Structure and Properties of Poly(Propylene Carbonate)

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Structure and Properties of Poly(Propylene Carbonate)

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Poly(propylene carbonate) (PPC), a new kind of aliphatic polycarbonate copolymerized by carbon dioxide and propylene oxide, was characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, DSC, TG, and viscosimetry. The copolymer chains consisted of alternative segments of carbon dioxide and propylene oxide and a small amount of homopolymer of propylene oxide. PPC fluid was pseudoplastic. Flow activation energy of PPC and quantitative relationship between apparent viscosity and molecular weight were obtained from their flow curves.

Keywords: Poly(propylene carbonate), rheological properties

INTRODUCTION

High content of carbon dioxide (CO_2) in the atmosphere is implicated in the "greenhouse effect", thus, the fixing of carbon dioxide has been extensively studied [1]. One method of fixing carbon dioxide is to copolymerize it with another monomer, a method which is more energy efficient than reducing it. Unfortunately, many catalysts reported have not enough efficiency to activate carbon dioxide, resulting in costly products [2].

Poly(propylene carbonate) (PPC), a new kind of aliphatic polycarbonate synthesized at our institute, is a copolymer of propylene oxide (PO) and carbon dioxide. This polymer is a potentially attractive material because the starting compounds are readily available and inexpensive. The characterization of PPC is described in this paper.
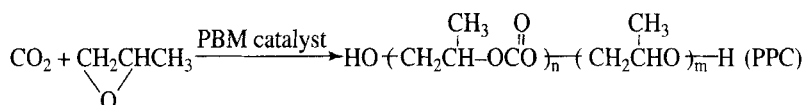
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EXPERIMENTAL

Synthesis

Poly(propylene carbonate) was prepared by copolymerization of carbon dioxide and propylene oxide in the presence of toluene and an inexpensive bimetallic catalyst (PBM) which was a zinc salt and triethylaluminum supported on an active proton containing polymer such as styrene and acrylic acid copolymer (PSAA) [3]:

$$CO_2 + CH_2CHCH_3 \xrightarrow{\text{PBM catalyst}} HO \left(CH_2\overset{CH_3}{\underset{|}{CH}}-O\overset{O}{\overset{\parallel}{C}}O \right)_n \left(CH_2\overset{CH_3}{\underset{|}{C}}HO \right)_m H \text{ (PPC)}$$

The copolymerization was carried out in a 5-L autoclave under 5 ~ 8 MPa pressure at 60°C for 8 h. The catalytic efficiency of PBM was as high as 10^4 g polymer/mol Zn. The yield of PPC was higher than 90%. The purified samples studied here have molecular weights ranging from 5,000 to 20,000. They are viscous fluids soluble in dichloromethane, chloroform, acetone, benzene, toluene, tetrahydrofuran, but insoluble in methanol, ethanol, and water. Samples decompose under basic conditions, at high temperature, and can be biologically degraded. Their density was tested using a MD-01 density gauge, and was found to be 1.31×10^3 kg/m^3.

Materials

The viscosity molecular weights of PPC samples were 20,700, 15,600, 9,200, 7,660, 4,160, and 500. PPC samples were dissolved in chloroform and byproducts of copolymerization and cyclic carbonate were extracted with water. The residual catalyst was removed by centrifugation at 1700 cycle/min, and PPC precipitated in methanol and vacuum dried to constant weight.

FTIR

A chloroform solution of 4wt% PPC was cast on a NaCl disk and dried in vacuum to constant weight. The infrared spectra were measured by a Model Analect RFX-65A Fourier transform infrared spectrometer (Analect Corp., Madison, WI, USA) between 4000 and 400 cm^{-1} with a resolution of 2 cm^{-1}. Every spectrum was scanned 32 times.

NMR

Both ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra of PPC were measured with a Bruker DRX-400 nuclear magnetic resonance spectrograph (Bruker Corp., Bruker-Spectrospin Vertriebsgemeinschaftag Spectrospinag, CH-8117, Fällanden, Switzerland) with deuteriochloroform (CDCl$_3$) as solvent and tetramethylsilane as internal standard. The concentrations of sample solutions in the NMR experiment were about 10%. Spectra were scanned 32 times for ^{1}H-NMR and 1500 times for ^{13}C-NMR.

