Pressure Dependence of the CO_2/Propylene Oxide Copolymerization Catalyzed by Zinc Glutarate

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ABSTRACT: The pressure dependence of the CO_2/propylene oxide copolymerization catalyzed by zinc glutarate was studied in this article. The effects of pressure on the product composition, yield, backbone structure of poly(propylene carbonate) (PPC), molecular weight and its distribution, and thermal stability were systematically investigated. Low pressure favored formation of byproducts (cyclic carbonate and polyether), whereas PPC still covered the majority of the product under 0.5 MPa. The copolymerization rate increased with pressure increasing under low pressures. Higher pressure led to a decline in the polymer yield because of catalyst/epoxide dilution. On the other hand, the carbonate linkage fraction decreased slightly with the drop of pressure, from 99% at 5.2 MPa to 96% at 0.5 MPa. All the PPCs synthesized under different pressures exhibited high molecular weights and broad distributions. However, the polymer prepared under 0.5 MPa possessed a relatively lower thermal stability than others. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 366–371, 2010

Key words: carbon dioxide; polycarbonates; copolymerization; zinc glutarate; pressure

INTRODUCTION

As a nontoxic, nonflammable, and naturally abundant material, CO_2 could be used as monomer to synthesize degradable polycarbonate plastics, which provides a green route of polycarbonate production without creating "white pollution" and introducing petroleum exhaustion problems.[1–3] This technique was first developed by Inoue et al.[4] in 1969, who fulfilled the task of copolymerization of CO_2 and propylene oxide (PO) into polymer. After that many researchers have been working on this subject, but mostly focusing on optimizing the catalytic efficiency and selectivity for the last 5 decades.[5,6] Many catalyst systems have been proposed in that time, such as $Zn(Et)_2$/active hydrogen compound,[7–9] zinc dicarboxylates,[10] organometallic compounds,[11–14] double metal cyanide,[15] and rare earth catalysts.[16,17] Among them, zinc glutarate (ZnGA) seems to be the most promising catalyst nowadays because of the low cost, relatively high catalytic efficiency, and the as-made poly(propylene carbonate) (PPC) exhibiting high molecular weight.[18–20]

CO_2/epoxide copolymerization occurs in the liquid phase of this gas–liquid two-phase system, where pressure determines the molar ratio of CO_2 in it. Therefore, it is of importance to investigate the influence of pressure on the polymerization process. In former researches of CO_2/PO copolymerization, most catalyst systems used higher pressure, whereas the status of experiments under low pressures was unknown.[21–23] Darensbourg et al.[24] investigated the influence of pressure on the CO_2/cyclohexene oxide (CHO) coupling reaction catalyzed by chromium salen complexes. Xiao et al.[25] found that pressure was of no influence on the copolymerization rate of CO_2/CHO catalyzed by intramolecularly dinuclear magnesium complex. Both catalyst systems were ineffective at homopolymerization of epoxide to form polyethers, and the only byproduct was cyclic carbonate. To those catalysts in favor of epoxide homopolymerization, low pressure may result in large proportion of polyether besides cyclic carbonate, and few literatures systematically investigated the role of pressure. Meanwhile, pressure links with the production costs closely, like equipment, safety, and process scale-up, etc.

We aim to the process development of PPC polymerization, which includes process optimization, scale-up, and industrialization. In this work, we systematically investigated the effects of pressure on the CO_2/PO copolymerization catalyzed by supported ZnGA in the following areas: product
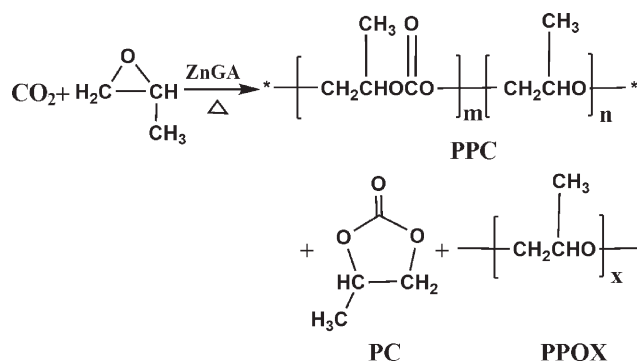
Scheme 1 Copolymerization of carbon dioxide and propylene oxide.

composition, yield, backbone structure, molecular weight and its distribution, and thermal stability.

