

Synthesis and Characterization of Alternating Copolymer from Carbon Dioxide and Propylene Oxide

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ABSTRACT: High yield and pure zinc glutarate catalysts used for copolymerization of carbon dioxide and propylene oxide have been synthesized in different solvents by ultrasonic methodology. For the purposes of comparison, low-yield zinc glutarates were also synthesized via mechanical stirring method with other synthetic conditions remaining unchanged. Fourier Transform Infrared Spectroscopy and wide-angle X-ray diffraction techniques confirmed the presence of high-quality zinc glutarate catalysts. Accordingly, poly(propylene carbonate) (PPC) can be synthesized from carbon dioxide and propylene oxide using the zinc glutarate catalysts. It was confirmed that the as-prepared PPC had an alternating copolymer structure together with high molecular weight. The thermal and mechanical properties of the obtained PPC copolymer were determined by means of differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile test. DSC and TGA results showed that the PPC copolymer exhibited high glass transition temperature (39.39°C) and decomposition temperature (278°C) when compared to their corresponding values reported in the literature. Tensile test showed that the PPC film exhibited superior mechanical strength. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2327–2334, 2002

Key words: copolymerization; polycarbonate; synthesis; catalysis

INTRODUCTION

Carbon dioxide (CO₂) is currently regarded as an environmental pollutant that causes the greenhouse effect.¹ Thus, the prevention of massive CO₂ emission to the atmosphere has been the subject of a variety of research works. Proper utilization and disposal of CO₂ are considered as effective means to reduce the release of green-

house gas to the atmosphere.² From the economy and ecology viewpoints, the utilization of CO₂ is preferred. The approach is to use carbon dioxide as a reacting monomer, and then fixing CO₂ as a resource into the polymeric materials. For a typical example, aliphatic polycarbonates can be synthesized via the direct copolymerization of CO₂ with epoxides such as ethylene oxide (EO), propylene oxide (PO), isobutylene oxide (BO), and cycloheptene oxide (CHO). Inoue and coworkers were the first to report the conversion of carbon dioxide and epoxide to polycarbonate in 1969. A catalyst derived from diethyl zinc/water was used to activate the carbon dioxide.³ Since then, a variety of related catalysts and catalyst precursors containing zinc or other metals have been re-

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vealed to improve the catalytic efficiency and copolymerization process.⁴

Among the catalysts reported, zinc dicarboxylates (e.g., zinc glutarate) are the most effective catalysts for the alternating copolymerization of CO₂ and epoxides to produce high molecular weight polycarbonates.⁵ However, the yield of the polymerization product is rather low, generally lower than 40 g polymer/g catalyst. More recently, Ree and coworkers have reported an efficient way to enhance the catalytic efficiency of zinc glutarate for the copolymerization of CO₂ and PO. Their method can produce very high yield poly(propylene carbonate).⁶ However, the starting material (zinc oxide) used in the synthesis of catalyst must be in the form of a very fine powder, and the resulting catalysts also need to be ground into fine powders of 2–3 μm prior to the polymerization process. To achieve a high interdispersion of powdered materials, the ultrasonic stirring method has been used to prepare catalysts for the gas-phase oxidation of saturated and unsaturated hydrocarbons.⁷ However, an ultrasonic approach for the fabrication of zinc dicarboxylates catalyst has not been reported in the literature. For this article, we attempted to synthesize zinc glutarate catalysts under ultrasonic stirring. Such catalysts were to be used for the copolymerization of CO₂ and PO. Alternating poly(propylene carbonates) with high molecular weight were achieved. The molecular structures and properties of PPC were analyzed by nuclear magnetic resonance spectroscopy (NMR), Ubbelohde viscometry, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile test.

EXPERIMENTAL

Materials

Propylene oxide with a purity of 99.5% was refluxed for 2 h over calcium hydride under dry nitrogen gas. It was then stored over 4 Å molecular sieves prior to use. Carbon dioxide, with a purity higher than 99.8%, was used as received. Glutaric acid (GA) of 98.0% purity, and solvents such as toluene, tetrahydrofuran, acetone, methylene dichloride, were of analytical reagent grade and used without further purification. Zinc oxides of 99.5 and 99.99% purity were used without further treatment.