Determination of Viscosity Molecular Weight of PPC

PPC was dissolved in benzene at a concentration of 0.01 g/mL. Intrinsic viscosity [η] of the PPC-benzene solution was obtained with a Ubbelodhe viscosimeter at $35 \pm 0.1°C$ by the one-point method [4]. Since the flow time of the solvent $t_0 > 100$ s, the intrinsic viscosity was calculated without kinetic energy correction:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln \eta_r)}}{c} = \sqrt{2\left(\frac{t - t_0}{t_0} - \ln \frac{t}{t_0}\right)}\Bigg/ c \qquad (1)$$

and the viscosity molecular weight of PPC was calculated from the following equation [3,5]:

$$[\eta] = (dL/g) = 1.11 \times 10^{-4} \times M_\eta^{0.8} \qquad (2)$$

Thermal Analysis

DSC measurements were carried out with a Perkin-Elmer DSC-7 (Perkin-Elmer Corp., Connecticut, CT, USA). The temperature range scanned was from $-50°$ to $150°C$ at a scanning rate of $20°C/min$ in all cases and indium was used as a standard. The sample weights were about 10 mg. All of the DSC tests were made in a N_2 atmosphere. The glass-transition temperature was taken to be the midpoint of the change in heat capacity.

The thermal stability of PPC was determined with a Perkin-Elmer TGS-2 analyzer (Perkin-Elmer Corp., Connecticut, CT, USA). The temperature range was from $30°$ to $500°C$ at a scanning rate of $10°C/min$ in a nitrogen atmosphere.

Rheological Properties

Rheological behavior of PPC fluid was carried on a Rheotest 2.1 rotary cone-and-plate viscosimeter (VEB MLW Corp., Berlin, Germany) at various temperatures. The sample under test was in a wedge-shaped gap between a fixed flat plate and a cone with radius R that rotated with an angular velocity ω. The gap angle of the cone-and-plate system was relatively small and amounts to only $\psi = 0.3$ angular degrees. The investigation of the material under test at a defined temperature was guaranteed by direct temperature regulation of the plate. This was attained by temperature regulating the cone-and-plate system with a water circulation thermostat. The cone with radius $R = 36$ mm required 0.1 mL of sample. According to the density of the PPC fluid (1.31×10^3 kg/m^3), the weight of sample tested was about 0.13 g. By Rheotest 2.1 rotary viscosimeter, shear stress τ, shear rate $\dot{\gamma}$ and apparent viscosity η_a were obtained from the following equation:

$$\tau = \frac{3 \cdot M}{2\pi \cdot R^3} \tag{3}$$

$$\dot{\gamma} = \omega / tg(\psi) \tag{4}$$

$$\eta_a = \tau / \dot{\gamma} \tag{5}$$

where ω is the rotation speed, M is the rotation tensor, which is given by the viscometer, R is the radius of cone, ψ is the angle of cone, and tg is the tangent function.

RESULTS AND DISCUSSION

Spectral Analysis

The FTIR spectra of PPC are shown in Figure 1. The bands around 1750 cm^{-1} in spectra 1 and 2 were split into 1780 and 1745 cm^{-1}, which indicated that the cyclic carbonate (a byproduct of PPC copolymerization) existed in the PPC products. This impurity was removed by water extraction until the split bands became a single band at 1750 cm^{-1}. The IR spectrum of purified PPC (spectrum 3 in Figure 1) showed a series of characteristic bands of carbonate group, that is, 1750, 1250, and 790 cm^{-1}. The former two strong absorption bands correspond to the carbonyl bond
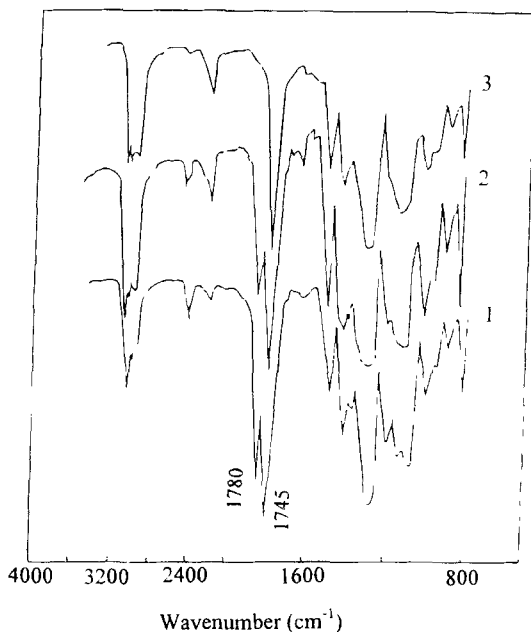
Wavenumber (cm^{-1})