EXPERIMENTAL

Materials

Carbon dioxide (purity more than 99.995%) was commercially obtained without further purification. Propylene oxide (PO) of 95.0% purity was pretreated by calcium hydride for 4 h and then distilled. It was stored over 4-Å molecular sieves for 48 h before use. Solvents, such as ethanol, acetone, and chloroform, were of analytical reagent grade and used as received. The catalyst was supported ZnGA, and the synthesis method was described in previous literature.[22]

Copolymerization of CO_2 and PO

The copolymerization of CO_2 and PO was carried out in a Parr reactor autoclave system (3.75 L capacity) equipped with a mechanical stirrer of two-layered six-bladed 45° pitch blade turbine. Forty-two grams of supported ZnGA was added into the reactor. The system was sealed and further dried for 24 h under vacuum at 100°C. Subsequently, the reactor was purged with 1200 mL purified PO as both reactant and solvent.[18] Then, the reactor was pressurized to a set pressure via a CO_2 cylinder and heated to 60°C under stirring for 40 h. Thereafter, the reactor was cooled to room temperature and the pressure was released. The resulting viscous mixture was taken out and dried in a vacuum oven at 60°C for 24 h, followed by weighing to get gross production. The drier was dissolved in a proper volume of chloroform. The catalyst residual was extracted from the product solution by using dilute HCl (5%), followed by washing three times with distilled water. PPC copolymer was precipitated out by pouring the solution into ethanol. The as-made PPC was filtered and dried at 80°C under vacuum for 24 h.

Measurements

The NMR spectra were recorded at 400 MHz in a Bruker NMR instrument (ADVANCE2B 400 MHz) using tetramethylsilane and chloroform-d1 ($CDCl_3$) as the solvent. Thermogravimetric analysis was carried out in a Perkin-Elmer thermogravimetric analyzer (TGA: Pyris-1) under a protective nitrogen atmosphere (100 mL/min) at a heating rate of 20°C/min. Number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of a polymer product were estimated using a gel permeation chromatography (GPC) system (PL-GPC 50 Plus) with multiple detectors: refractive index (PL-RI), viscometer (PL-BV 400RT), and light scattering (PL-LS).

RESULTS AND DISCUSSION

Product composition and yield

In the copolymerization of CO_2 and PO with ZnGA as catalyst, besides PPC, there are two byproducts: propylene carbonate (PC) and poly(propylene oxide) (PPOX), as depicted in Scheme 1.

The product composition in the dried reaction mixture can be determined by ^{1}H-NMR spectroscopy.[26] The chemical shifts of each product are listed, PPC: 5.0 [$CH(CO_3)$], 4.2 [$CH_2(CO_3)$]; PPOX: 3.4–3.9 [$CH_2(O)$ and $CH(O)$]; PC: 4.85, 4.56, and 4.04. Figure 1 is the ^{1}H-NMR spectra of the dried reaction mixtures prepared under 0.5, 2.6, and 5.2 MPa, from which the PC, PPC, and PPOX peaks and the trend that the portion of byproducts decreases with pressure increasing are observed. The mole ratio (x) of each product can be calculated by the area of the listed peaks,
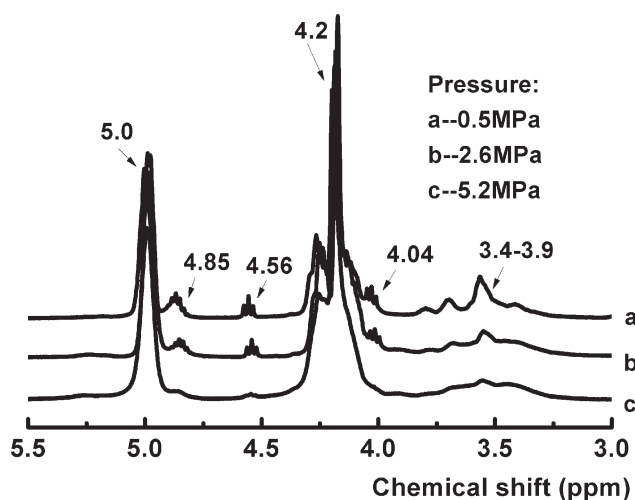

