Melt Processable and Biodegradable Aliphatic Polycarbonate Derived from Carbon Dioxide and Propylene Oxide

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ABSTRACT: Alternating poly(propylene carbonate)s (PPC)s were successfully synthesized from carbon dioxide and propylene oxide in higher yield than previously reported. Such thermally stable and high molecular weight copolymers were achieved by optimizing the reaction conditions. The molecular structural change and mechanical properties of the alternating copolymer subjected to melt extrusion were examined by means of modulated differential scanning calorimetry (MDSC), thermogravimetric analysis (TGA), NMR, and tensile tests. The MDSC and TGA results showed that the alternating copolymer generally exhibits a high glass-transition temperature of above 40°C and a decomposition temperature of above 250°C. These PPCs can be readily melt processed under conditions similar to those for commercial polyolefins. For instance, they can be melt extruded in a temperature range from 150 to 170°C under varying extrusion pressures. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3301–3308, 2003

Key words: polycarbonates; processing; biodegradable; extrusion

INTRODUCTION

Climate warming or the greenhouse effect is attributed to the release of carbon dioxide into the atmosphere.[1] It is estimated that carbon dioxide causes about 66% of climate warming.[2] Thus, the utilization of CO_2 has attracted increasing attention recently as an effective approach to reduce the release of greenhouse gas.[3] Among these applications, the most advantageous is to employ carbon dioxide to produce degradable polymeric materials. Plastic waste, which is called "white-pollution," is mainly derived from packaging materials such as trash bags, agricultural mulch films, and food wrappers. This challenging project has forced scientists to develop new degradable materials. Polyolefins can be degraded by the presence of oxygen and UV rays,[4,5] but the process is extremely slow. However, the copolymerization of CO_2 with other organic compounds such as epoxides can form aliphatic polycarbonates and renders them biodegradable.

According to the literature, aliphatic polycarbonates derived from carbon dioxide and propylene oxide (PO) can be synthesized using various catalysts, such as organometallic compounds and their complexes, metallic complexes, as well as polymer-supporting bimetallic catalysts.[6] However, there is a big hurdle for large-scale commercialization of the new polymers. The catalytic efficiency of the these catalysts remains rather low. For example, the most effective catalyst reported by Ree et al. is zinc glutarate, which has a yield of only 64 g polymer/g catalyst[7]; and extremely strict experimental conditions have to be employed to afford the highest yield.[8] In previous work, we prepared zinc glutarate catalysts under magnetic stirring followed by supporting them on perfluorinated compounds.[9] By optimizing the reaction conditions, high molecular weight poly(propylene carbonate) (PPC) with an exact alternating structure was achieved with an extremely high yield (126 g polymer/g catalyst).
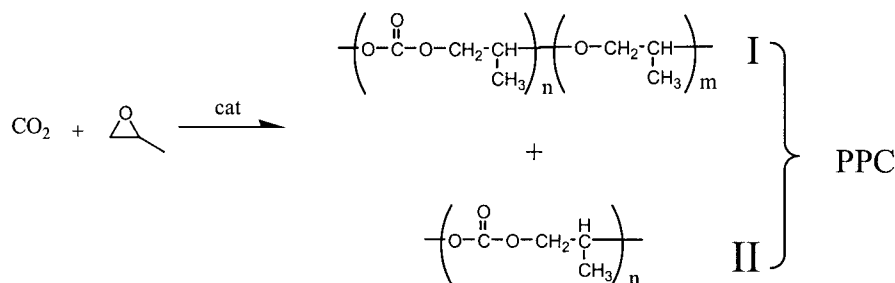
Scheme 1

The PPCs also exhibit good biodegradability in both soil burial and buffer solution immersion tests.[10b]

Most PPCs synthesized by using different catalysts exhibit thermally unstable properties. This behavior mainly results from the presence of high ether bond content in the backbone and hydroxyl groups in the polymer chain ends. Accordingly, the glass-transition temperature (T_g) and decomposition temperature are lower than 30 and 180°C, respectively.[11] Because of the strict alternating structure, the PPCs synthesized in our lab contain about 43 wt % carbon dioxide. The new polyaliphatic carbonates therefore exhibit superior thermal and mechanical properties,[9] and the PPC made in this manner could be melt processed like commercial polypropylene. In this work, the mechanical properties and the molecular structure change of the PPC prior to and after melt processing are examined by the means of modulated differential scanning calorimetry (MDSC), thermogravimetric analysis (TGA), NMR, and tensile tests. The results demonstrate that the alternating copolymer can be melt extruded at temperatures ranging from 150 to 170°C under varying extrusion pressures.