FIGURE 1 FTIR Spectrum of poly(propylene carbonate): (1) before purifying, (2) during purifying, (3) after purifying.

(C=O) and the ether linkage (C-O-C) vibration band, respectively. The ether linkage (C-O-C) is related not only to $(-CH_2CH(CH_3)OCH_2-)_m$ but also to $(-CH_2CH(CH_3)OC(=O)O-)_n$. The 790 cm^{-1} may be responsible for the inplane deformation vibration band of the $-CH_3$ group. Weaker absorption at 1065 cm^{-1} corresponds to the ether chain whose strength is related to the content of propylene oxide homopolymeric segments ($\frac{CH_3}{-CH_2CHO-_m}$) in PPC.

The content of carbonate segments (-O-$\overset{O}{\overset{\|}{C}}$-O-) in the polymer chains is represented by fc (fc is segmental fraction of CO_2 units in total polymer, here the total PPC polymer consists of the following segment units) that can be calculated from the ^{1}H-NMR spectrum of PPC. The spectrum (Figure 2) had four chemical shift bands: $\delta = 5.0$, 4.2, 1.2, and 3.5 ppm which correspond to >CH-, $-CH_2$-, $-CH_3$ in the copolymer segment and $-CH_2$- with >CH- in the homopolymer segment of propylene oxide [1]. The
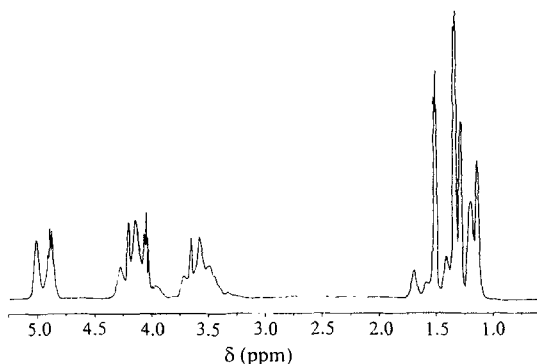
FIGURE 2 ^{1}H-NMR spectrum of poly(propylene carbonate).

areas of the bands (A_i) can be obtained from the integral curves, from which fc can be calculated by Equation (6).

$$fc = \frac{A_{5.0} + A_{4.2}}{2 \times (A_{5.0} + A_{4.2}) + A_{3.5}} \tag{6}$$

Equation (6) is derived as follows:

(1) PO (propylene oxide) unit in alternative copolymer segment, and expressed as [PO(CO_2)]
(2) CO_2 unit, expressed as [CO_2]
(3) PO unit in PO homopolymer segment, expressed as [PO(PO)] so that,
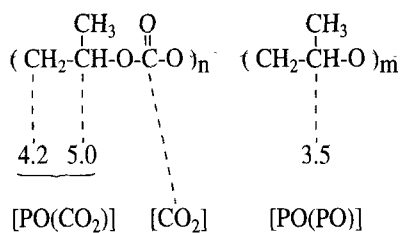
$$fc = \frac{[CO_2]}{[PO(CO_2)] + [CO_2] + [PO(PO)]} \tag{7}$$

Because CO_2 is not able to self polymerize, it only is present in the copolymer chain segments, therefore, in ^{1}H-NMR measurement,

$$[PO(CO_2)] = [CO_2] = A_{5.0} + A_{4.2} \tag{8}$$

$$[PO(PO)] = A_{3.5} \tag{9}$$

Equation (6) is obtained by substitution of Equation (8) and (9) into (7).