Figure 1 ^{1}H-NMR spectra of the dried reaction mixtures produced (a) after 40 h under 0.5 MPa, (b) after 16.5 h under 2.6 MPa, and (c) after 40 h under 5.2 MPa, at 60°C.
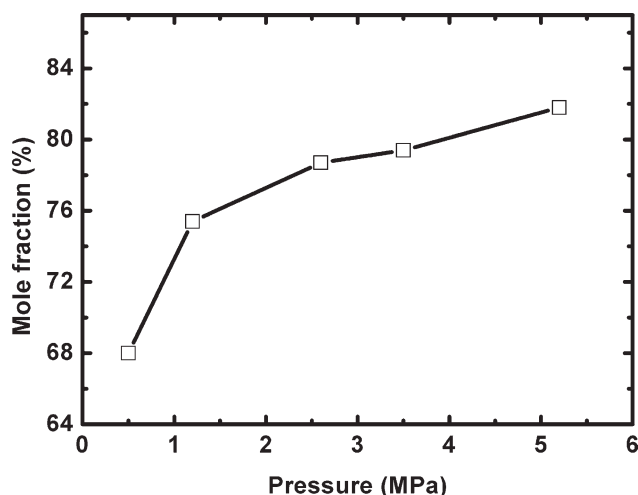
Figure 2 Effect of pressure on the content of PPC in the CO_2/PO copolymerization.
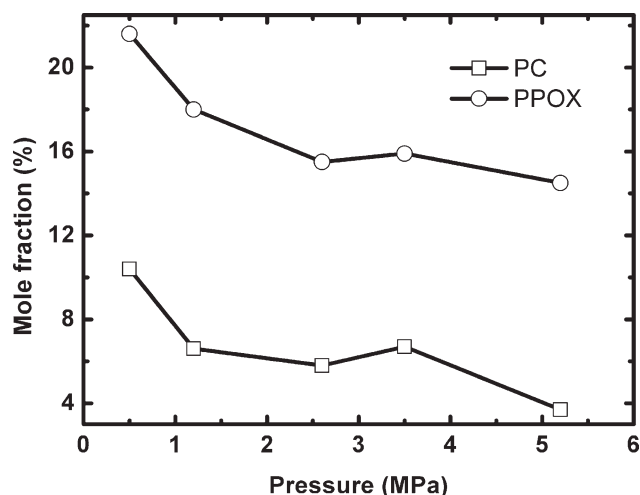

Figure 3 Effect of pressure on the content of PC and PPOX in the CO_2/PO copolymerization.

$$x_{pc}/x_{ppc}/x_{ppox} = (A_{4.85} + A_{4.56} + A_{4.04})$$
$$/(A_{5.0} + A_{4.2})/A_{3.4-3.9}, \quad (1)$$

where A is the calculated area of the peak. The mole ratio PC/PPC/PPOX under 0.5 MPa can be got with eq. (1), i.e., 10/68/22. Composition data under other pressures were obtained in the same way. The changes of molar ratio of PPC, PC, and PPOX with pressure are displayed in Figures 2 and 3, respectively. A general uprising trend in the ratio of PPCs with pressure and a descending trend in the ratio of PCs and PPOXs with pressure are observed. With the increase of pressure, PPCs ratio increased from 68 to 82%, whereas PCs ratio decreased from 10 to 4% and PPOXs ratio from 22 to 14%. The content of PPC increased with increasing CO_2 pressure up to 2.6 MPa and then leveled off. Noticeably, byproducts did not increase significantly under low pressure (0.5 MPa), and PPC still covered the majority of the production (68%). According to the mechanism proposed by Darensbourg et al.,[24] a PO unit insertion, a CO_2 unit insertion, and a backbiting to form PC are three com-