EXPERIMENTAL

Materials

The purification of 99.5% pure PO was carried out by distillation over calcium hydride under a dry nitrogen gas flow for 2 h. In some cases, the PO was further purified by simultaneous distillation over sodium hydroxide and calcium hydride under dry nitrogen gas for 6 h. The as-treated PO was then stored over 4 Å molecular sieves prior to use. Carbon dioxide with a purity of higher than 99.8% was used as received. Glutaric acid (GA) was 98.0% pure. Solvents such as toluene, methanol, acetone, and methylene dichloride were analytical reagent grade and used without further purification. Zinc oxide of 99.99% purity and perfluorinated compounds were also used without further treatment.
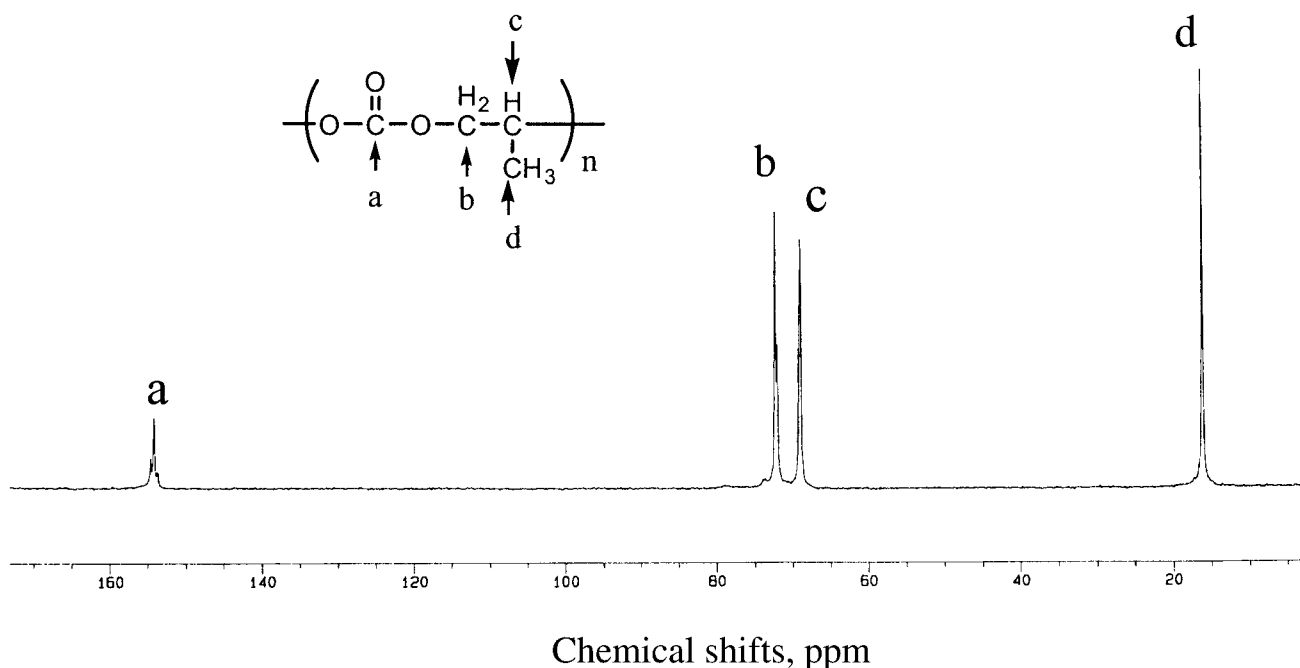

