.5$	39.0	16.0	11.0	14.0	1.25
Time, $h = 2.0$	41.0	12.0	11.0	12.0	1.14
Time, $h = 1.0^a$	25.0	25.0	11.0	13.0	1.14
Time, $h = 2.0^a$	29.0	32.0	11.0	14.0	1.23
Effect of agitation: $P = 15$ bar, $T = 50^\circ\text{C}$ , $M_o/I_o = 2000:1$ , time: 2 h					
RPM = 700 <sup>b</sup>	—	—	—	—	—
RPM = 1100 <sup>b</sup>	—	—	—	—	—
RPM = 700	—	50.0	—	—	—
RPM = 800	11.0	45.0	8.0	10.0	1.30
RPM = 900	41.0	14.0	8.0	9.0	1.14
RPM = 1100	41.0	12.0	11.0	12.0	1.14
RPM = 1450	40.0	12.0	8.0	11.0	1.31
Effect of $M_o/I_o$ : $P = 15$ bar, $T = 50^\circ\text{C}$ , time: 2 h					
$M_o/I_o = 1500:1$	17.9	43.0	8.0	10.0	1.13
$M_o/I_o = 2000:1$	41.0	12.0	11.0	12.0	1.13
$M_o/I_o = 3000:1$	37.0	8.0	14.0	16.0	1.08
$M_o/I_o = 4000:1$	33.0	19.0	4.0	4.0	1.08
Effect of pressure: $M_o/I_o = 2000:1$ , $T = 50^\circ\text{C}$ , time: 2 h					
$P = 7$ bar	7.0	8.0	10.0	13.0	1.24
$P = 15$ bar	41.0	12.0	11.0	12.0	1.14
$P = 25$ bar	56.0	12.0	13.0	15.0	1.16
Effect of temperature: $M_o/I_o = 2000:1$ , $P = 15$ bar, time: 2 h					
$T = 25^\circ\text{C}$	—	—	—	—	—
$T = 50^\circ\text{C}$	41.0	12.0	11.0	12.0	1.14
$T = 70^\circ\text{C}$	29.0	31.0	11.0	14.0	1.23
Effect of initiator/co-initiator ratio [In/Co-in]: $M_o/I_o = 2000:1$ , $P = 15$ bar, $T = 5^\circ\text{C}$ , time: 2 h					
In/Co-in = 0.5	20.0	41.0	11.0	14.0	1.29
In/Co-in = 1.0	41.0	12.0	11.0	12.0	1.14
In/Co-in = 2.0	29.0	41.0	5.0	6.0	1.13

PD: polydispersity.

<sup>a</sup>Reaction time studied at  $70^\circ\text{C}$ .

<sup>b</sup>Agitation speed at  $25^\circ\text{C}$ .

mass distribution of the resulting PPC as evident from the polydispersity (PD) (nearly unity, calculated from GPC data, Table I) was obtained.

### Monomer/Initiator Ratio

The reactions were carried out at different monomer-to-initiator ( $M_o/I_o$ ) ratios at a constant pressure of 15 bar and a temperature of  $50^\circ\text{C}$  (Table I and Figure 5). At the lowest studied  $M_o/I_o$  ratio of 1500:1, the molar mass and conversion are both low. At  $M_o/I_o$  of 2000:1 and above, the conversion first increases and then decreases again. At lower  $M_o/I_o$  ratio, the amount of initiator is relatively high, and hence probably a

greater number of initiating sites are available for polymerization, resulting in the formation of several shorter polymer chains along with an increased amount of oligomers (thereby giving rise to a polymer with low molecular weight). It is interesting to note that at 1500:1 the reaction becomes more favorable for cyclic carbonate conversion.