Preparation of Catalysts

Zinc glutarate was synthesized from zinc oxide and glutaric acid by two different routes. In the

first method, zinc glutarate was prepared under mechanical stirring as described elsewhere,⁸ and zinc oxide powders were used as received without further grinding. Accordingly, to a 250-mL three-neck round-bottom flask equipped with mechanical stirrer, condenser, and a Dean-Stark trap were added 100 mmol zinc oxide (purity 99.5 or 99.99%) and 150-mL toluene. To this mixture was added 98 mmol glutaric acid, and the mixture was slowly heated up to 55°C for several hours under vigorous stirring. Upon cooling, the resulting mixture was filtered. The resulting solid was continuously washed with acetone several times followed by drying overnight in a vacuum oven at 80°C. The obtained zinc glutarate was a fine powder of white color. In the second route, the reaction was performed under ultrasonic stirring instead of mechanical stirring. To a 250-mL round-bottom flask equipped with condenser, Dean-Stark trap, and ultrasonic bath (120 W, 40 kHz) were added 100 mmol zinc oxide (purity 99.5 or 99.99%), 98 mmol glutaric acid and 150 mL toluene. The mixture was stirred ultrasonically for a constant period of time. The temperature of the reaction mixture increased automatically up to about 50–53°C during ultrasonic stirring. Upon termination of the reaction, the resulting mixture was filtered and washed with acetone for several times. The pure zinc glutarate powders were dried at 80°C overnight in a vacuum oven.

Copolymerization

The copolymerization of CO₂ and PO was carried out in a 100 mL autoclave, which was equipped with a magnetic stirrer. The clean autoclave was dried at 100°C for 24 h in a vacuum oven, and quickly transferred into a dry glove box. Zinc glutarate was dried at 100°C for 24 h prior to being used for the polymerization process; 0.4 g dry zinc glutarate was charged into the autoclave. The autoclave was then capped with its head, and the entire assembly was connected to the reaction system equipped with a vacuum line. The autoclave, with zinc glutarate in it, was further dried for 48 h under vacuum at 100°C in an oil bath. Meanwhile, the catalyst was dried *in situ* under vacuum at the same temperature for another 48 h. After drying, the autoclave was purged with carbon dioxide and evacuated alternately three times, followed by adding 40 mL purified PO using a syringe. The autoclave was then pressurized to 51.5 atm with CO₂ cylinder. The copolymerization was performed at 60°C with a stirring speed

Table I Preparation of Zinc Glutarates by Different Methods

Cat. No	Preparing Method	Purity of Zinc Oxide	Reaction Time, h	Conversion of Glutaric Acid (%) ^a
1	mechanic stirring	99.50%	5	57.52
2	mechanic stirring	99.50%	10	94.94
3	Ultrasonic stirring	99.50%	4	75.94
4	Ultrasonic stirring	99.50%	8	98.40
5	Ultrasonic stirring	99.50%	10	100
6	Ultrasonic stirring	99.99%	10	60.00
7	Ultrasonic stirring	99.99%	20	95.75
8	Ultrasonic stirring	99.99%	25	97.27

^aThe conversion of glutaric acid was calculated from the amount of unreacted glutaric acid after removal of the used toluene and acetone from the filtrate.

of about 100 rpm. After a 40-h reaction the autoclave was cooled to room temperature and the pressure was released. The resulting viscous mixture was taken out, dissolved in 200 mL methylene chloride, and transferred to a separating funnel. The catalyst residue was extracted from the copolymer by using 200 mL dilute hydrochloric acid (5%). The extracting process was repeated three times, and the resulting copolymer solution was subsequently washed with water. The final mixture was concentrated by using a rotary evaporator, and the PPC product was precipitated out by pouring the copolymer solution into methanol. The precipitate was filtered, drying in a vacuum oven at room temperature. Subsequently, the resulting filtrate was distilled to remove methanol and methylene chloride to yield the copolymer product that was soluble in methanol.

