

Copolymerization of Carbon Dioxide and Propylene Oxide Using Zinc Adipate as Catalyst

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ABSTRACT: Zinc adipate was synthesized from zinc oxide with adipic acid by different methods. Their chemical structure and crystalline morphology were determined by Fourier transform infrared spectroscopy (FTIR), wide-angle X-ray diffraction (WXR), and scanning electron microscopy (SEM) techniques. The results showed that the zinc adipate synthesized under magnetic stirring possessed higher degree of crystallinity than that synthesized under mechanical stirring due to the different stirring strength, and therefore exhibited greater catalytic activity for the copolymerization between CO₂ and propylene oxide (PO). The optimum condition for the copolymerization of CO₂ and PO

was also investigated. Very high catalytic activity of 110.4 g polymer/g catalyst was afforded under optimizing copolymerization condition. NMR spectra revealed that the synthesized poly(propylene carbonate) (PPC) had a highly alternating copolymer structure. DSC and TGA examinations showed that the glass transition temperature and decomposition temperature of the PPC with $M_n = 41,900$ Da were 27.7 and 248°C, respectively. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 200–206, 2006

Key words: zinc adipate; carbon dioxide; crystallinity; copolymerization; poly(propylene carbonate)

INTRODUCTION

Carbon dioxide (CO₂), methane, nitrous oxide, and Freon gases are currently regarded as major environmental pollutants that cause global warming or greenhouse effect.^{1–5} Among these gases, CO₂ gives the greatest contribution to the climatic warming. It has been reported that the contribution is about 66%.⁵ Thus, the reduction of CO₂ emission has attracted considerable attention of scientists all over the world.^{5,6} The capture and disposal of CO₂ are actively sought as means to avoid massively releasing this greenhouse gas into atmosphere.⁷ However, from the viewpoints of economy and ecology, the utilization of CO₂ as polymeric monomer is more desirable.

A cost-effective utilization approach is to fix CO₂ into a range of polymers with tailored properties. For example, the aliphatic polycarbonate and the block copolymers of polycarbonate and polyether can be synthesized via the direct copolymerization of CO₂ with epoxides such as ethylene oxide (EO), propylene oxide (PO), isobutylene oxide (BO), or cycloheptene oxide (CHO).⁸ Inoue and coworkers first reported the copolymerization of CO₂ with PO to produce aliphatic polycarbonate using a diethyl zinc/water complex catalytic system.^{9,10} Since then, the copolymerization of CO₂ and epoxides has been widely investigat-

ed.^{8,11–16} In copolymerization process, high active catalyst was needed to activate the inherently low reactivity of CO₂; thus, researchers have developed a number of related catalysts to increase the catalytic activity and improve the copolymerization process^{11–28}. Motika et al. invented zinc carboxylate catalysts for the copolymerization of CO₂ and epoxides by the reaction of zinc oxide with glutaric or adipic acid in an aprotic reaction solvent.²⁸ Darensbourg and coworkers synthesized a group of soluble zinc (II) phenoxides for the copolymerization between CO₂ and cyclohexene oxide.^{29,30} Tan et al. prepared the ternary rare-earth-metal coordinated catalyst consisting of Y(CF₃CO₂)₃, diethylzinc, and glycerine for the copolymerization of CO₂ and propylene oxide.²⁵ Ree et al. improved the catalytic activity of zinc glutarate for the copolymerization of CO₂ with PO under optimized copolymerization conditions, and a high yield of about 70 g polymer per gram of catalyst was achieved.¹⁴ Meng and coworkers optimized the preparation conditions of zinc glutarate from zinc oxide and glutaric acid and fragmented the catalyst particle in a size of 0.2–0.3 μm by ball-milling or ultrasonication so that an extremely high yield of 160.4 g polymer per gram of catalyst was afforded.¹⁶ Among the catalytic systems for the copolymerization of CO₂ with PO reported so far, zinc dicarboxylates (*e.g.*, zinc glutarate) have proved to be the most effective catalysts for the production of aliphatic polycarbonate with reasonably high molecular weight. In particular, zinc glutarate exhibits the highest catalytic activity in the synthesis of poly(propylene