Increasing the  $M_o/I_o$  ratio to 2000:1 and 3000:1 leads to an increase in  $M_w$  of the polymer. It is estimated that at high  $M_o/I_o$  ratio the amount of initiator required for the reaction is relatively less and the number of initiating sites for polymer chain growth decreases, resulting in longer polymer chains with high molar

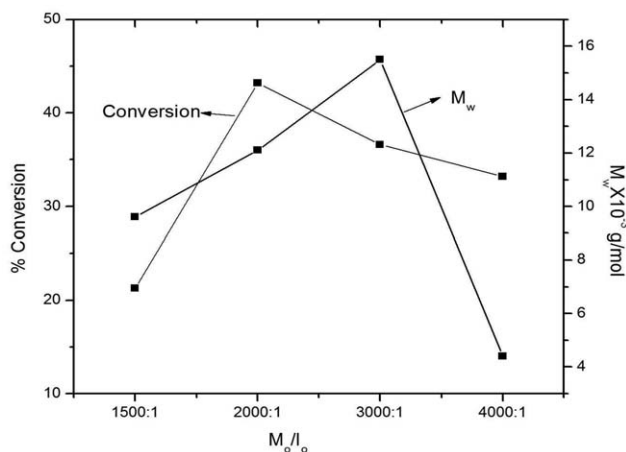


Figure 5. Effect of  $M_o/I_o$  ratio on PPC conversion and  $M_w$ .

mass and conversion. Further increasing the  $M_o/I_o$  ratio to 4000:1 (with the small amount of initiator required), decreases the number of initiating sites, and thus a smaller number of propagating chains probably result in chain termination by the impurities and moisture present in the system (which will have a significant effect on the molar mass). The size exclusion chromatography (SEC) results (Figure 6) show that at a  $M_o/I_o$  ratio of 3000:1 the molar mass obtained is the highest, showing the lowest retention volume, and at a ratio of 4000:1 the molar mass obtained is the lowest with maximum retention volume.

The increase in  $M_n$  with increase in  $M_o/I_o$  can also be explained by the simple relation

$$DP_n = 1 + \frac{M_o}{I_o}$$

Here  $DP_n$  is the degree of polymerization. In the absence of detailed kinetic rate constants, the above relation can be used for the ring-opening polymerization. This relation is valid for the polymerization where the initiation step is very fast and there is no termination. Thus for other situations this relation should be used only as an approximation and for qualitative estimates.<sup>31,32</sup>

#### Effect of Initiator/Co-initiator Ratio

It is known that organic base and Lewis base co-initiators increase the selectivity for PPC formation.<sup>20,21</sup> The co-initiator binds the epoxide from the vacant axial site and thus assists in the polymer chain growth (Figure 4). In the present study, the amount of initiator was kept fixed, and the amount of co-initiator was varied with three different initiator/co-initiator ratios of 0.5, 1, and 2. It is observed that the selectivity for PPC first increases with an increase in initiator/co-initiator ratio and then decreases with a further increase in this ratio (Table I). Because the co-initiator also increases the number of chain-propagating sites, these results can be explained in the same way as the role of an initiator at optimum  $M_o/I_o$  ratio (see the section titled Monomer/Initiator Ratio). A greater amount of co-initiator will lead to an increase in initiating sites for polymer chain growth, giving PPC with low molecular weight and conversion.

#### Effect of Pressure

The effects of pressure on the percent conversion and  $M_w$  are shown in Table I. It is seen that for a given  $M_o/I_o$  ratio the conversion changes appreciably with pressure, while there is only a little change in  $M_w$  values. The conversion is only around 6% at 7 bar, increasing to around 41% at 15 bar and 55% at 25 bar. The change in pressure evidently increases the concentration of carbon dioxide and thereby the yield of the product. However, an increase in molecular weight with an increase in pressure is not always continuous, and it instead reaches a limiting value at a certain pressure. Since at a given monomer-to-initiator ratio (i.e., 2000:1) the number of chain-initiating sites for chain growth is nearly the same at all pressures, there is only a little change in  $M_w$ . The average molecular weight of the product is dependent on the individual rate constants of initiation, propagation, and termination. Thus, when the initiator/co-initiator system is changed, it is expected that the  $M_w$  value trend will be different for different initiator/co-initiator systems, depending on system conditions.