Characterization

Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature using a Rigaku D/max-1200X diffractometer to analyze the structure of zinc glutarate. The 2°C scan data were collected at a 0.05° interval over a range of 4–90°. The WAXD patterns were deconvoluted according to the method described elsewhere.⁹ An interactive curve-fitting technique based on the nonlinear least-squares estimation algorithm was used to fit the WAXD profile. From the deconvoluted peak, coherence length (L_c) was estimated from its full width at half-maximum (FWHM) with an instrumental broadening of 0.15° by using the Scherrer equation.¹⁰ The glass transition temperature was determined on a Perkin-Elmer 7 DSC instrument at a heating rate of 20°C/min under nitrogen flow. The decomposition process of

the polymers from 30 to 500°C was determined with a Seiko thermogravimetric analyzer (TGA/DTA; model SSC-5200) under a protective nitrogen atmosphere (200 mL/min). The heating rate employed was 20°C/min⁻¹. NMR data were recorded at 400 MHz in a Bruker NMR instrument (Model: DRX 400MHz), and listed in parts per million downfield from tetramethylsilane (TMS). Chloroform-*d*₁ (CDCl₃) was used as the solvent. The molar fraction of CO₂ units in the copolymer products was determined by ¹H-NMR spectroscopy. The inherent viscosities [η] of the synthesized copolymers were measured at 30°C and at a concentration about 0.5 g/dL using an Ubbelohde suspended level capillary viscometer. The [η] was determined by extrapolation of the reduced and inherent viscosities to infinite dilution. Mechanical properties of the films were measured at 23°C using an Instron tester (Model: 4206).¹¹ The samples with dimensions of 0.03 × 5.0 × 50 mm³ were prepared from methylene chloride by the solution casting method. They were tested at a crosshead speed of 5 mm/min. At least five samples were tested, and the average value is reported.

RESULTS AND DISCUSSION

Zinc Glutarate Catalysts

Table I summarizes the results of Zinc glutarate synthesized via different methods. Zinc glutarate was obtained via the slurry reactions by reacting glutaric acid with zinc oxide due to the insolubility of zinc oxide in toluene. As described in literature, zinc oxide should be ground to a fine powder prior to the reaction to afford a high yield of product. Moreover, the slurry reaction should be

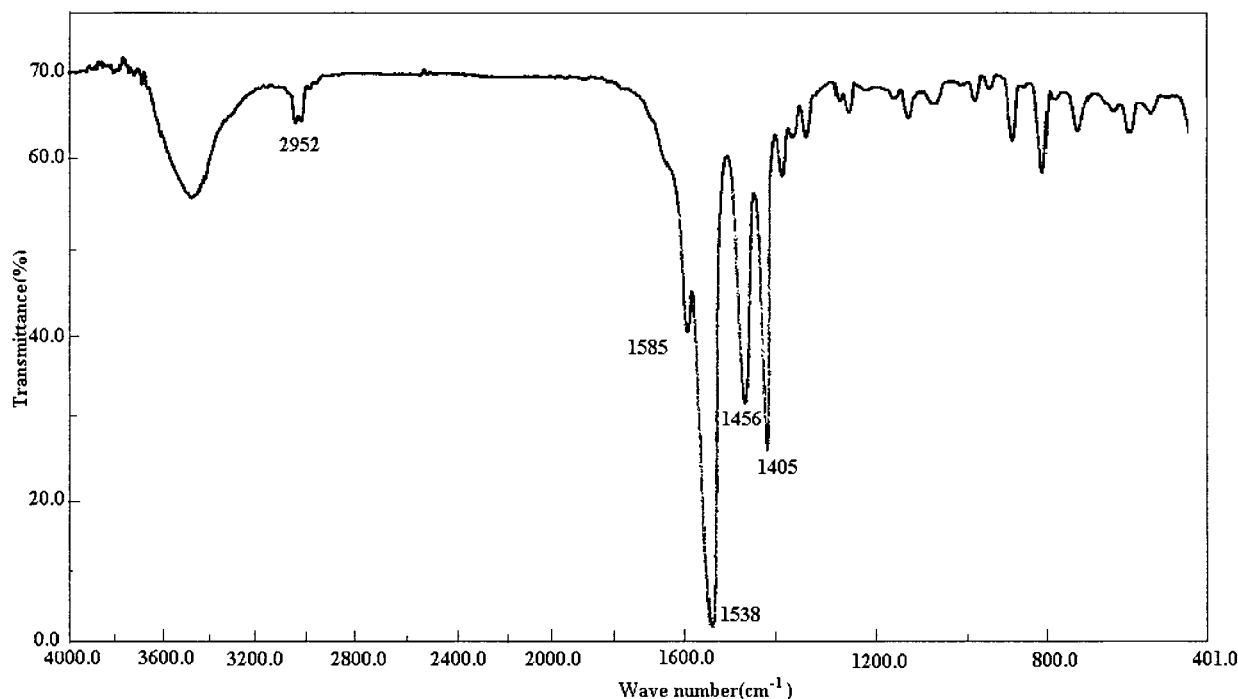


Figure 1 FTIR spectrum of the zinc glutarate (Cat 5) synthesized by ultrasonic stirring.