In this study, fc was in the 0.4 ~ 0.45 range for most of the PPC samples. This means that the alternative segments fraction was in a range of 80 to 90% for the present copolymerization conditions, that is, PPC molecular structure was as follows:

$$\cdots -(\underset{\underset{CH_3}{|}}{CH_2-}\overset{\overset{O}{||}}{CH}-OCO)_{0.8-0.9} \cdot (\underset{\underset{CH_3}{|}}{CH_2}CHO)_{0.2-0.1}$$
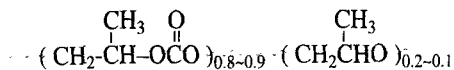
These results demonstrate that PPC was mainly an alternating copolymer of propylene oxide and carbon dioxide. The simplicity of the ^{13}C-NMR spectrum of PPC (shown in Figure 3) also proves the regularity of the copolymer's structure because PPC is an alternating copolymer of propylene oxide and carbon dioxide. The chemical shift for various carbon atoms of PPC can be calculated according to Grant's empirical formula [6]:
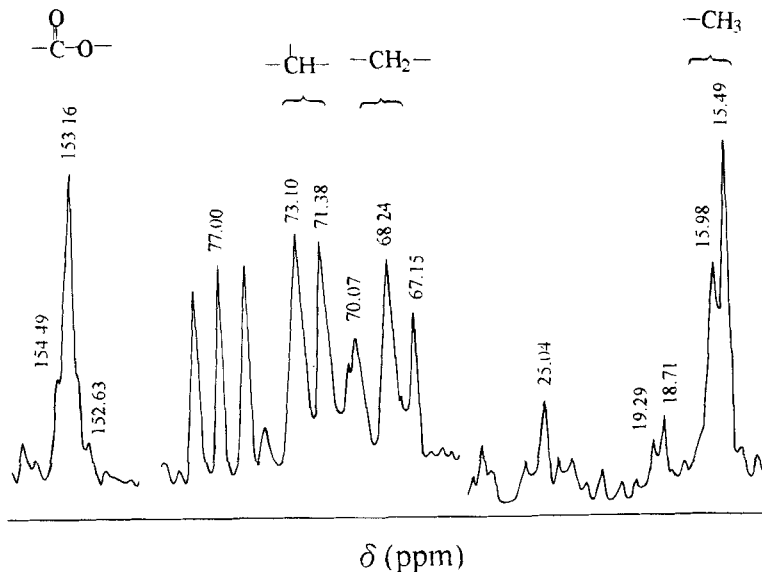
$$\delta(K) = -2.1 + \Sigma N_{ik} A_i \tag{10}$$

FIGURE 3 ^{13}C-NMR spectrum of poly(propylene carbonate).

where N_{ik} is the number of carbon atoms, and A_i is an empirical constant. The calculated results (Table I) are in good agreement with the experimental results. This also indicates that PPC is mainly an alternative copolymer.

Thermal Analysis

The glass-transition temperature of PPC was related to its molecular weight: −7°C was obtained for the 20,700 sample and −18°C for the 9,200 sample. Figure 4 is the thermogravimetric analysis curves of PPC with molecular weight 20,700 and 9,200 showing that there were different initial decomposition temperatures, but almost the same major decomposition temperature for different molecular weight PPC. PPC with a molecular weight 20,700 started to decompose at 250°C (weight loss 8.5%) and decomposed quickly at 295°C. PPC with a molecular weight 9,200 started to decompose at 164°C (weight loss 6.4%) and decomposed quickly at

TABLE I   The Chemical Shift for Various Carbon Atoms of Poly(Propylene Carbonate).