#### Effect of Temperature

From Table I it can be seen that no conversion of propylene oxide was observed at 25°C, but increasing the temperature to 50°C gave 41% PPC conversion. With a further increase of temperature to 70°C, the PPC conversion decreases, and the reaction becomes more favorable for the synthesis of cyclic carbonate. It probably happens due to the backbiting reactions that takes place at higher temperature. The polymerization temperature significantly affects the yield of the polymer but has little influence on the molar mass of polymer formed at two different temperatures, i.e., 50 and 70°C at constant  $M_o/I_o$  ratio. At a particular  $M_o/I_o$  ratio the number of initiating sites available for polymer chain growth remains the same, so the average molar mass remains nearly constant. It is believed that PPC conversion is affected by kinetic and thermodynamic factors. Thus polymerization temperature affects only the yield of the PPC by shifting the equilibrium. But this trend can only be seen up to a limiting value because the backbiting of the polymer chain is expected to take place at still higher temperature. The above trend may show a little variation with a change in initiator/co-initiator system where significant change in

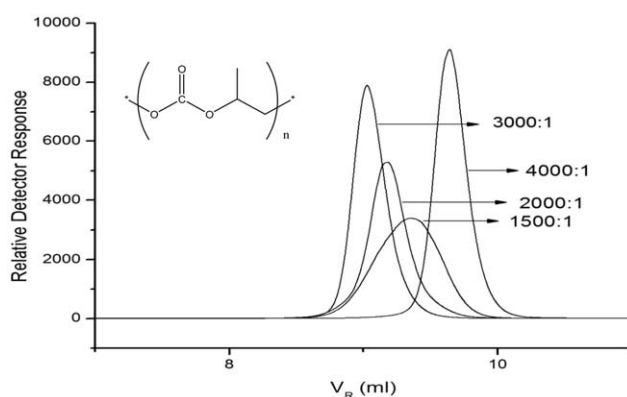
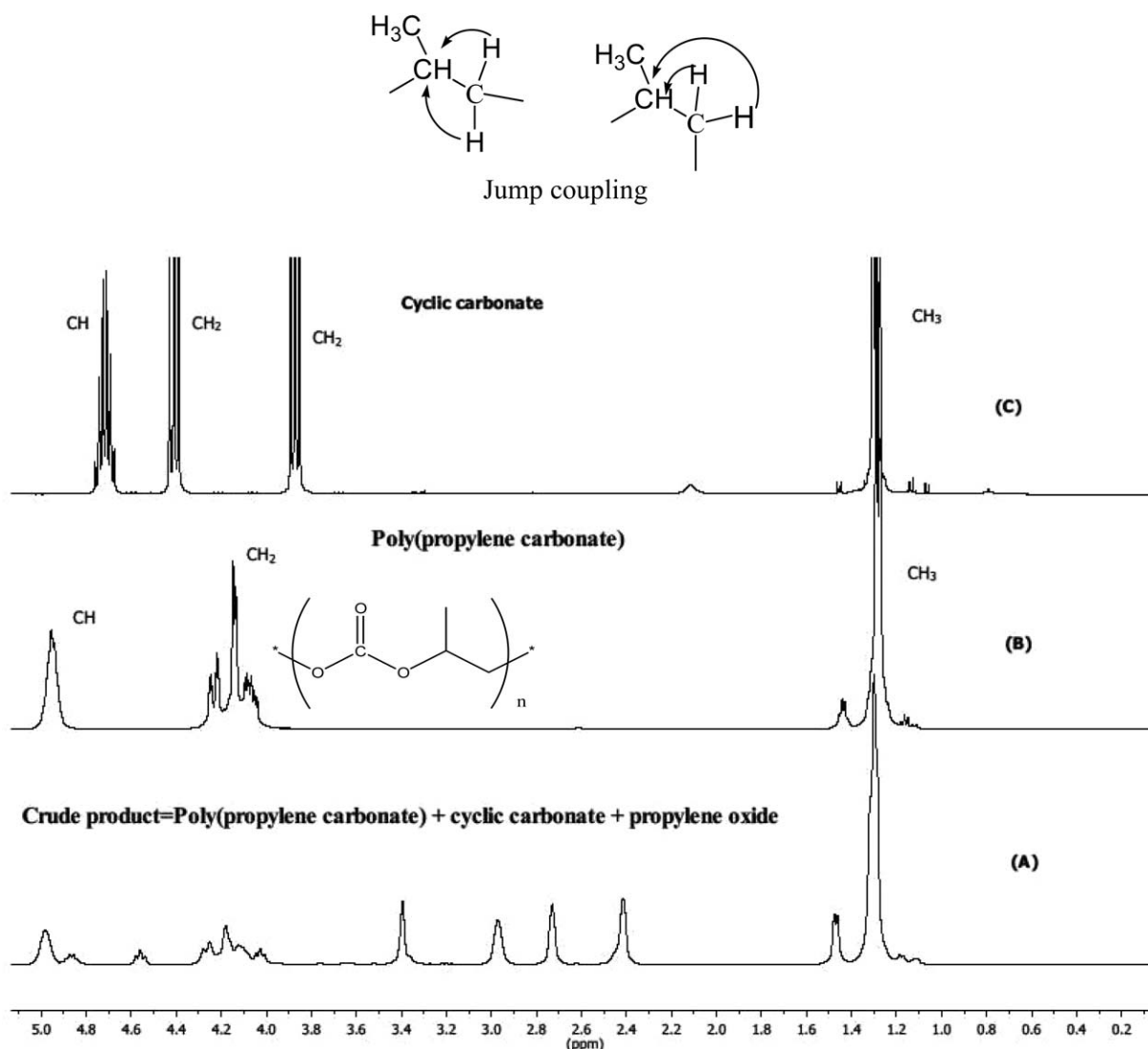


