Synthesis and Degradation Behavior of Poly(propylene carbonate) Derived from Carbon Dioxide and Propylene Oxide*

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Abstract: High molecular weight and regular molecular structure poly(propylene carbonate) (PPC) was successfully synthesized from carbon dioxide and propylene oxide. The PPC copolymer structure was an exact alternating copolymer as evidenced by the ^{13}C NMR technique. Degradative behavior of the PPC was conducted by soil burial and buffer solution immersion (pH = 6) tests, respectively. The results showed that the weight loss of soil buried PPC films increased more slowly than that immersed in the buffer solution after 6-month exposure. However, the weight loss of sample immersed in the buffer solution increased rapidly during the first two months and reached a value of 4.59%. Water sorption measurement also revealed that the PPC membranes immersed in buffer solution were more hydrophilic than those in soil burial tests. The degradation mechanism of PPC membranes was correlated with the sample morphologies, FTIR and ^1H NMR spectra. The SEM morphologies were consistent with the weight loss and water sorption measurements.

Key words: degradation; poly(propylene carbonate); carbon dioxide; propylene oxide
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1 Introduction

Environmental pollution associated with the plastic waste disposal has attracted considerable attention to develop new degradable materials. Plastic waste is mainly derived from the packaging materials such as rubbish bags, agricultural mulch films, and food wrappers. We called this problem as "white-pollution" compared with the "black-pollution" problem caused from tires. Synthetic polymers such as polyolefins are degraded by the presence of oxygen and ultraviolet ray[1,2]. However, the degradation process of polyolefins is extremely slow. Various approaches to render synthetic polymers degradable have been considered.

Starch-based polymer blends are initial alternatives to produce degradable materials for many practical applications due to the fact that starch is abundant, inexpensive and degradable natural raw material. Generally, because of its poor physical and mechanical properties[2,3], starch is unsuitable for most applications as a thermoplastic. Many efforts have been devoted to develop degradable polymer blends with better mechanical performance. Particular attention is paid on the blends based on polycaprolactone (PCL)[4]. PCL is an aliphatic polyester that can degrade in soil and seawater[5,6]. It is believed that hydrolysis is the main explanation for the degradation of aliphatic polyesters. In the process, aliphatic polyesters begin with a water uptake phase followed by the hydrolytic splitting of ester bonds. The degradation rate of PCL is relatively slow because of its high crystallinity[7]. Such shortcomings of PCL can be improved via copolymerization with other monomers[8].

ABA type block copolymer of poly(caprolactone)-poly(ethylene glycol) comprising PCL (A) and PEG (B) segments by copolycondensation of ε-CL with PEG mixtures has been reported by Wang and Qiu[9]. The biodegradability of the new copolymer is increased with decreasing crystallinity of the copolymer, and can be controlled by adjusting the ratio of PCL to PEG[9]. However, the high cost is still the main hurdle for massive production of these polymers.

More recently, we have successfully synthesized high molecular weight poly(propylene carbonate) (PPC) from carbon dioxide and propylene oxide by using supported-catalysts[10-13]. The production cost of PPC is much lower than PCL or PCL/PCE copolymers due to the use of cheap waste carbon dioxide. PPC exhibits high transparency, and superior mechanical strength. Accordingly, it shows promise for use as packaging materials and food wrappers. In terms of the presence of

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aliphatic ester linkages within the new polymer, and its amorphous microstructure, the PPC is considered to exhibit reasonable degradation properties. In this regard, we attempt to prepare degradable PPC thin film specimens via solution casting method. The degradation behavior of PPC is examined by the soil burial and buffer solution immersion.

2 Experimental

2.1 Materials

Propylene oxide (PO) with a purity of 99.5% was further purified by distillation for 2 h over calcium hydride. It was then stored over 0.4 nm molecular sieves prior to use. Carbon dioxide with purity higher than 99.8% was used as received. Toluene, acetone, were of analytical reagent grade, methanol, chloroform, were of industrial reagent grade. All these solvents were used without further purification to produce catalysts and purify polymer. Analytical reagent grade chloroform was used for preparing degradable poly(propylene carbonate) (PPC) film specimens by the solution casting method. Glutaric acid (GA) of 98.0% purity, zinc oxide of 99.99% purity and perfluorined compounds were also used without further treatment.

2.2 Preparation of catalysts and poly(propylene carbonate)

Zinc glutarate was synthesized from zinc oxide and glutaric acid under magnetic stirring as described in literature[12]. 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 toluene. To this mixture were then charged 58.8 mmol glutaric acid and 1.176 mmol perfluorined compound, and the mixture was slowly heated up to 55 ℃ for 6 to 8 hours under vigorous stirring. Upon cooling, the resulting mixture was filtered. The resulting solids were continuously washed with acetone for several times followed by drying overnight in a vacuum oven at 100 ℃.