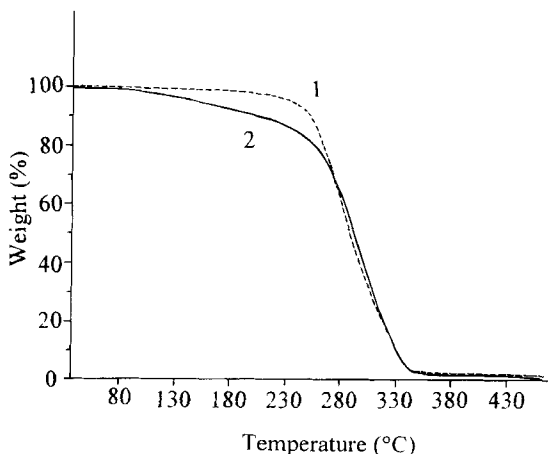| Carbon	−CH3	−CH2−	>CH−	C=O
Calculated result (ppm)	15.21, 15.50	69.40, 71.39	72.34, 74.66	154.73
Experimental result (ppm)	15.49, 15.98	68.24, 70.07	71.83, 73.10	153.16

FIGURE 4 Thermogravimetric analysis curve of poly(propylene carbonate): (1) M_η = 20,700 (2) M_η = 9,200.

291°C. This behavior resulted because these samples had the same main structure.

Rheological Analysis

Rheological behavior of PPC with molecular weight 9,200 at various temperature is shown in Figure 5. At the same temperature, shear stress increased with increasing shear rate, because the shear stress varied with the conformation of the main chain of PPC. PPC macromolecules presumably disaggregated, and oriented along the flow direction with increasing shear rate. After a critical shear rate, PPC macromolecules oriented at the maximum degree which did not change with shear stress, at which time the apparent viscosity became constant, indicating that PPC was a pseudoplastic fluid.

Temperature has a great effect on apparent viscosity. At the same shear rate, the Arrhenius equation is applicable to pseudoplastic fluids [7]:
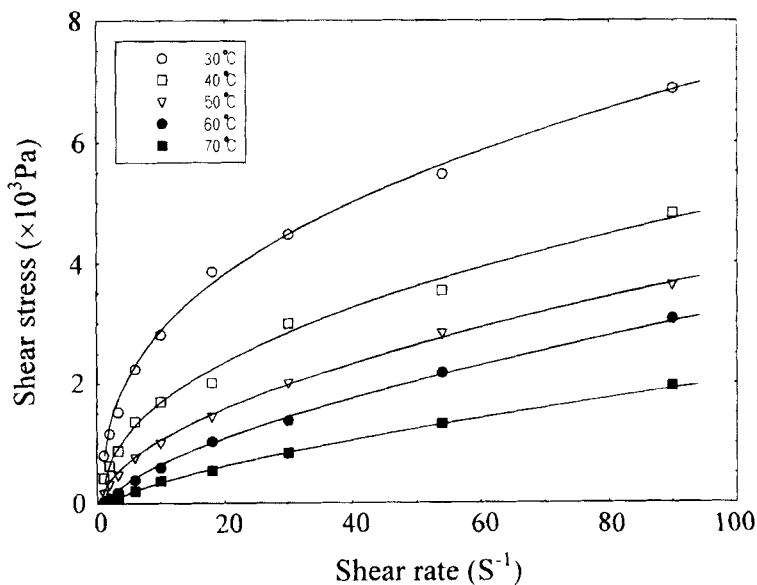
$$\eta_a = A \exp(E_a/RT) \tag{11}$$

FIGURE 5   Flow curves of poly(propylene carbonate) ($M_\eta = 9,200$).

where A is a constant, Ea is the flow activation energy, R is the gas constant, and T is the temperature. A plot of $\ln \eta_a$ vs. $1/T$ should be linear as shown in Figure 6 of PPC ($M_\eta = 9,200$) at various shear rates. Flow activation energy was calculated from the slope and is listed in Table II. As indicated, E_a decreases with increasing shear rate suggesting that PPC fluid has a lower temperature sensitivity at higher shear rate than at lower shear rate. This trend was caused by various entanglement structures of the polymer which had different temperature sensitivities at various shear rates.