Figure 6. SEC chromatograms of PPC; column: SHODEX GPC KF 806L, detector: ELSD, eluent: THF.



**Figure 7.**  $^1\text{H}$ -NMR spectra of (A) crude product (where the chemical shift at 3.4 is a sharp peak due to methanol since polymerization was terminated with acidified methanol). For propylene oxide, the shifts around 2.4 and 2.7 are due to  $\text{CH}_2$  protons and that around 2.9 ppm is due to CH protons. (B) Poly(propylene carbonate) obtained after separation from reaction mixture and (C) cyclic carbonate (as obtained at 700 rpm).

molecular weight of PPC can be observed with a change in temperature.

#### Characterization of Poly(propylene carbonate)

Figure 7 shows the  $^1\text{H}$ -NMR spectra of crude product, poly(propylene carbonate) obtained after precipitation from the crude mixture, and cyclic carbonate. In the case of  $^1\text{H}$ -NMR spectra of PPC, the shift at 1.3 ppm corresponds to  $\text{CH}_3$  protons of PPC and at 4.2 and 4.8 ppm to  $\text{CH}_2$  and CH protons, respectively (Figure 7). In the case of  $^{13}\text{C}$ -NMR, the shift around 154 ppm corresponds to carbonyl carbon of PPC and at 16, 69, and 72 ppm to  $\text{CH}_3$ ,  $\text{CH}_2$ , and CH carbons, respectively (Figure 8). The  $^{13}\text{C}$ -NMR also helps in explaining the regiochemistry of PPC (Figure 9). The shift at 153.8 ppm corresponds to head-to-head linkages and at 154.2 and 154.7 ppm to head-to-tail and tail-to-tail linkages. Most of the synthesized samples show an abundance of head-to-tail linkages (>90%).<sup>24</sup> HSQC spectroscopy (Figure 10) clearly shows the correlation