petitive pathways after a PO unit inserting in the chain forming alkoxide intermediate. The pressure increase leads to CO_2 content rising in the system, which is favorable for CO_2 insertion to form the carbonate linkage and reduces lifetime of the alkoxide intermediate necessary for backbiting mechanism to produce PC.

As shown in Table I, the feeds were uniformly 1000 g PO and 42 g supported catalyst. The reaction time of Run 2 and Run 3 did not meet the set point of 40 h because the systems were too viscous to be stirred at the time of 17 and 16.5 h. However, the yields were relatively high with shorter time, which demonstrated that the copolymerization rates were faster. When the pressure kept rising, the yield decreased slightly from Run 4 to Run 5. Generally, the copolymerization rate has a first rising, then descending trend with pressure increasing.

One control experiment without CO_2 addition was also conducted under the same temperature of 60°C and catalyst loading of 42 g for 40 h, with a PPOX yield of 21.4 g/g of Zn. Compared with Run 1 yield of 53.7 g PPC/g of Zn and 9.9 g PPOX/g of Zn, the huge advance in yield under 0.5 MPa with small

TABLE I
Effect of Pressure on PPCs Yield, Molecular Weight, and Its Distribution

Run	Pressure (MPa)	Reaction time (h)	PPC yield (g/g of Zn)	$M_n \times 10^{-5}$ (g mol^{-1})	$M_w \times 10^{-5}$ (g mol^{-1})	PDI ($= M_w/M_n$)
1	0.5	40	53.7	0.65	2.73	4.2
2	1.2	17	51.0	0.93	5.88	6.3
3	2.6	16.5	60.2	0.75	3.63	4.8
4	3.5	40	61.2	1.04	5.20	5.0
5	5.2	40	58.8	0.78	2.90	3.8

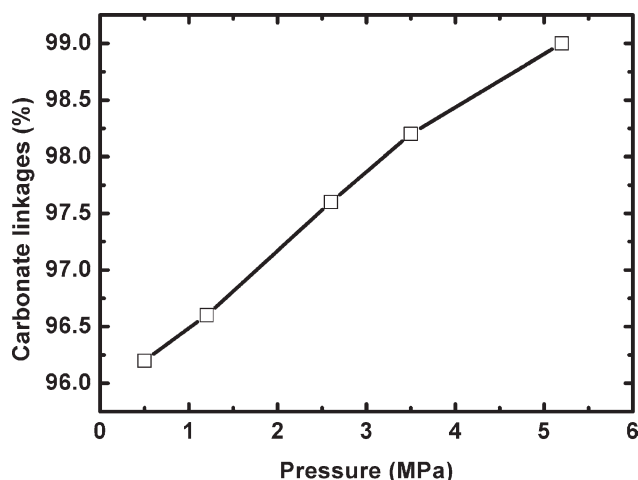Copolymerization reactions performed with 1000 g PO and 42 g supported catalyst at 60 °C

Figure 4 Effect of pressure on carbonate linkage fraction in PPC chain.

CO_2 concentration in the liquid phase illustrates that the CO_2 insertion into the polymer chain is fast.

The pressure determines the molar ratio of CO_2 in the liquid phase and thus influences the concentration of CO_2, PO, and catalyst in the system. Rough estimation by using Peng-Robinson equation suggests that under 0.5 MPa, the mole fraction of CO_2 in the liquid phase is 0.04 and the system volume slightly changes, whereas under 5.2 MPa, the mole fraction of CO_2 in the liquid phase reaches 0.55 and the system volume almost doubles. The increase of pressure leads to the increase of concentration of CO_2 and dilution of catalyst/epoxide concentrations, both of which are competing factors determining the copolymerization rate.