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TABLE I
Preparation of Zinc Adipate under Different Reaction Conditions

Number	Zinc oxide (mmol)	Adipic acid (mmol)	Stirring methods	Reaction temp. (°C)	Reaction time (h)	Yield (%)
1	20	19.2	Magnetic	55	10	87.14
2	20	19.2	Magnetic	70	10	90.07
3	20	19.2	Magnetic	80	10	98.58
4	20	19.2	Magnetic	90	10	92.91
5	20	19.2	Magnetic	100	10	89.36
6	20	19.2	Magnetic	80	4	71.43
7	20	19.2	Magnetic	80	6	91.49
8	20	19.2	Magnetic	80	8	94.29
9	20	19.2	Magnetic	80	12	99.29
10	20	19.2	Mechanical	80	8	99.29

carbonate) (PPC) from CO₂ and PO.^{14,16} However, the cost of zinc glutarate synthesized from zinc oxide and glutaric acid is relatively high, which limits the practicable application of this kind of catalyst for the preparation of PPC. In comparison with zinc glutarate, inexpensive zinc adipate synthesized from zinc oxide and adipic acid has been reported to show relatively high catalytic activity for the copolymerization (polymer yield: 7–19 g/g of catalyst).²⁸ In this regard, the improvement of the catalytic activity of zinc adipate is much significant for commercial usage of CO₂.

In this work, zinc adipates with high catalytic activity were synthesized from zinc oxide and adipic acid *via* different stirring routes. By using the synthesized zinc adipate, high molecular weight alternating PPC in an extremely high yield (110.3 g polymer per gram of catalyst) was achieved by optimizing the reaction conditions.

EXPERIMENTAL

Materials

Propylene oxide (PO) with a purity of 99.5% was purified by distillation for 2 h over calcium hydride under dry nitrogen gas flow. The as-treated PO was then stored over 4 Å molecular sieve prior to use. CO₂ with a purity of higher than 99.8% was used as received. Adipic acid (AA) of 99.0% purity and zinc oxide (ZnO) of 99.0% purity were used without further treatment. Solvents such as toluene and acetone were of analytical reagent grade, whereas chloroform and methanol were of industrial reagent grade. All these solvents were used without further purification for producing catalysts and polymer.

Preparation of catalysts

Zinc adipates were synthesized from the reaction of zinc oxide with adipic acid via magnetic or mechanical stirring route. Adipic acid of 19.2 mmol was dissolved in 150 mL toluene using a 250 mL round-bottom flask equipped with a Dean-Stark trap and a reflux con-

denser with a drying tube for separation and removal of byproduct-water. Fine powdery ZnO (20 mmol) was added to the adipic acid solution in toluene, and then, the slurried mixture was slowly heated to 80°C for 8–12 h under vigorous stirring. The resulting reaction mixture was cooled to room temperature, filtered, and washed several times with acetone. Finally, white powdery zinc adipate was obtained. The reaction yield was estimated by measuring the amount of unreacted adipic acid obtained from the filtrate after removal of toluene and acetone. Each zinc adipate product was dried under vacuum at 100°C for two days, followed by grinding in a mortar. The fine powdery catalysts were dried further at 100°C in a vacuum oven for 3 days before use.

Copolymerization between CO₂ and propylene oxide

All copolymerizations of CO₂ and PO were carried out in a 500 mL autoclave equipped with a sealed mechanical stirrer, a heating jacket, and a programmable temperature controller. The above catalysts were further dried at 100°C for 24 h before being used for the polymerization process. Dry catalyst was then introduced into the autoclave as quickly as possible. The autoclave was finally capped with its head, and the entire assembly was connected to the reaction system equipped with a vacuum line. The autoclave with catalyst inside was further dried for 24 h under vacuum at 100°C. Subsequently, the autoclave was purged with carbon dioxide and evacuated alternatively for three times, followed by adding purified PO using a large syringe. Then the autoclave was pressurized to 5.2 MPa via a CO₂ cylinder. The copolymerization was performed at 60°C under stirring for 40 h. Thereafter, the autoclave was cooled to room temperature and the pressure was released. The resulting viscous mixture was removed from the autoclave, then dissolved in a proper volume of methylene chloride, and transferred to a separating funnel. The residual catalyst was extracted from the product solution