between  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra. It is observed in the  $^1\text{H}$ -NMR spectra of the polymeric product that  $-\text{CH}_2$  protons have  $-\text{CH}$  protons in their neighborhood and they should give a doublet in  $^1\text{H}$ -NMR, but probably due to the jump coupling in the case of  $\text{CH}_2$  protons a multiplet (small peaks on the side of the middle intense peak) is observed (Figure 7). This result is further found to be in agreement with the HSQC results, which show the presence of no additional protons and carbons around the region (4.0–4.2 ppm). The FTIR spectra of PPC and cyclic carbonate are shown in Figure 11. The bands at  $1246\text{ cm}^{-1}$  and  $1740\text{ cm}^{-1}$  correspond to C—O stretching and C=O stretching of PPC, respectively, and the bands at  $1120\text{ cm}^{-1}$  and around  $1790\text{ cm}^{-1}$  correspond to C—O and C=O stretching of cyclic carbonate, respectively.

In order to understand the reaction mechanism on a broader scope, a PPC end-group analysis was carried out using  $^{19}\text{F}$ -NMR and Energy Dispersive Spectroscopy (EDS). In the case of  $^{19}\text{F}$ -NMR, the spectrum exhibited resonances at  $\delta = -140.49$ ,

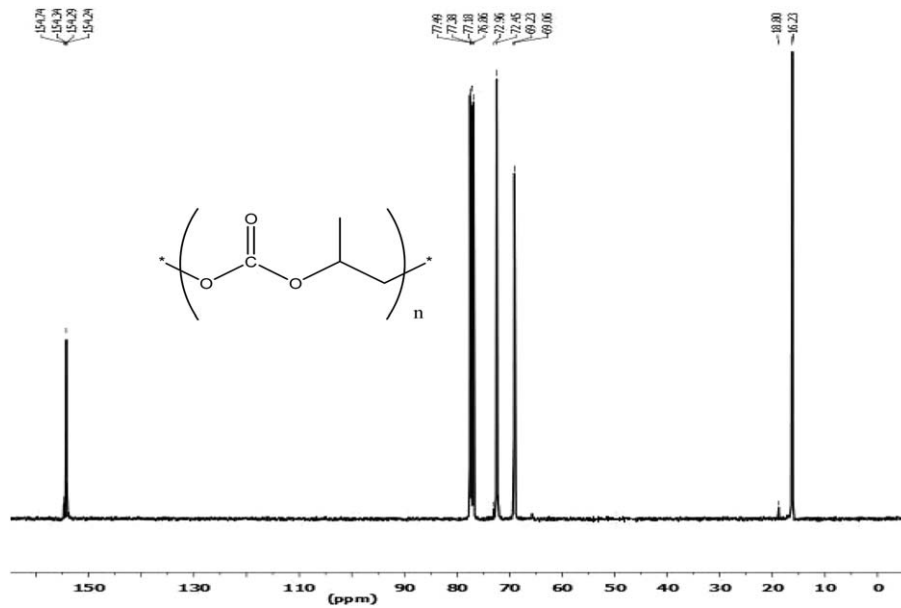


Figure 8.  $^{13}\text{C}$ -NMR of poly(propylene carbonate).