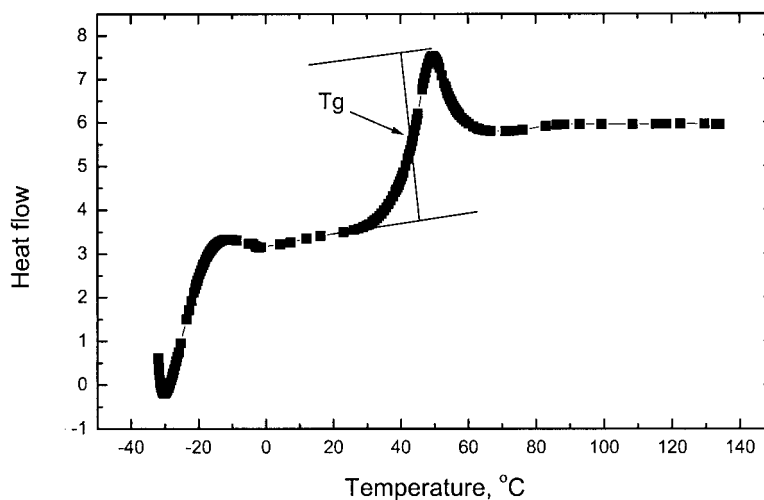**Figure 1** The ^{13}C-NMR spectrum of the alternating PPC copolymer.

Figure 2 A typical DSC trace for the alternating PPC copolymer.

Preparation of aliphatic polycarbonates

Zinc glutarate was synthesized from zinc oxide and GA under magnetic stirring as described in the literature.[12] The supported catalyst was synthesized according to previous work.[9,10] To a 150-mL three-neck round-bottom flask equipped with a magnetic stirrer, condenser, and a Dean Stark trap were added 60 mmol zinc oxide and 90 mL of toluene. Then 58.8 mmol GA and 1.176 mmol perfluorinated compound were introduced into it, and the mixture was slowly heated to 55°C and maintained at this temperature for 6–8 h under vigorous stirring. After purification, a white fine powder catalyst was attained. The copolymerization of CO$_2$ and PO was carried out in a 2-L autoclave equipped with a mechanical stirrer. Supported zinc glutarate was dried at 100°C for 24 h prior to the polymerization process. Then the dried sup-

ported zinc glutarate was introduced into the autoclave as quickly as possible. The autoclave was capped, and the entire assembly was connected to the reaction system equipped with a vacuum line. The autoclave with the catalyst inside was further dried for 24 h under a vacuum at 100°C. Subsequently, the autoclave was purged with carbon dioxide and alternately evacuated 3 times, followed by adding purified PO with a large syringe. The autoclave was then pressurized to 5.0 MPa via a CO$_2$ cylinder. The copolymerization was performed at 60°C under stirring for 40 h. The resulting viscous mixture was removed and dissolved in a proper volume of methylene chloride. The residual catalyst was extracted from the product solution by using 500 mL of dilute hydrochloric acid (5%), followed by washing 3 times with distilled water. The viscous solution was concentrated by using a rotary
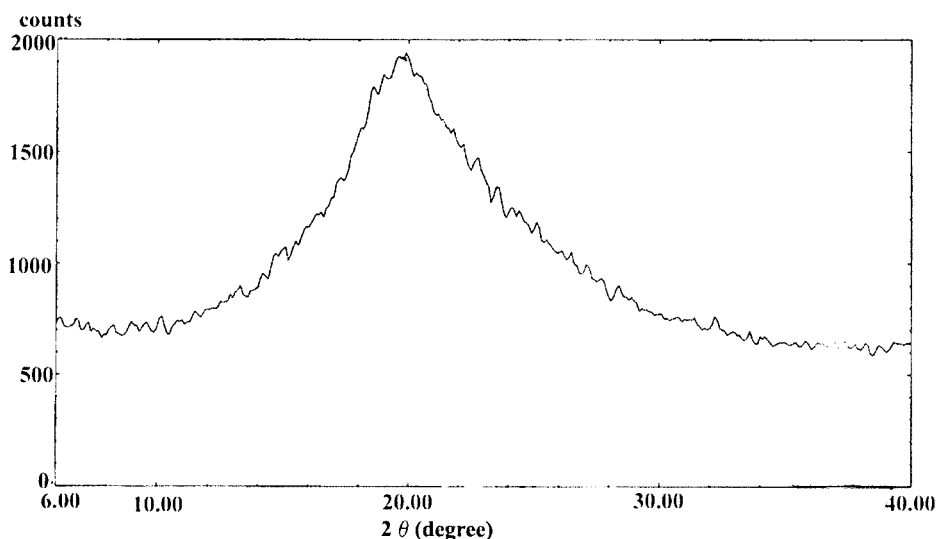

Figure 3 A typical wide-angle X-ray diffraction spectrum of the alternating PPC copolymer after annealing.