To study the effect of molecular weight of PPC on its flow properties, flow curves of several PPC samples with various molecular weights were tested at 40°C and are shown in Figure 7. When the molecular weight of PPC was low, interaction between macromolecule was not strong enough and the weak shear stress at low shear rate was not easy to detect by the
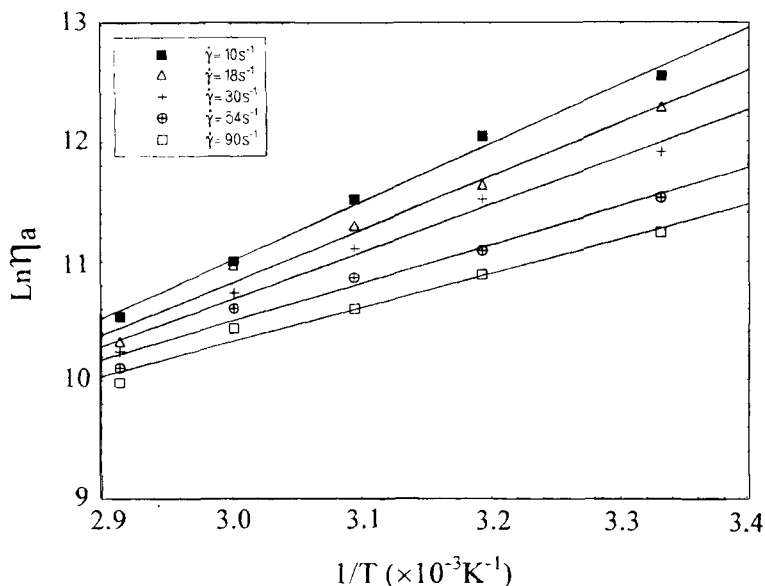

FIGURE 6   Apparent viscosity of PPM ($M_\eta = 9,200$) vs. temperature.

TABLE II   Flow Activation Energy of PPC ($M_\eta = 9,200$) at Various Shear Rates

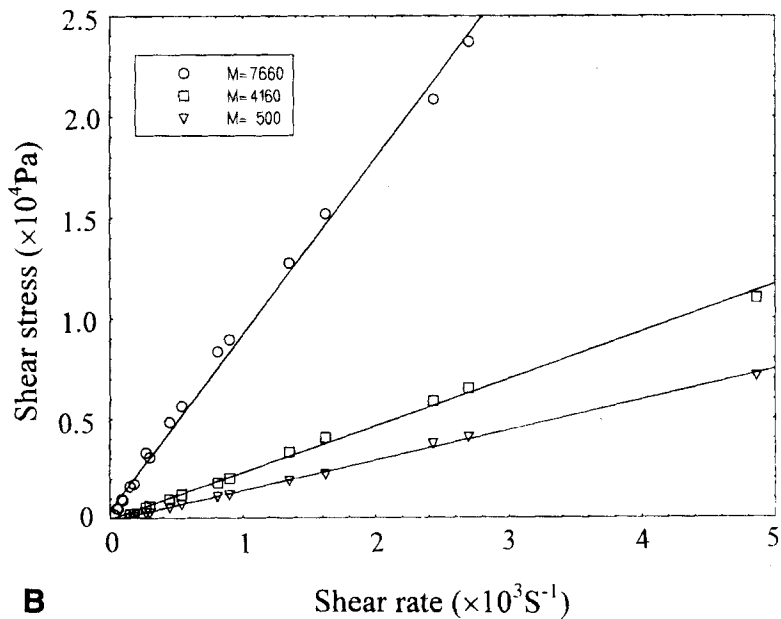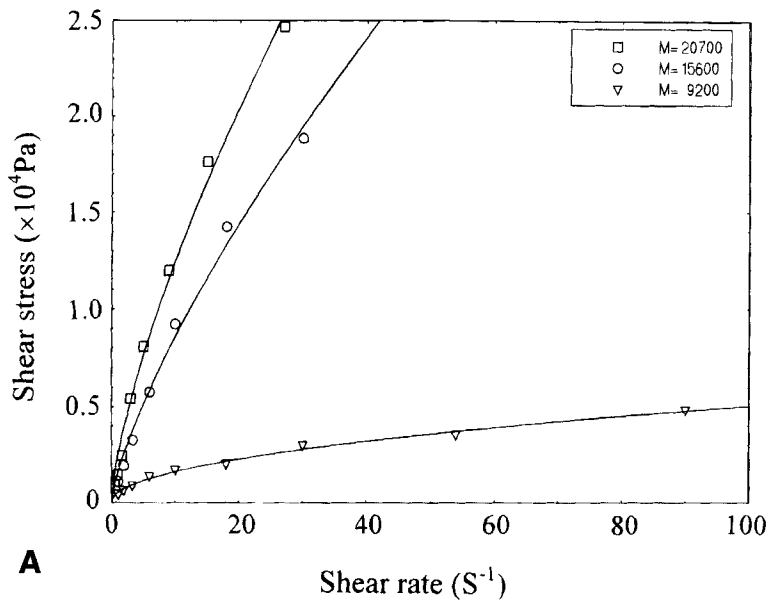| Shear rate (s^{-1})	10	18	30	54	90
Flow activation energy (kJ/mol)	40.6	36.9	32.9	26.7	23.9