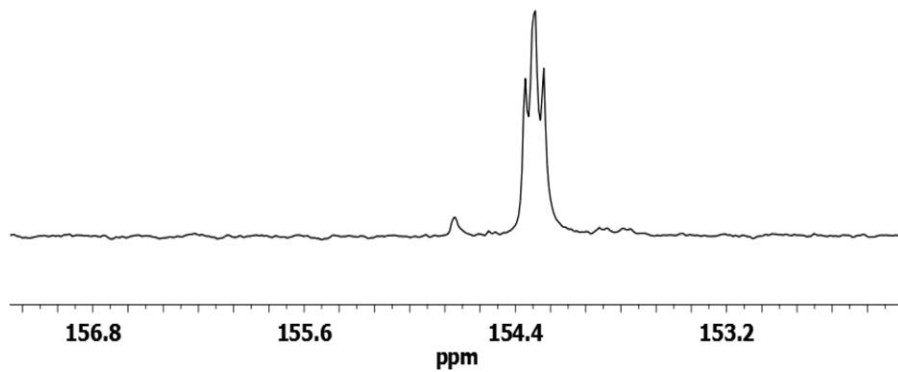


Figure 9. Regiochemistry of poly(propylene carbonate) determined by  $^{13}\text{C}$ -NMR.

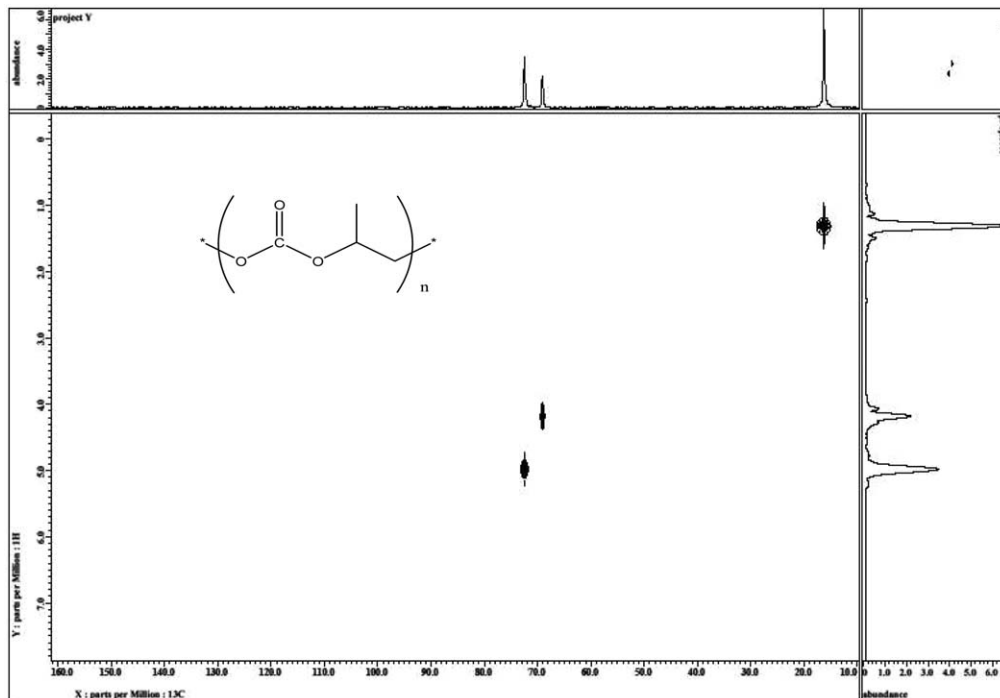


Figure 10. HSQC spectra of poly(propylene carbonate).