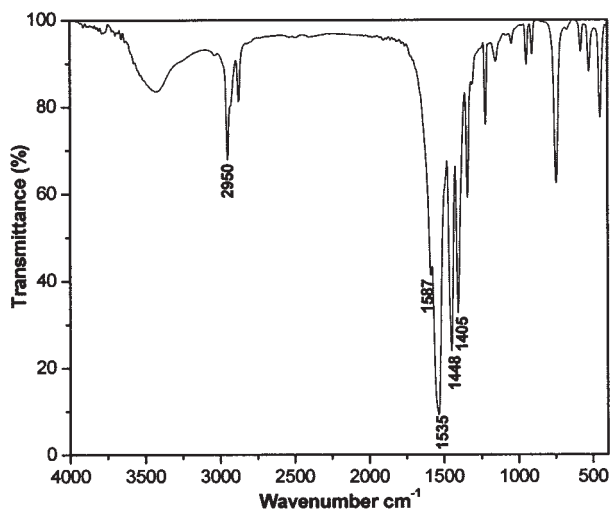


Figure 1 FTIR spectrum of zinc adipate.

by using 200 mL dilute HCl (5%) and then washed three times with distilled water. The viscous solution was concentrated using a rotary evaporator. Finally, PPC copolymer was precipitated out by pouring the concentrated solution into vigorously stirred methanol. The as-made PPC was filtered and dried for two days at 80°C under vacuum. The solvents used were removed from the filtrate by distillation, consequently giving the polymer product that was soluble in methanol.

Characterization

Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a Rigaku D/max-1200 to analyze the structure of catalyst. The 2θ scan data were collected at 0.05° intervals over a range of 2–80°. Infrared spectra were recorded on an Analect RFX-65A FTIR spectrophotometer, using the KBr pellet. The morphology of catalysts was examined by scanning electron microscopy (JSM6330F). The surface areas were determined by the Brunauer-Emmett-Teller (BET) technique, using a Quantachrome BET

analyzer (model: NOVA 1000). The NMR spectra were recorded at 400 MHz in a Bruker NMR instrument (Model: DRX 400 MHz), using Chloroform- d_1 ($CDCl_3$) and Benzene- d_6 (C_6D_6) as the solvent. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined using a gel permeation chromatography (GPC) system (Waters HPLC Pump, Waters 2414 detector) with a set of three columns (Waters Styragel 500A, 10,000A, and 100,000A). The GPC system was calibrated by a series of polystyrene standards with polydispersities of 1.02 supplied from Shodex Inc. THF (HPLC grade) was used as an eluent. In addition, the glass transition temperature (T_g) was determined in a modulated TA DSC instrument (model NETZSCH 204) at the heating rate of 20°C/min under a nitrogen flow of 100 mL/min. The T_g value was recorded from the second scan after first heating and quenching. Thermogravimetric analysis was carried out in a Pekin-Elmer thermogravimetric analyzer (TGA/DTA; model TGS-2) under a protective nitrogen atmosphere (100 mL/min) at the heating rate of 10°C/min.

RESULTS AND DISCUSSION

Preparation and characterization of zinc adipate catalysts

Zinc adipates were synthesized from zinc oxide and adipic acid via magnetic and mechanical stirring methods. Zinc oxide is insoluble in toluene; thus, zinc adipate catalyst has been prepared with adipic acid via a slurry reaction. In the process, zinc adipate gradually precipitated out from the reaction solution because of the insolubility of zinc dicarboxylate in toluene. Upon completion of the reaction, the products in white powder were filtered off and washed several times with acetone, followed by drying under vacuum at 100°C. The yields of zinc adipate are summarized in Table I.