TABLE I
Thermal Properties for Alternating PPC Copolymer with Varying Number-Average Molecular Weights (M_n)

| Sample | (M_n) | T_g (°C) | TGA$_{-5\%}$ (°C) | | T_{max} (°C) |
			He$_2$	O$_2$	He$_2$
1	56.1	38.24	233.0	230.1	256.1
2	62.5	41.01	256.6	254.7	271.6
3	142.8	45.83	252.1	249.0	279.5
4	144.6	46.46	255.8	250.8	275.8

TGA$_{-5\%}$, 5% weight loss temperature; T_{max}, maximum weight loss temperature.

evaporator to give a concentration of about 10 wt %. Finally, PPC was precipitated by pouring the concentrated PPC solution into vigorously stirred methanol. The PPC product was filtered and dried for 2 days at room temperature under a vacuum.

Melt extrusion of PPC copolymers

The alternating copolymers with number-averaged molecular weights of 56,000, 88,000, and 114,000 were melt extruded in a melt indexer (μPXRZ-400B) equipped with a standard die at various temperatures. The die has a smooth straight bore with a diameter of 2.0955 ± 0.0051 mm and a length of 8.000 ± 0.025 mm. The measurements and melt extrusion of the PPCs were performed according to the ASTM D1238-82 standard. The investigated temperatures ranged from 150 to 180°C. Two different loads were employed at each temperature during the melt extrusion process. The appearance of extrudates was imaged using a digital camera.

Characterization

The T_g was determined in a modulated thermal analysis DSC instrument (model 2910) at a heating rate of 20°C/min under a nitrogen flow of 100 mL/min. The decomposition process of the PPCs from 30 to 400°C was carried out using a Seiko TG analyzer (TGA/dynamic thermal analysis, model SSC-5200) under a protective helium or nitrogen atmosphere (100 mL/min) and a ramping rate of 20°C/min. Wide-angle X-ray diffraction measurements were performed at room temperature using a Rigaku D/max-1200X diffractometer. NMR data were recorded at 400 MHz in a Bruker NMR instrument (model DRX) and were listed in parts per million (ppm) downfield from tetramethylsilane. Chloroform-d_1 (CDCl$_3$) was used as the solvent. The molar fraction of CO$_2$ units in the copolymer products was determined by ^{1}H-NMR spectroscopy. In addition, intrinsic viscosity [η] measurements were carried out in benzene at 35°C using an Ubbelohde suspended level capillary viscometer. The molecular weight was calculated from the equation [η] = 1.11 × 10^{-4} [M_n]$^{0.8}$ (dL/g).[13] The static mechanical properties of the PPC copolymer were measured at 17°C using an Instron tester (model 4206). The measurement was performed at a cross-head speed of 5 mm/min. Thin film specimens with dimensions of 0.1 × 80 × 5 mm^3 were cast from methylene chloride.
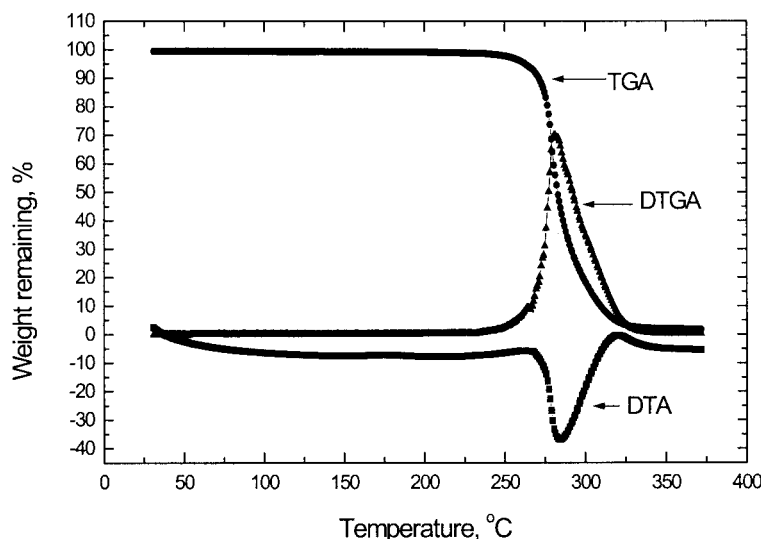

Figure 4 The thermogravimetric analysis (TGA), dynamic thermal analysis (DTA), and derivative TG analysis (DTGA) curves for the alternating PPC copolymer.