The supported zinc glutarate was obtained as white fine powder and at yield greater than 99.5%. The copolymerization of CO_2 with PO was performed out in a 500 mL autoclave equipped with a mechanical stirrer. Supported zinc glutarate was further dried at 100 ℃ for 24 h prior to being used for the polymerization process. The detailed process was reported in previous work[10].

2.3 Degradation measurements

Degradation experiments were carried out by means of the soil burial and buffer solution processes, respectively. The initial weights of the specimens were measured prior to tests. Thin film specimens were prepared by casting $w = 5\%$ PPC/chloroform solution. The round specimens with a diameter of 120 mm and thickness of 40 ~ 50 μm were used. In the soil burial test, specimens with a diameter of 120 mm and thickness of 40 ~ 50 μm were placed in a rectangle box (50 cm × 25 cm × 20 cm) containing enriched garden soil. We drilled 32 cavities with a diameter of 10 mm in the bottom of the box. Specimens were placed about 90 mm under the topsoil and 60 mm above the bottom. Water the soil every three days to make it wetness. The total exposure period was 6 months. The specimens were periodically removed from the box, i.e., monthly to determine their weight loss. In the process, the films were thoroughly rinsed in a stream of water, followed by immersion in distilled water until clear, and dried at room temperature in a vacuum oven to constant weight.

In the buffer solution immersion experiment, the specimens were immersed in a glass container filled with buffer solution (pH = 6.0). These films were separated by polyethylene meshworks. The buffer solution was composed of 0.2 mol/L potassium benzene dicarbonic acid and a small amount of NaOH. The container was then placed in a thermobath regulated at 45 ℃. The films were removed from the buffer solution for various specified durations. Upon washing with distilled water, they were dried at room temperature under vacuum to constant weight. The film specimens, both from soil burial and buffer solution experiments, were dried with filter paper after washed with distilled water, and weighed(m_1). The film specimens were dried in a vacuum oven to a constant weight(m_2). The amounts of water absorbed by the specimens were determined from the following equation:

$$\text{Water sorption} = \frac{m_1 - m_2}{m_2} \times 100\%$$

2.4 Characterization

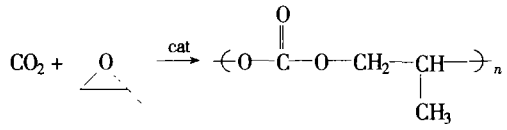
FTIR spectroscopic analysis was carried out by using an Analect RFx-65A FTIR spectrometer. NMR data were recorded at 400 MHz in a Bruker NMR instrument (Model: DRX 400 MHz) and were listed in parts per million downfield from tetramethylsilane (TMS). Chloroform-d_1 ($CDCl_3$) was used as the solvent. The molar fraction of CO_2 units in the copolymer products was determined by ^1H NMR spectroscopy. The surface morpho- logies of degraded membranes were examined in scanning electron microscope (JEOL JSM 820). In addition, instrinsic viscosity [η] measurements were carried out in benzene at 35.0 ℃ using an Ubbelohde suspended level capillary viscometer. The molecular weight (M_n) can be calculated from the equation:

$$[\eta] \times 10^{-2} = 1.11 \times 10^{-4} M_n^{0.8} (\text{mL/g})$$

3 Results and discussion

3.1 Molecular structure and properties of poly (propylene carbonate)

Poly(propylene carbonate) derived from CO_2 and PO and catalyzed by perflurorine compound supporting zinc glutarate has been previously reported in the literature[14-18]. The reaction scheme is depicted as follows,



PPC

In order to improve the copolymerization process and to enhance the catalytic efficiency, perfluorine compound supporting zinc glutarate was prepared and used as the catalyst in this work[10]. The copolymerization was carried out under a 5.0 MPa pressure with PO as either monomer or solvent. The resulting PPC copolymer exhibits white color that can be cast into a tough and transparent film. By adjudging the PO/cat ratio from 100(mL/g cat) to 400(mL/g cat), an optimum PO/cat ratio of 200(mL/g cat) can be achieved (Tab. 1). This table reveals that high molecular weight PPC can be afforded in a very high yield of 126 g polymer/g cat, which is the highest value that has never been reported in literature.