The synthesis procedure of zinc adipate is similar to that of zinc glutarate.^{14,16} Considering the crystalline nature of adipic acid and high melting point of 152–

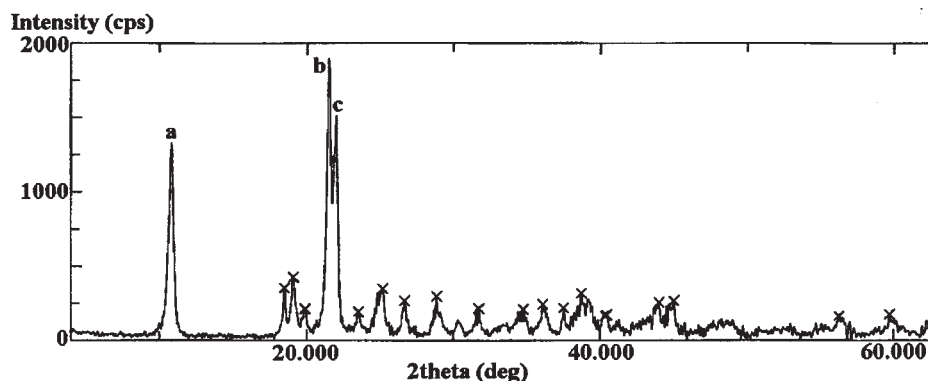


Figure 2 Wide-angle X-ray diffraction pattern of zinc adipate.

TABLE II
Surface Area and XRD Data of Zinc Adipate Synthesized via Different Stirring Methods

Catalyst	Surface area (m ² /g)	Intensity/FWHM			Lc		
		Peak a	Peak b	Peak c	Peak a	Peak b	Peak c
Cat. 1 ^a	8.92	8404	8610	6241	355	299	300
Cat. 2 ^b	11.86	5638	6716	10702	355	299	599

^a Cat. 1 synthesized via magnetic stirring method.

^b Cat. 2 synthesized via mechanical stirring method.

154°C, high reaction temperature is favorable for the reaction of zinc oxide with adipic acid. As shown in Table I, it can be seen that the yield increases with increasing temperature up to 80°C, and thereafter decreases with further increasing temperature. Moreover, the yield of zinc adipate increases with increasing reaction time up to about 10 h and then levels off at a high yield of > 99%. Purer zinc adipate can be obtained at a prolonged reaction time. Finally, the reaction under the mechanical stirring processes faster than that under magnetic stirring, indicating that strong stirring favors the diffusion of adipic acid into the surface of zinc oxide.

Figure 1 shows a typical FTIR spectrum of zinc adipate. The characteristic absorption peaks are assigned as follows: FTIR (KBr), 1587 cm⁻¹ (COO⁻ antisymmetric stretching), 1535 cm⁻¹ (COO⁻ antisymmetric stretching), 1405 cm⁻¹ (COO⁻ symmetric stretching), 2950 cm⁻¹ (—CH₂— stretching), and 1448 cm⁻¹ (—CH₂— scissoring). All vibrational peaks are similar to those for zinc glutarate.¹⁴ The stretching peak of carbonyl group (C=O) at around 1700 cm⁻¹, a vibrational characteristic peak of adipic acid, was not observed, demonstrating the completed reaction of adipic acid.

Figure 2 shows a typical X-ray diffraction pattern of zinc adipate. To determine the crystalline characteristics of catalysts synthesized via different stirring routes, three peaks a–c located at around 11.8, 21.5, and 22.0° were selected to calculate their intensity/FWHM (full width at half-maximum) values and Lc's (coherence length) as listed in Table II. By comparing the intensity/FWHM and Lc values, the crystallinity of magnetic-synthesized zinc adipate is much higher than that of mechanical synthesized one. However, their crystal sizes (Lc) remained almost same for both catalysts. This suggests that both overall crystallinity and crystal perfection of zinc adipate are influenced by stirring strength. Strong stirring can result in a faster formation of zinc adipate, but lower crystallinity and smaller particle sizes. As shown in Table II, the surface area of Cat. 2 is greater than that of Cat. 1.