Below 2.6 MPa, the pressure increase leads to the increase of the CO_2 concentration in the system while the dilution of catalyst/epoxide concentration is insignificant, thus accelerating the reaction rate. Above 2.6 MPa, the system volume expansion results in the dilution of the catalyst/epoxide concentration,[27–29] which accounts for the rate decline. A similar trend has been observed by Darensbourg et al.[24] for the CHO/CO_2 copolymerization, where the catalyst system of SalenCrX was ineffective at homopolymerization of epoxide to form polyethers.

As listed in Table I, all the polymers prepared under different pressures exhibited high molecular weights and broad distributions, which show that influence of pressure on these aspects is insignificant. According to the former researches,[21,26] the high molecular weight and broad distribution are due to the high activity and multiple active sites of ZnGA.

Backbone structure

In the copolymerization of CO_2/PO, highly alternating structure in the polymer chain is expected. The
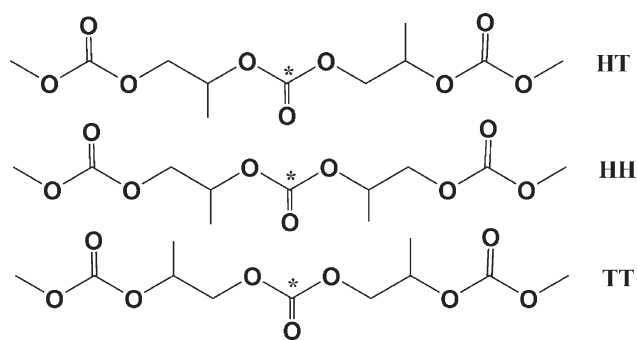
Scheme 2 Three regiosequences for carbonate carbons in PPC chain.

chain may include two structural units: the carbonate linkage and the ether linkage. The carbonate linkage fraction can be determined by ¹H-NMR spectroscopy.[30] The chemical shifts: ¹H-NMR (d, $CDCl_3$), 5.0 [$CH(CO_3)$], 4.2 [$CH_2(CO_3)$], and 3.4–3.9 [$CH_2(O)$ and $CH(O)$]. The ¹H-NMR data confirmed the existence of carbonate linkages and small fraction of random incorporated ether units in PPC backbone. The carbonate content was determined via ¹H-NMR by integrating the peaks corresponding to the protons of the PPC copolymer. The calculation was conducted using the following equation,

$$f_c = (A_{5.0} + A_{4.2})/[2 \times (A_{5.0} + A_{4.2}) + A_{3.4-3.9}], \quad (2)$$

where A is the integration of correlated proton signals in ¹H-NMR, f_c is the ratio of carbonate units to all units in the backbone. The maximum value of f_c is 50%, which denotes completely alternating structure. Figure 4 displays the effect of pressure on the carbonate linkage fraction. The carbonate linkage fraction decreased gradually as the pressure decreased, whereas under low pressure (0.5 MPa), it still reached 96%, showing the almost alternating PPC.
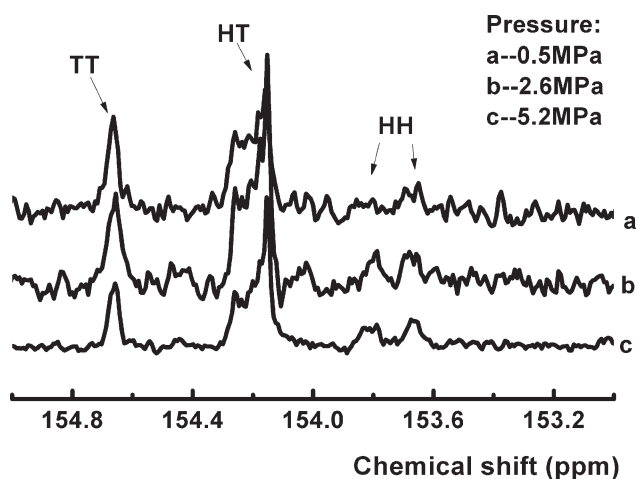