FIGURE 7a and 7b   Flow curves of poly(propylene carbonate) with various molecular weights.

viscometer. When the molecular weight of the PPC was high, only the rheological behavior at low shear rate was observed. There was a critical molecular weight M_c of PPC. PPC fluid with a lower or higher M_w had different rheological properties.

Figure 8 shows ln η_a vs. ln M_η of PPC with various molecular weights. Apparent viscosity increases slowly with increasing molecular weight when $M_\eta < M_c$, and rapidly when $M_\eta > M_c$. M_c may be a critical molecular weight when polymer chains start to entangle. From Figure 8, M_c was calculated to be 5400. When $M_\eta < M_c$,

$$\eta_a = 0.42 \, M_\eta^{0.2} \tag{12}$$

When $M_\eta > M_c$,

$$\eta_a = 1.4 \times 10^{-16} \, M_\eta^{4.36} \tag{13}$$

Equations (12) and (13) are different than Equation (2). According to Equations (12) and (13), we can calculate the apparent viscosity of PPC with various molecular weight at low shear rate just from its viscosity mol-
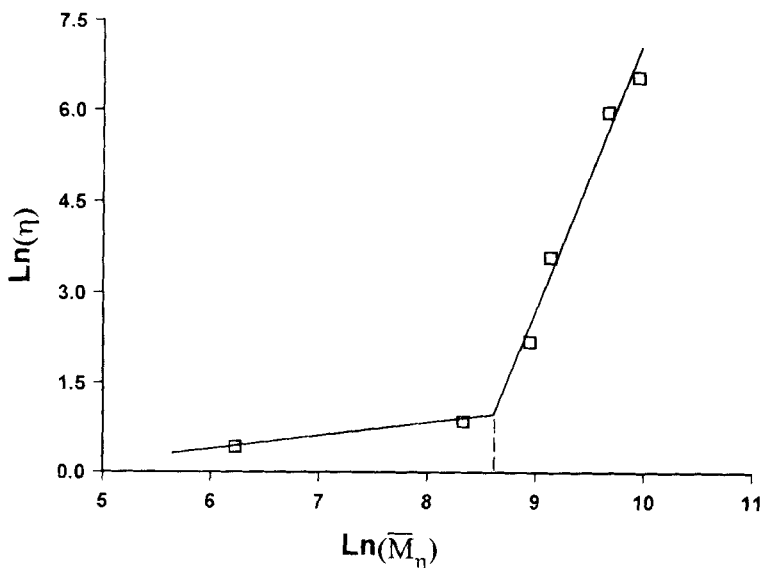

FIGURE 8   ln η_a vs. ln M_η of poly(propylene carbonate).

ecular weight, because the apparent viscosity at low shear rate is difficult to measure for high molecular weight PPC.

CONCLUSION

Poly(propylene carbonate) (PPC), a copolymer of propylene oxide and carbon dioxide, is composed of alternating segments of carbon dioxide and propylene oxide and a small amount of homopolymer of propylene oxide. It is pseudoplastic with a density of 1.31×10^3 kg/m^3. From ^{1}H-NMR, the content of carbonate segments in the polymer chains was in the 0.40 ~ 0.45 range for most of the PPC samples, implying an alternating copolymer structure of propylene oxide and carbon dioxide. PPC decomposed quickly at about 291°C. The quantitative relationship between apparent viscosity and molecular weight of PPC was obtained, from which, the apparent viscosity of PPC with various molecular weights at low shear rate can be calculated just from its viscosity-molecular weight.

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