A typical SEM image of zinc adipate (Cat. 1) is given in Figure 3. It exhibits a rectangular crystal with a particle size of about 200 nm. As determined by TGA

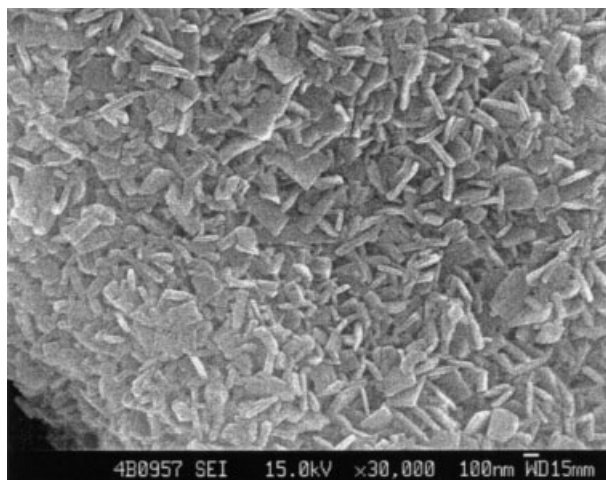


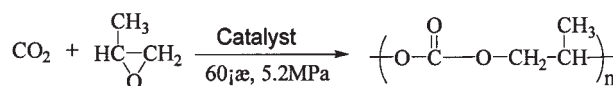
Figure 3 Typical SEM micrographs of zinc adipate particle.

method, the weight loss of Cat. 1 started at 376°C, indicating the high thermal stability of zinc adipate.

Copolymerization of CO₂ and PO

As depicted in Scheme 1, the copolymerization of CO₂ and PO has been extensively studied elsewhere in literature using zinc dicarboxylates as catalyst.^{14,16,31,32} According to previous work,^{16,31} polymer yield and molecular weight depended on reaction condition, such as CO₂ pressure, temperature, and time. In addition, the autoclave and catalyst must be dried thoroughly prior to copolymerization because trace water can reduce largely the catalytic activity of catalyst and in turn give low yield of PPC with low molecular weight.

The copolymerization results are summarized in Table III. By changing catalyst/PO ratio, an optimum catalytic activity can be achieved as seen in Table III. The PPC with a high molecular weight of 53,400 Da was obtained in an extremely high yield (110.4 g polymer/g of catalyst) when the catalyst/PO ratio was fixed at 0.3/100. Smaller catalyst/PO ratio led to lower yield of PPC because of the lower catalyst concentration in reaction system. In contrast, higher ratio led to a higher viscous polymerization system that restricts the diffusion of living polymer end and then reduces the yield of copolymer. Meanwhile, the molecular weight of copolymer shows a decreasing trend with increasing the catalyst concentration. As shown in Table III for the relationship between the crystallinity of zinc adipate and its catalytic activity, it can be seen



Scheme 1 Copolymerization between carbon dioxide and propylene oxide.

TABLE III
Results of Copolymerization Between CO₂ and PO

Catalyst	Weight of catalyst (g)	Loadings of PO (ml)	Yield (g/g of catalyst)	M_n (10 ³)	M_w (10 ³)	PI
Cat. 1	0.20	100	57.3	44.1	274.4	6.2
Cat. 1	0.25	100	95.9	41.9	115.9	2.8
Cat. 1	0.30	100	110.4	53.4	172.9	3.2
Cat. 1	0.40	100	103.1	41.9	104.7	2.5
Cat. 1	0.50	100	88.3	40.1	91.9	2.3
Cat. 1	0.60	100	82.2	37.7	6.5	2.0
Cat. 1	0.80	100	69.7	34.4	69.3	2.0
Cat. 1	1.0	100	52.4	38.6	84.3	2.2
Cat. 2	0.40	100	88.9	47.9	160.6	3.4
Cat. 2	0.50	100	79.3	28.4	65.2	2.3
Cat. 2	0.60	100	73.9	39.2	81.7	2.1

Reaction conditions: CO₂ pressure, 5.2 MPa; temperature, 60°C; and time, 40 h.

that Cat. 1 with high crystallinity exhibited very high catalytic activity, while, Cat. 2 with low crystallinity showed apparently lower catalytic activity. Similarly, Ree et al. reported that the high crystallinity of zinc glutarate was desirable for the fixation of CO₂ into a polymer chain.¹⁴ Generally, higher crystallinity of catalyst can lead to a higher catalytic activity. For each copolymerization, the polymer product insoluble in methanol was obtained with > 99% of the total yield; instead, the polymer product soluble in methanol was obtained in a very small portion, <<1% of the total yield.