TABLE II
Melt Index of Alternating PPC Copolymers At Three Number-Average Molecular Weights

Extrusion condition	Melt Index (g/10 min)		
	56,000	89,000	114,000
150°C and 2.16 kg	0.1789	0.0579	0.0185
150°C and 21.6 kg	10.120	4.0365	1.0706
170°C and 2.16 kg	0.6930	0.4200	0.3878
170°C and 21.6 kg	39.870	29.647	—
180°C and 2.16 kg	1.6250	1.2903	1.0744

RESULTS AND DISCUSSION

Molecular structure of aliphatic polycarbonate

The copolymerization of CO_2 and PO has been extensively reported by other researchers.[14] The reaction is depicted in Scheme 1.

In previous work[9] the copolymerization of CO_2 and PO was performed in 100- and 500-mL autoclaves, respectively, using a perfluorinated compound supported zinc glutarate as a catalyst that was synthesized under ultrasonic stirring. Highly alternating PPC copolymer was afforded in very high yield. The copolymerization was carried out under a pressure of 5.0 MPa with PO as either a monomer or solvent. In this process the autoclave must be dried thoroughly because the trace water on or in the reactor can seriously reduce the activity of the catalyst and in turn yield low molecular weight PPC. Therefore, the autoclave and the catalyst in the reactor were simultaneously dried at 100°C under a vacuum for 24 h prior to the copolymerization. The purified alternating PPC copolymer exhibits a white color, and it can be cast into a flexible transparent film using a solution of about 10 wt % concentration followed by drying under ventilation.

The ^{1}H-NMR and ^{13}C-NMR spectra for the PPC copolymer are assigned as follows: ^{1}H-NMR ($CDCl_3$, δ): 1.34 (d, 3H, —CH_3), 4.17 (m, 2H, —H_2C—), 5.00 (m, 1H, —OCH—); ^{13}C-NMR (ClD_3, δ): 16.1 (—CH_3), 69.0 (—CH_2CH—), 72.2 (—CH_2CH—), 154.2 ($OCOO$). When comparing the spectrum of random the PPC copolymer synthesized by other workers, there is no evidence for the presence of any trace amount of ether units [poly(PO)] that would appear at 1.16 and 3.58 ppm (Scheme 1, structure I): ^{1}H-NMR ($CDCl_3$, δ): 1.16 (d, 3H, —CH_3), 3.58 (2H, —CH_2CH—), 3.45 (1H, —CH_2CH—).[6h,6i] This result demonstrates that the synthesized PPC copolymer exhibits a strict alternating molecular structure (Scheme 1, structure II), implying that the carbon dioxide content in the PPC is greater than 43 wt %. Moreover, the ^{13}C-NMR spectrum (Fig. 1) also indicates an exact alternating molecular structure for the synthesized PPC with only four different kinds of carbon species. The