Figure 5 Carbonyl region of the ¹³C-NMR spectra of the PPC prepared (a) after 40 h under 0.5 MPa, (b) after 16.5 h under 2.6 MPa, and (c) after 40 h under 5.2 MPa, at 60°C.
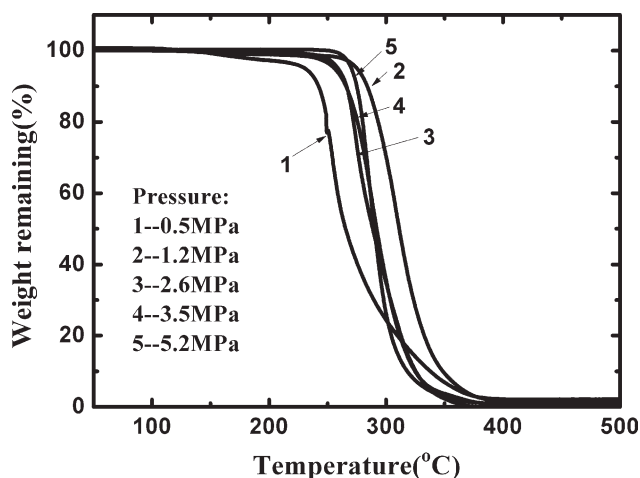
Figure 6 Effect of pressure on TGA curves of PPC.

In addition, ^{13}C-NMR spectrum of the polycarbonate product can determine the ratio of tail-to-tail (TT), head-to-tail (HT), and head-to-head (HH) junctions in the microstructure of the polycarbonate product (Scheme 2).[26] Investigation on the ^{13}C-NMR spectra of the PPCs under different pressures revealed that the ratio of TT : HT : HH was in a fixed order of 1 : 3 : 1 and pressure had little influence on it (Fig. 5). Chen and coworkers[31] observed that the HT content was stable with the variation of temperature and pressure in the CO_2/PO copolymerization catalyzed by (R,R)-SalenCo^{III}-(2,4-dinitrophenoxy). The result shows that the ratio of TT : HT : HH is determined by the catalyst system.

Thermal stability

The PPC thermal stability depends greatly on both molecular structure and molecular weight of the PPC copolymer.[32] As shown in the TGA curves of PPC prepared under different pressures (Fig. 6), the onset temperature of decomposition rose as the pressure increased. This is due to the gradually increasing carbonate linkage fraction in the backbone chain. Meanwhile, the relatively higher molecular weight contributes to the better thermal stability of Run 2 (1.2 MPa). Noticeably, all the PPCs possessed high degradation temperature more than 250°C other than the PPC under 0.5 MPa. Lower molecular weight and less alternating structure in the backbone chain contribute to the low thermal stability of Run 1 (0.5 MPa).

CONCLUSIONS

High pressure may cause problems in the scale-up process and thus hinder the industrialization of PPC synthesis. After a systematic investigation of the effect of pressure on the CO_2/PO copolymerization catalyzed by supported ZnGA, we found that high pressure was not a necessity. High pressure (3.5–5.2 MPa) favored PPC selectivity and the alternating structure in the polymer chain. However, the PPC selectivity was slightly improved under high pressures. Under low pressures (0.5–2.6 MPa), the copolymerization rate increased with the increasing pressure due to the CO_2 concentration increase, whereas high pressure resulted in the catalyst/epoxide dilution, which accounted for the rate decline. Meanwhile, all the PPCs prepared under different pressures exhibited high molecular weights and broad distributions, which were determined by the high activity and multiple active sites of the ZnGA. Other than the one prepared under 0.5 MPa, all the PPCs possessed a relatively good thermal stability. Considering the higher copolymerization rate and relatively stable properties, the pressure is suggested to be set between 2.6 and 3.5 MPa for the CO_2/PO copolymerization catalyzed by ZnGA. This trend may apply to other catalyst systems while the catalyst differences should be taken into consideration.

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