As listed in Table IV, the yield of copolymer increased with increasing reaction time, up to 40 h, and then leveled off with further increasing reaction time. This is because the resulting viscous reaction system precluded the diffusion of living polymer end, resulting in no further increase of the polymer yield. The molecular weight increased with increasing reaction time up to 30 h, and thereafter decreased slightly with the further increase. Presumably, this is due to subsequent degradation or depolymerization of resulting copolymer in the presence of catalyst in the polymerization system during the long reaction time.

The relationship between reaction temperature and copolymerization can be seen in Table V. The yield of

copolymer increased with increasing temperature up to about 60°C, and then decreased dramatically with the further increase. The decrease of polymer yield at higher temperature is presumably due to the polymer degradation during the polymerization.

As shown in Table VI, the copolymer yield increased with increasing CO₂ pressure, followed by decreasing with further increasing CO₂ pressure under pressure > 5.2 MPa. The possible reason is due to the solubility change of produced polymer in the mixture of PO and CO₂. In general, CO₂ content increases with increasing its pressure, while CO₂ is a nonsolvent for the resulting polymer. However, the molecular weight of resulting polymer increased with increasing the CO₂ pressure owing to the concentration increase of reactant in a nonsolvent.

Structure and properties of synthesized PPC

As described in experimental section, the structure of methanol insoluble polymer was investigated by ¹H NMR and ¹³C NMR spectroscopy, respectively. For ¹H NMR spectrum (Fig. 4), the observed peaks were assigned as follows: ¹H NMR (CDCl₃), δ (ppm) 1.34 (*d*, 3H; —CH₃), 4.18 (m, 2H; —CH₂CH—), and 5.00 (m, 1H; —CH₂CH—). For ¹³C NMR spectrum (Fig. 4), the peaks were assigned as follows: ¹³C NMR (C₆D₆), δ

TABLE IV
Effect of Reaction Time on the Copolymerization of CO₂ and PO

Reaction time (h)	Weight of catalyst (g)	Loadings of PO (ml)	Yield (g/g of catalyst)	M_n (10 ³)
10	0.4	100	18.8	51.5
20	0.4	100	61.2	52.5
30	0.4	100	80.8	61.0
40	0.4	100	103.1	41.9
48	0.4	100	105.1	40.1

Reaction conditions: CO₂ pressure, 5.2 MPa; temperature, 60°C.

TABLE V
Effect of Reaction Temperature on Copolymerization of CO₂ and PO

Reaction temperature (°C)	Weight of catalyst (g)	Loadings of PO (ml)	Yield (g/g of catalyst)	M_n (10 ³)
40	0.4	100	7.3	59.0
50	0.4	100	57.4	62.9
60	0.4	100	103.1	41.9
70	0.4	100	0.5	—

Reaction conditions: CO₂ pressure, 5.2 MPa; time, 40 h.

TABLE VI
Effect of CO₂ Pressure on Copolymerization of CO₂ and PO

CO ₂ pressure (Mpa)	Weight of catalyst (g)	Loadings of PO (ml)	Yield (g/g of catalyst)	M_n (10 ³)
2.0	0.4	100	65.7	31.4
4.0	0.4	100	85.5	40.1
5.2	0.4	100	103.1	41.9
6.0	0.4	100	88.9	40.2
6.5	0.4	100	16.6	57.2

Reaction conditions: temperature, 60°C; time, 40 h.