performed under vigorous stirring. Herein, we report on the efficiency of a synthetic method for zinc glutarate using ultrasonic stirring. As shown in Table I, the conversions of glutaric acid into zinc glutarate by the ultrasonic method are obviously higher than those by the mechanical method. Very high yield of 98.40% was achieved after an 8-h reaction under ultrasonic stirring. Furthermore, there was no need to heat the reaction mixture because the ultrasonic stirring caused an increase of the reaction temperature up to about 50–60°C during stirring. In general, this process of self-heating requires about 20 to 30 min. For zinc oxide with 99.50% purity, the 100% conversion of glutaric acid can be achieved within 10 h of ultrasonic stirring, demonstrating that ultrasonic stirring can obviously accelerate the reaction. The effect of ultrasound on chemical reactions has been extensively reviewed during the past few years,¹³ and is considered to result primarily from cavitation. This refers to the formation, growth, and implosive collapse of bubbles created in the dispersion medium. When a bubble collapses near an extended surface of the solid-liquid systems, high-speed liquid jets that are produced impinge on the surface. This can lead to particle fracture or erosion.¹⁴ In addition, the shock waves generated during the collapse can

cause small particles to collide into one another at a speed of about half the sound velocity. It is believed that the high yield of zinc glutarate prepared by the ultrasonic method results from a high interdispersion of the starting materials. In contrast, it is difficult to afford 100% conversion of zinc oxide of 99.5% purity by mechanical stirring, as shown in Table I. It is worth mentioning that a low yield of zinc glutarates is obtained when very pure zinc oxide (99.99% purity) is used under ultrasonic stirring. Only 60% yield is achieved even for 10 h reaction time, indicating that the ultrasonic effect for synthesis is different for zinc oxides of various purities. Low yield is presumably due to purer zinc oxide having a more perfect crystal structure. As a result of this, a high yield of zinc glutarate of 97.27% from very pure zinc oxide can be obtained only by extending reaction time to 25 h.

It is well known that purer materials are more active for use as catalysts. Figure 1 shows the FTIR (KBr) spectrum of catalyst No 5 with 100% yield. In this spectrum, the coordination characteristic absorption peaks of zinc glutarate are detected as: 1585 cm^{-1} (COO^- antisymmetric stretching), 1538 cm^{-1} (COO^- antisymmetric stretching), 1405 cm^{-1} (COO^- symmetric stretching), 2952 cm^{-1} (CH stretching), and 1456 cm^{-1}