alternating PPC copolymer behaves as an amorphous copolymer because no melting point is observed prior to its decomposition in MDSC measurements (Fig. 2). A wide-angle X-ray diffraction spectrum (Fig. 3) also reveals that the PPC does not exhibit any crystallinity, even after being annealed at 100°C for 48 h.
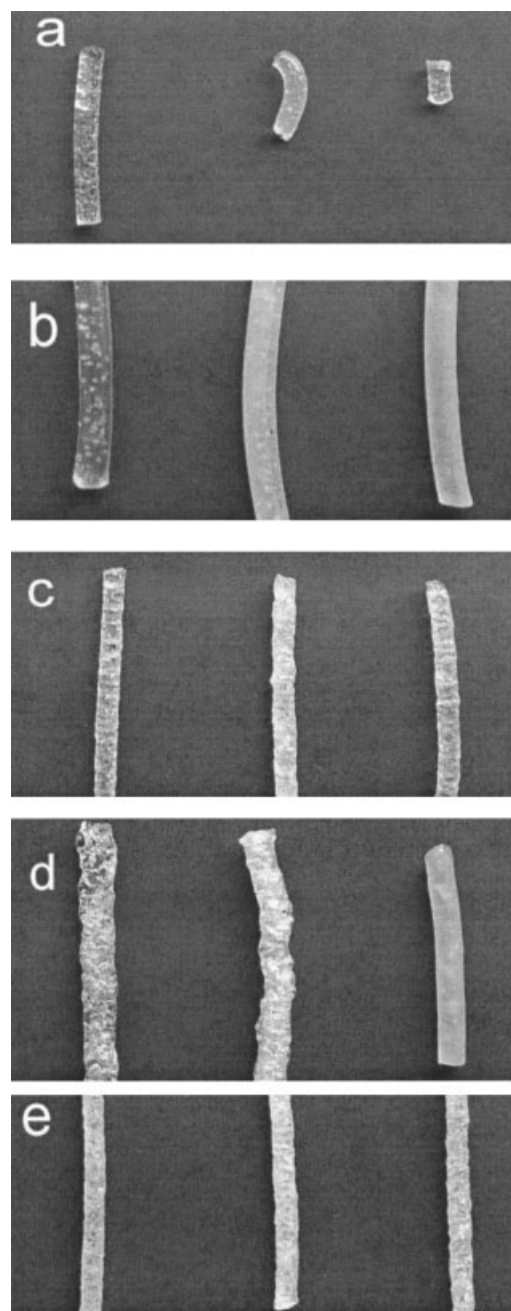

Figure 5 The appearance of the alternating PPC copolymer extrudates obtained under varying extrusion conditions. The molecular weights of the PPCs from left to right are 56,000, 89,000, and 114,000, respectively. Melt extrusion conditions: (a) 150°C and 2.16 kg, (b) 150°C and 21.6 kg, (c) 170°C and 2.16 kg, (d) 170°C and 21.6 kg, and (e) 180°C and 2.16 kg.
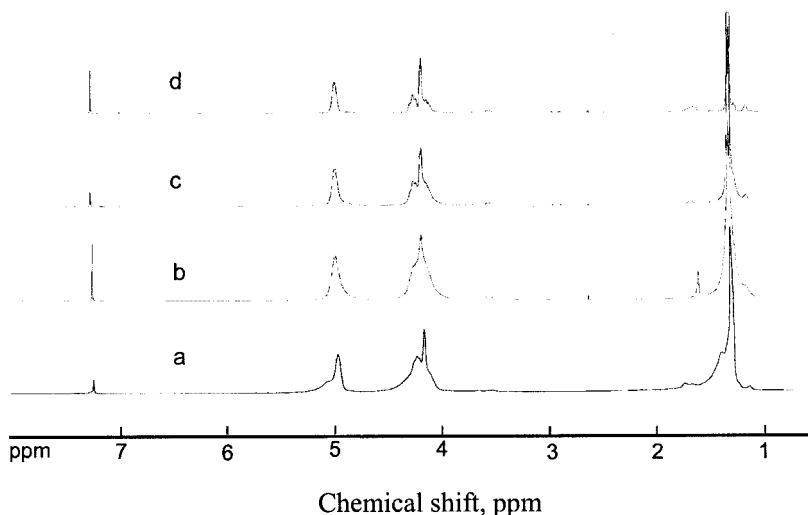
Figure 6 The ^{1}H-NMR spectra of the alternating PPC copolymers before and after melt extrusion: original PPC copolymer (spectrum a), melt extruded at 150°C (spectrum b), melt extruded at 170°C (spectrum c), and melt extruded at 180°C (spectrum d).