(ppm) 15.9 (—CH₃), 69.2 (—CH₂CH—), 72.5 (—CH₂CH—), and 154.8 (—OCOO—). Compared with the results in literature,¹⁴ the NMR data prove that the as-made PPC has an alternating structure. However, in ¹H NMR spectrum, two very weak peaks at ~1.16 and 3.58 ppm were observed. These peaks may correspond to the protons of CH₃ and CH₂CH in

poly(propylene oxide) (PPO), respectively. According to literature,¹⁴ the NMR data of PPO are as follows: ¹H NMR (CDCl₃), δ (ppm) 1.16 (*d*, 3H; —CH₃), 3.58 (2H; —CH₂CH—), and 3.45 (1H; —CH₂CH—); ¹³C NMR (C₆D₆), δ (ppm) 17.8 (—CH₃), 73.8 (—CH₂CH—), and 75.7 (—CH₂CH—). Therefore, it can be concluded that the polymer had highly alternating structure (Scheme 1) together with very small amount of PPO. In addition, the FTIR spectrum of as-made PPC demonstrated characteristic absorption of ester group at 1745 cm⁻¹ (*s*, C=O), 1235 cm⁻¹ (*s*, C—O), and 787 cm⁻¹ (*s*, C—O).

The obtained PPC was amorphous as reported previously in the literature.^{14,31} Thermal properties of the PPC were determined by DSC and TGA techniques. The DSC and TGA curves with molecular weight of 41,900 Da were given in Figure 5. Glass transition temperature (*T_g*) was detected to be 27.7°C in the DSC run under a nitrogen atmosphere, and thermal degradation temperature (*T_d*) appeared to be 248°C in the

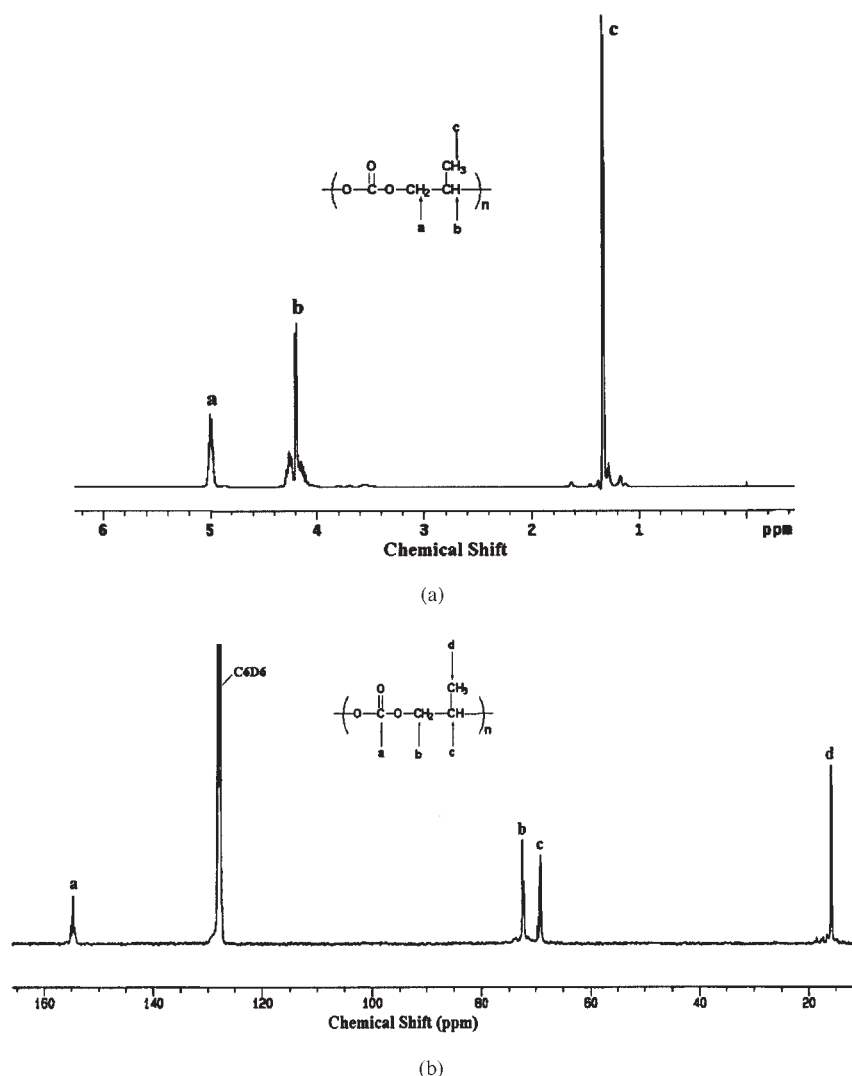


Figure 4 ¹H NMR (4a) and ¹³C NMR (4b) spectra of the obtained PPC.