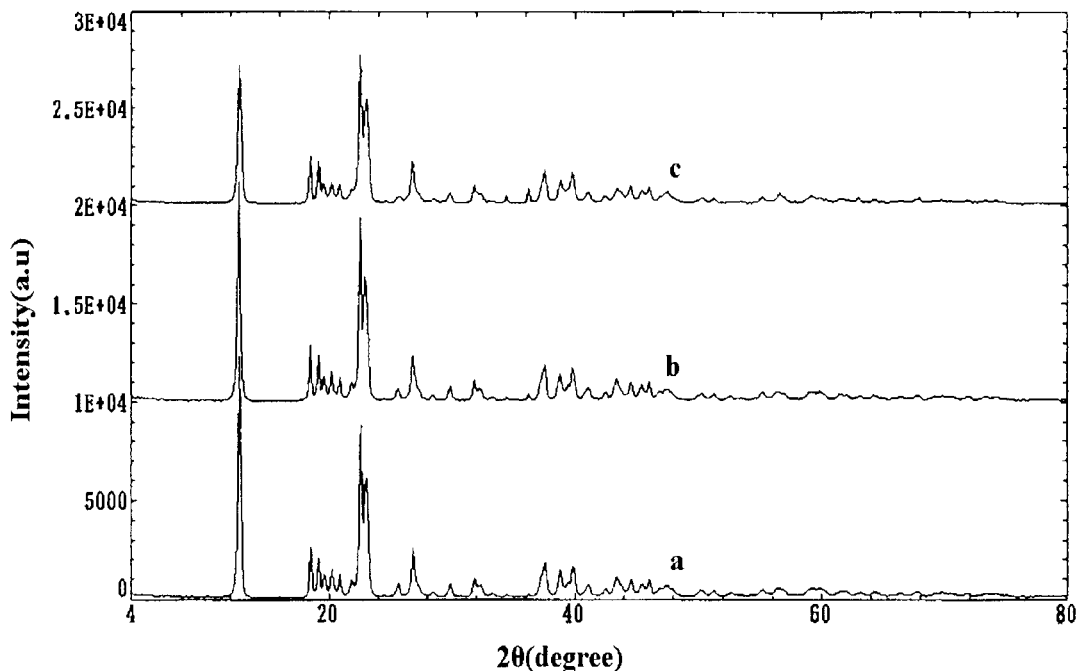


Figure 2 Wide-angle X-ray diffraction patterns of the zinc glutarates synthesized by (a) ultrasonic stirring (10 h); (b) mechanical means (24 h); (c) mechanical means (10 h).

(CH₂ scissoring). All the IR peaks are in accordance with the results reported by other researchers.⁶

Figure 2 shows the WAXD pattern of the catalyst 5. The diffraction pattern of the catalyst is similar to that of zinc glutarate reported by Ree et al.,⁶ indicating that the catalyst synthesized by ultrasonic stirring possesses the same crystalline structure. Ree et al. pointed out that zinc glutarate exhibits the same crystal structure regardless of the synthetic route. However, the size and quality (perfection) of crystal are different for various catalysts synthesized from different starting materials. The broadness of peaks in the corresponding diffraction patterns can be used to assess the size of crystallites. Based on the calculation from Figure 2, we can conclude that the crystal size of zinc glutarate, synthesized by the ultrasonic route, is slightly smaller than those by mechanical stirring. Nevertheless, the overall crystallinity is difficult to calculate exactly. By careful calculation from WAXD results, it is estimated that the overall crystallinity of zinc glutarate prepared by the ultrasonic process is about 5% higher than that by the mechanical method. It is believed that the reason is that the former process can produce high yield products.

The thermal stabilities of the zinc glutarate catalysts were analyzed by TGA, and the 5 wt %

weight loss temperature of catalyst 5 was determined to be 422.79°C. All zinc glutarates were very thermally stable, with their 5 wt % loss temperatures generally higher than 400°C. This implies that these catalysts can be heated up to a relatively high temperature to dry or activate the catalysts.

Copolymerization of CO₂ and PO

The copolymerization process of propylene oxide and carbon dioxide has been extensively studied^{6,14} because both PO and CO₂ are commercially available at reasonable prices. It is well established that both yield and molecular weight of the resulting copolymer depend upon the carbon dioxide pressure, temperature, and reaction time. Accordingly, the copolymerization was carried out at 50–60°C for 40 h under a carbon dioxide pressure of 51.5 atm using PO as either monomer or solvent.

The autoclave needs to be dried prior to the polymerization because the water absorbed on its wall can seriously affect activity of zinc glutarate catalysts. The process generally takes an extended period of time, for example, 2 or 3 days.⁶ In this work, we adopted an *in situ* drying process, i.e., the catalyst that was charged in the reactor and autoclave was simultaneously dried at 100°C under vacuum for 2 days prior to use.