Thermal properties for alternating PPC copolymers

The thermal properties for the PPC with varying molecular weights are listed in Table I. It can be seen that the T_g and decomposition temperatures (5% weight loss temperature, TGA$_{-5\%}$; and maximum weight loss temperature, T_{max}) for the alternating PPC tend to increase with increasing molecular weight. The alternating PPC with a molecular weight greater than 140,000 exhibits the highest T_g (i.e., above 45°C as shown in Fig. 2) and TGA$_{-5\%}$ (above 250°C as shown in Fig. 4). These are the best results that have been

disclosed in the literature. Compared with the PPCs obtained via a complex catalyst, the T_g and TGA$_{-5\%}$ of this alternating PPC are 25 and 100°C higher, respectively, than those of PPC synthesized via a complex catalyst.[9b] The high thermal stability presumably results from the PPC's regular molecular structure because the thermal properties greatly depend upon the molecular structure and molecular weight. In other words, the strict alternating structure of this PPC plays a crucial role in its thermal stability: different catalysts can lead to different molecular structures,
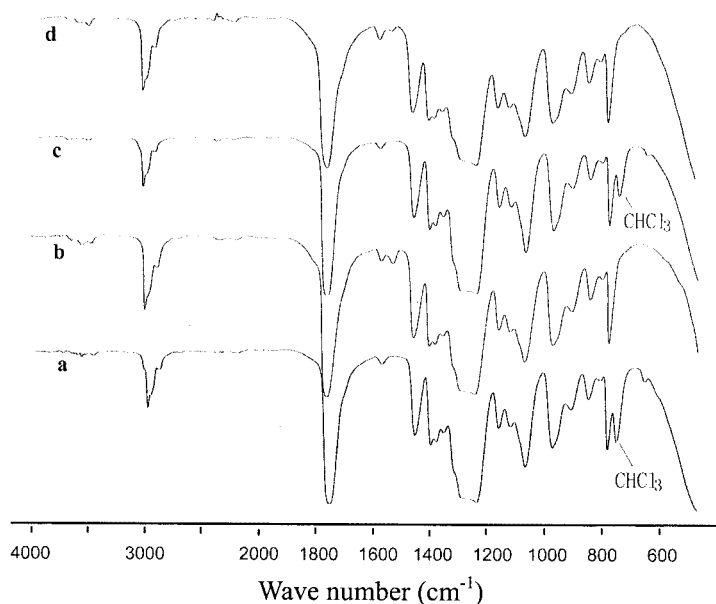

Figure 7 The IR spectra of the alternating PPC copolymers before and after melt extrusion: the original PPC copolymer (spectrum a), melt extruded at 150°C (spectrum b), melt extruded at 170°C (spectrum c), and melt extruded at 180°C (spectrum d).

TABLE III
Effects of Melt Extrusion on Thermal Properties of PPCs with Varying Number-Average Molecular Weights (M_n)

		Sample	
M_n		Before melt extrusion	Melt extruded at 180°C and 2.16 kg
56,000	T_g (°C)	38.24	36.01
	TGA$_{-5\%}$ (°C) N$_2$	256.0	250.7
89,000	T_g (°C)	40.77	38.72
	TGA$_{-5\%}$ (°C) N$_2$	251.0	250.0
114,000	T_g (°C)	42.07	39.88
	TGA$_{-5\%}$ (°C) N$_2$	258.0	260.0

and zinc dicarboxylates can produce PPCs with a regular molecular structure.

Melt extrusion of alternating PPC copolymers

Based on the flow rate standard adopted for polyethylene and polypropylene (ASTM D1238-82), the melt indices (MIs) of the PPC copolymers as determined under varying extrusion conditions are listed in Table II. The melt extrusion temperatures we selected ranged from 150 to 180°C. It can be seen that the MI of the PPC decreases with increasing molecular weight because of the high molecular weight yielding high melt viscosity. Moreover, the MI also increases with an increase in the extrusion temperature. By comparing it with commercial polyethylene and polypropylene, the as-prepared PPC exhibits a similar flow rate or MI at a temperature of 170°C.