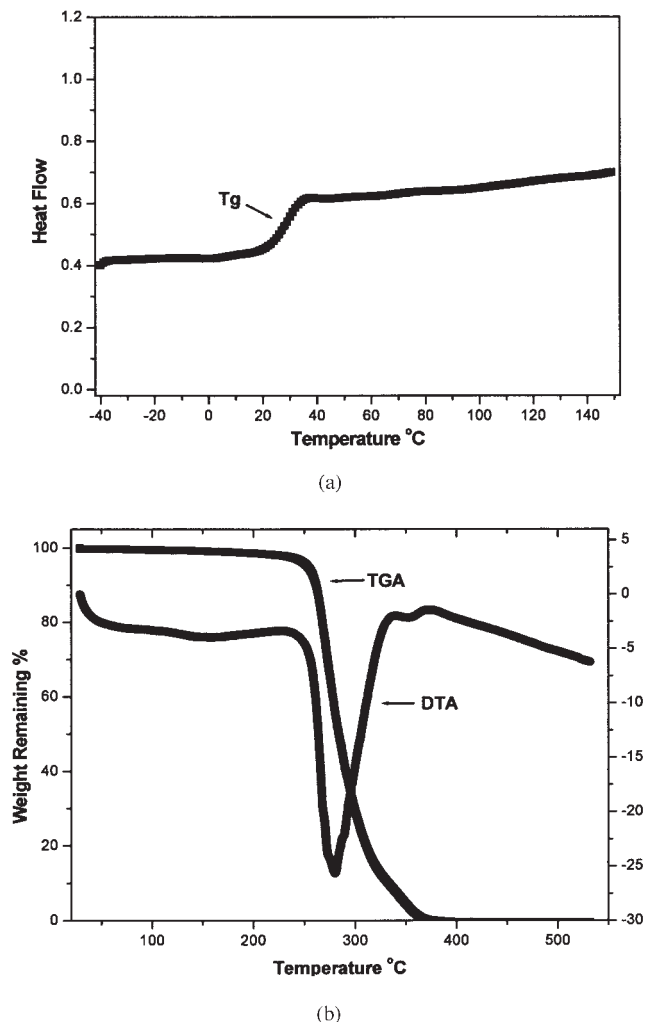


Figure 5 DSC (5a) and TG/DTA (5b) curves of the obtained PPC ($M_n = 41,900$ Da).

TG run under a nitrogen atmosphere. Both results demonstrate good thermal properties for the as-prepared PPC.

CONCLUSIONS

Zinc adipates can be synthesized from zinc oxide and adipic acid via magnetic stirring and mechanical stirring routes. The experimental results showed that zinc adipates synthesized by magnetic stirring demonstrated high crystallinity and low surface area, whereas the zinc adipates synthesized by mechanical stirring had low crystallinity and high surface area. The results also showed that catalyst with high crystallinity exhibited higher catalytic activity than that with low crystallinity. Poly(propylene carbonate)s with high molecular weight can be afforded in an extremely high yield of 110.4 g polymer/g catalyst by optimizing the catalyst/PO ratio. The optimum reaction conditions for the copolymerization of CO_2 and PO catalyzed by zinc adipate are as follows: 60°C,

40 h, and 5.2 MPa CO_2 pressure. The NMR data revealed that the obtained PPC had a highly alternating molecular structure. The obtained PPC copolymer also exhibited a high glass transition temperature of 27.7°C and decomposition temperature of 248°C. The low cost zinc adipate with high catalytic activity is favorable for the potential and practical application in the copolymerization of CO_2 and propylene oxide.

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