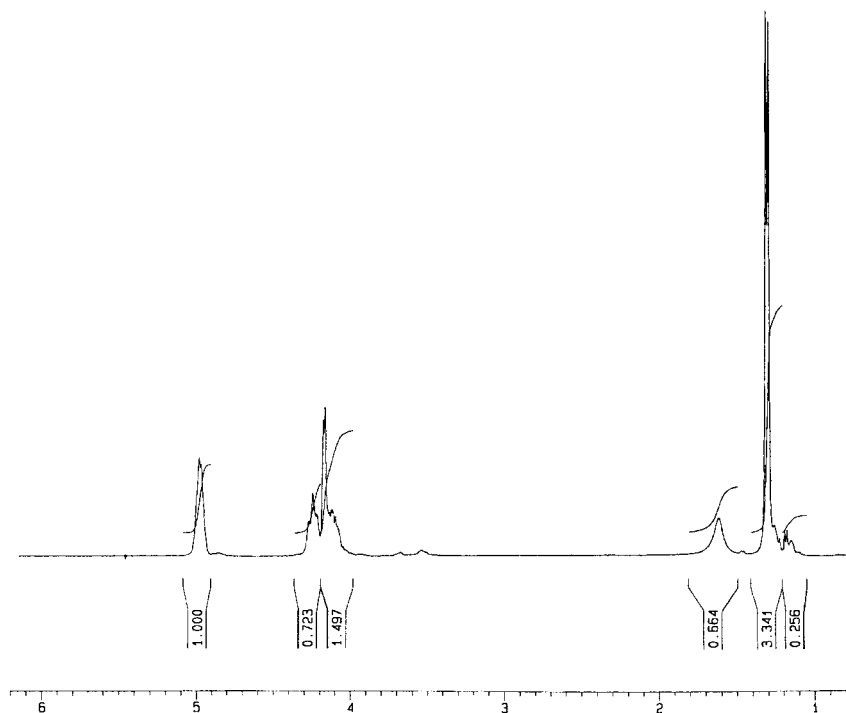


Figure 3 $^1\text{H-NMR}$ spectrum of the alternating copolymer from carbon dioxide and propylene dioxide catalyzed by zinc glutarate prepared by ultrasonic stirring.

The synthesized zinc glutarate with the highest yield (Cat 5) was used for the copolymerization of CO_2 and PO. A high yield of about 40 g polymer/g catalyst for the alternating poly(propylene carbonate) was achieved. Meanwhile, polymer containing more ether linkages and soluble in methanol was separated and collected in a very small portion (less than 1 wt %). The $^1\text{H-NMR}$ spectrum for the alternating poly(propylene carbonate) is shown in Figure 3, that is, $^1\text{H-NMR}$ (CDCl_3): δ (ppm) 1.34 (d, 3H; CH_3 $J = 5.5$ Hz), 4.17 (m, 2H, CH_2CH), 5.00 (m, 1H, CH_2CH). From the NMR data, an alternating poly(propylene carbonate) was indeed made by the zinc glutarate. After purification according to the procedure stated in the Experimental section, the as-prepared alternating poly(propylene carbonate) had a white color and could be cast into a tough and transparent film. The inherent viscosity measurements of the alternating copolymer in benzene indicated that the copolymer had a molecular weights (\overline{M}_n) $> 50,000$.

Properties of the Alternating Copolymer

The glass transition temperature (T_g) of the alternating PPC was measured to be 39.39°C from the

DSC run under a nitrogen atmosphere (Fig. 4). The 5 wt % weight loss temperature (T_d) from TGA appeared at 278°C under nitrogen atmosphere, as shown in Figure 5. Both the T_g and decomposition temperatures of the alternating PPC in this work are much higher than those revealed elsewhere. The high decomposition temperature implies that the as-prepared PPC could be melt processed at a temperature of about $100\text{--}140^\circ\text{C}$, and, therefore, a conventional extrusion process could be used to produce PPC extrudates. Despite the fact that the decomposition of PPC synthesized in this work takes place suddenly above its decomposition temperature, the decomposition temperature of 278°C is much higher than the possible processing temperature of 140°C .

The synthesized alternating PPC with a molecular weight of 50,000 can be cast into a thin film with a thickness of about 0.05 mm. The static mechanical behavior of the alternating PPC is depicted in Figure 6. Apparently, the PPC demonstrates a high tensile strength of 32 MPa and tensile modulus of 950 MPa at 23°C . The synthesized PPC exhibits superior mechanical strength that is comparable to polypropylene and polyethylene.