Figure 5 shows the appearance of the PPC extrudates processed under varying conditions. Numerous bubbles are observed in the extrudates with low molecular weight, in spite of the different temperatures and loads we employed. This implies that the thermal stability is increased with an increase in the molecular weight. The thermal decomposition of the PPC copolymers mainly results from the hydroxyl end groups in the PPC molecular chain. Moreover, a higher extrusion temperature can lead to serious decomposition of the PPC copolymer as shown in Figure 5(c–e). The surface of the extrudate becomes much coarser when the temperature is higher than 170°C. The decomposition products are believed to be small organic compounds such as cyclic carbonates and carbon dioxide.[15] These small organics act in turn as a foaming agent during the melt processing. It should be mentioned that the extrusion pressure of an extruder or an injection molder is much higher than that employed for the MI instrument. Therefore, the PPC copolymer can be melt processed at a temperature of about 150°C by using an extruder or injection molder. Taking into account the thermal decomposition of PPC copoly-

mers, a lower temperature and higher processing pressure are preferred. In conclusion, the PPC copolymers can be readily melt processed like commercial polyethylene and polypropylene.

Property changes of PPC during melt extrusion

The ^{1}H-NMR and IR spectra for the PPC copolymers before and after melt extrusion are given in Figures 6 and 7, respectively. The integral values of the characteristic peaks for the PPC are calculated from Figure 6, and there is no obvious change in the proton ratio of the PPC. The IR spectra of the PPCs before and after melt extrusion also show similar absorption peaks, indicating that slight degradation does not result in any molecular structural change.

The effects of melt extrusion on the thermal properties of the PPC are summarized in Tables III and IV. For the PPCs with varying molecular weights (Table III) and melt extruded under varying conditions (Table IV), the T_g decreases slightly after the melt extrusion but the 5% weight loss temperature remains almost unchanged. A slight decrease in the T_g is considered to indicate possible thermal decomposition during the melt extrusion process. PPCs with different molecular weights show a similar decreasing tendency for the above-mentioned temperatures, implying that the molecular structure (carbonate content) plays a crucial role in the thermal stability. The static mechanical properties of the PPC subjected to different melt extrusion conditions were determined, and the results are given in Table V. For lower molecular weight PPC, melt processing can lead to a deterioration in the mechanical properties in terms of the tensile strength and elongation. However, this influence on the tensile strength becomes negligible for high molecular weight PPC. This is because the higher the molecular weight, the lower is the residual hydroxyl group content in the PPC. Finally, it remains unclear why the elongation decreases dramatically after the melt extrusion process, although the PPC exhibits superior mechanical strength. The PPC has a yield strength of about 29.5 MPa at 17°C, which is similar to

TABLE IV
Effects of Melt Extrusion Condition on Thermal Properties of PPC with M_n 114,000

Melt extrusion condition	T_g (°C)	TGA$_{-5\%}$ (°C) N$_2$
Original	42.07	258
150°C and 2.16 kg	42.19	258
150°C and 21.6 kg	42.04	260
170°C and 2.16 kg	39.73	263
170°C and 21.6 kg	38.82	260
180°C and 2.16 kg	39.88	260
180°C and 21.6 kg	38.87	255

TABLE V
Static Mechanical Properties of PPCs Subjected to Different Melt Extrusion Conditions

M_n	Melt extrusion condition	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
56,000	Original	29.86	30.08	255
	Melt extruded at 150°C and 2.16 kg	29.53	29.63	70
	Melt extruded at 170°C and 2.16 kg	26.35	26.55	88
	Melt extruded at 180°C and 2.16 kg	23.29	23.37	30
89,000	Original	27.79	27.90	147
	Melt extruded at 180°C and 2.16 kg	28.87	28.97	40
114,000	Original	30.25	30.36	200
	Melt extruded at 180°C and 2.16 kg	29.67	29.72	50

that of polyolefins such as polypropylene (about 27 MPa) and polyethylene (about 22 MPa).

CONCLUSION

Alternating copolymers derived from carbon dioxide and PO with high molecular weights were successfully synthesized in high yield under optimized reaction conditions. The alternating molecular structure of the resulting PPC was confirmed by the NMR technique. The PPC copolymer exhibited the highest T_g of 46.46°C and a 5% weight loss temperature of 255.8°C. Melt extrusion led to a slight deterioration of the PPC's mechanical properties in terms of the tensile strength and elongation, especially for the PPCs with lower molecular weights. By optimizing the extrusion condition, the PPC copolymer can be readily melt processed at temperatures ranging from 160 to 180°C, similar to polyethylene. The PPC copolymers show potential applications as substitutes for thermoplastic polyolefins, binder resins, and degradable "green" polymers.

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