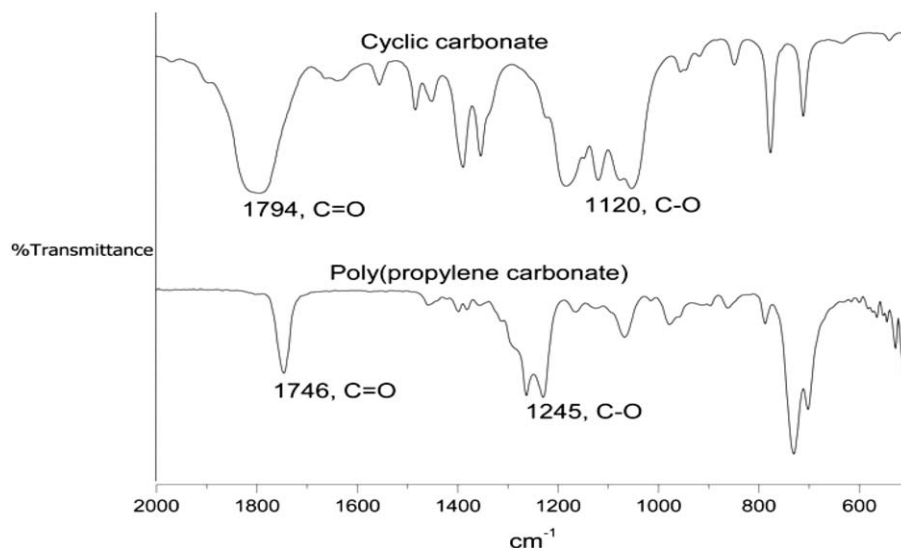


Figure 11. FTIR spectra of poly(propylene carbonate) and cyclic carbonate (as formed at 700 rpm).

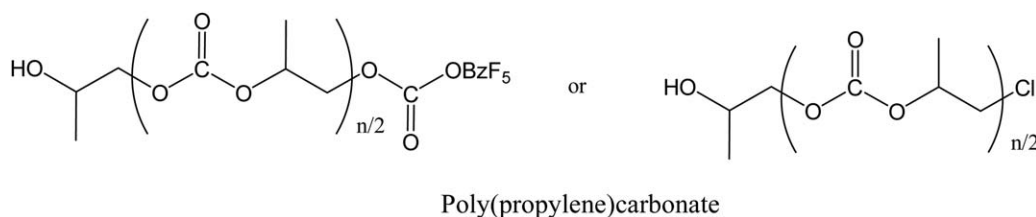


Figure 12. Possible end groups for poly(propylene carbonate).

–148.5, –155.7, –157.1, and –160.7 ppm, which were consistent with a  $\text{OBzF}_5$  moiety of the catalyst attached with PPC. Energy Dispersive X-Ray Spectroscopy (EDX) analysis showed the atomic percent of various elements as C = 52.2, O = 46.5, F = 0.44, and Cl = 0.27 (Figure S1). Thus, from the presence of fluorine and chlorine (nucleophilic groups of catalyst and cocatalyst), it is indicated that both the catalyst and cocatalysts are playing a role in initiating the reaction. It is expected that one end of the polymer chain is either attached to pentafluorobenzoate or chlorine nucleophile while the other end of the chain has a hydroxyl group because the termination of the reaction was carried out using acidified methanol (Figure 12).<sup>34</sup> Because no cobalt is observed in the EDX analysis, we suppose that cobalt has been removed from the polymer chain during the termination.

## CONCLUSION

Poly(propylene carbonate) has been successfully synthesized using a system with an inexpensive achiral  $(\text{Salph})\text{CoOBzF}_5$  as initiator and  $[\text{PPN}]^+\text{Cl}^-$  as co-initiator. Various reaction parameters such as  $M_0/I_0$  ratio, initiator/co-initiator ratio, pressure, temperature, and reaction time affect the molecular weight, yield, and selectivity of the reaction. A significant effect of stirring has been observed, in which PPC conversion increases with increased stirring rate and then becomes almost constant. Low-pressure and high-temperature conditions favor the formation of cyclic carbonate. Increasing pressure to 25 bar and temperature to 50°C significantly increases the yield of

PPC. Also, as expected, the average molar mass  $M_w$  of the polymer first increases with rising  $M_0/I_0$  ratio and then decreases. The polydispersity of all PPC samples was found to be close to unity, as calculated from the SEC results. The maximum  $M_w$  of  $14.8 \times 10^3$  g/mol has been obtained at 25 bar and 50°C.

## ACKNOWLEDGMENTS

This work was supported in part by the All India Council of Technical Education, New Delhi (India) under Project No. 8023/RID/RPS/068/11/12. The support of Sophisticated Analytical Instrumentation Laboratory, Thapar University, Patiala (Punjab), India is gratefully acknowledged.

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