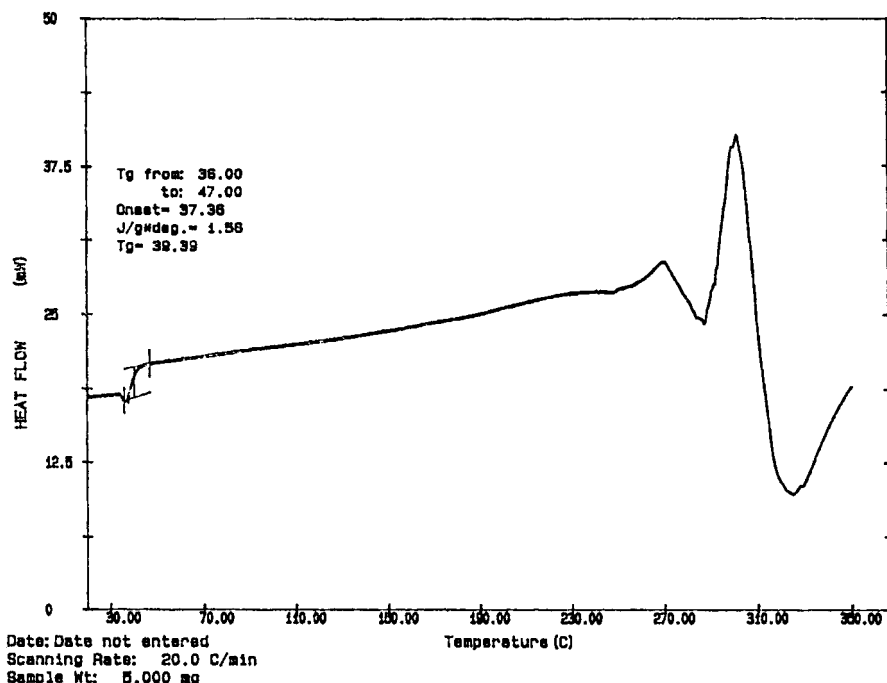


Figure 4 DSC curve of the alternating PPC copolymer.

CONCLUSIONS

Zinc glutarates were prepared by ultrasonic stirring from various zinc oxides of various purities. The synthesized zinc glutarates exhibited high crystallinity together with crystallites in small size and perfection. Alternating polycarbonate was successfully synthesized from carbon dioxide and propylene oxide in the presence of zinc glutarate catalysts. The catalytic efficiency of the zinc glutarate prepared by the ultrasonic method was

higher than that by mechanical means. The activities of these catalysts can be further improved by grinding the zinc glutarates into fine powders. High yields and high molecular weights of the alternating polycarbonates were obtained. Accordingly, the PPC exhibited a high glass transition temperature of 39.39°C, and 5% weight loss temperature of 278°C. Superior static mechanical properties of the resulting alternating PPC were afforded. The PPC with a molecular weight of 50,000 had a tensile strength of 32 MPa and tensile modulus of 950 MPa at 23°C. The PPC copol-

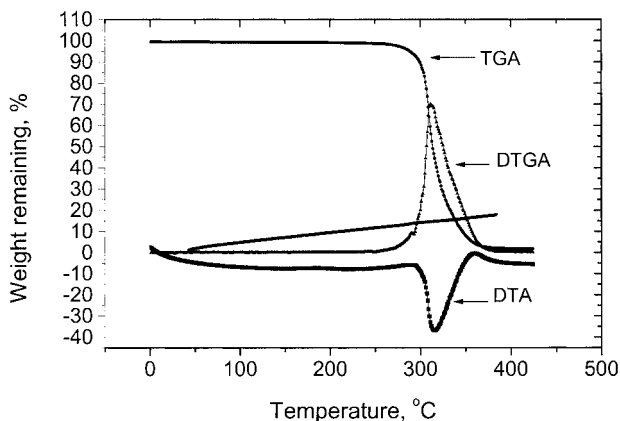


Figure 5 TGA, DTA, and DTG curves for the alternating PPC copolymer.

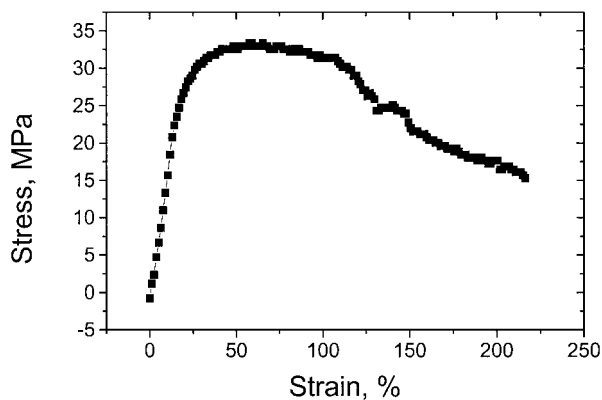


Figure 6 Typical stress-strain curve of the alternating PPC copolymer obtained at 23°C.

ymer shows potential applications as the substitutes for thermoplastic polyolefins and degradable green polymers.

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