Tab. 1 Effect of catalyst/PO ratio on the yield and molecular weight of PPC

$\frac{V(PO)}{mL}$	$\frac{m(Cat)}{g}$	$\frac{V(PO)}{m(cat)}$	$\frac{\gamma}{(g \cdot g_{cat}^{-1})}$	$\frac{M_n}{1000}$
100	0.25	400	46.6	51.4
100	0.30	333	48.4	53.6
100	0.35	286	65.3	66.3
100	0.45	222	87.7	62.5
100	0.50	200	126.0	56.1
100	0.75	133	88.8	36.2
100	1.0	100	68.3	55.0

Copolymerization conditions: Pressure of CO_2, 5.0 MPa, stirred at 100 rpm in a 500 mL autoclave at 60 ℃ for 40 h.

Fig. 1 shows the ^{13}C NMR (ClD_3) spectrum for the PPC δ: 16.1 (CH_3), 69.0 (CH_2CH), 72.2(CH_2CH), 154.2 (OCOO). It is apparent that there is no poly (propylene oxide) units present in the copolymer product. The chemical shifts of all carbons in the PPC are assigned as shown in Figure 1, demonstrating its exact alternating molecular structure. If there are any poly (propylene oxide) units in the copolymer product, their amounts would be very small.

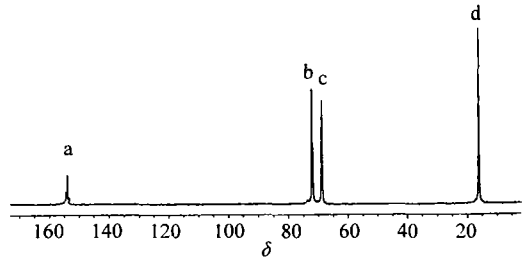
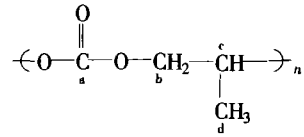


Fig. 1 Typical ^{13}C NMR spectrum of the alternating PPC copolymer derived from carbon dioxide and propylene dioxide



3.2 Degradation behavior

3.2.1 Weight loss

PPCs with M_r of 362000 and 1206000 respectively are selected as target materials for the investigation of their degradation behavior. Figure 2 shows the weight loss of PPC versus degradation time after soil and buffer solution immersion tests, respectively. For the soil burial test, it can be seen that the weight loss of PPC rapidly reaches to 1.69% in the first month, and then continues to increase up to about 3.00% after four months exposure. Thereafter, the weight loss value shows little increase with further exposure in wet soil. Such small weight loss value is in consistent with the results of other workers[19-21]. According to their works, the copolymer of CO_2 and ethylene oxide exhibits better biological or natural degradation ability than PPC.

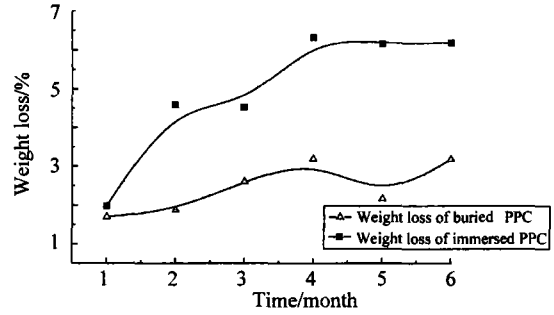


Fig. 2 Weight loss versus time for poly(propylene carbonate) in soil burial and buffer solution

It has been reported that the copolymers of carbon dioxide and epoxides can be degraded either in acidic and alkaline solutions[22] or in the peritoneal cavity of rats without causing any visible inflammation reaction[20]. Ming Zhou et al[19] have studied the enzyme-catalyzed degradation of copolymers of carbon dioxide and epoxides. They reported that the aliphatic polycarbonates containing oxyethylene units (ether linkages) can be degraded with a

single enzyme. In order to evaluate the similar degradation properties, the degradation behavior of PPC in buffer solution with a low acid concentration close to that in human stomach is also investigated. Fig.1 shows that the weight loss of PPC in buffer solution increases rapidly during the first two months and reaches to 4.59%. After four month's exposure, the weight loss further increases up to about 6.32% followed by leveling off. Presumably, the slow down in weight loss with prolonged exposure speed is resulted from the change of pH value in degradation vessel. Apparently, the degradation of PPC in buffer solution is much faster than that in soil burial. It is considered that the acidic environment favors the hydrolysis of aliphatic polycarbonate. This agrees with the work of Midori Takanashi et al[22] who reported a similar degradation behavior of aliphatic polycarbonate exposed in a strong acidic solution with pH = 1.

3.2.2 Morphology observation

It is well known that the morphology changes of degraded specimens can provide direct information or evidence for their degradation characteristics. Fig.3(a) and Fig.3(b) are SEM micrographs showing the surface morphologies of the PPC after soil burial for 1 and 6 months, respectively.

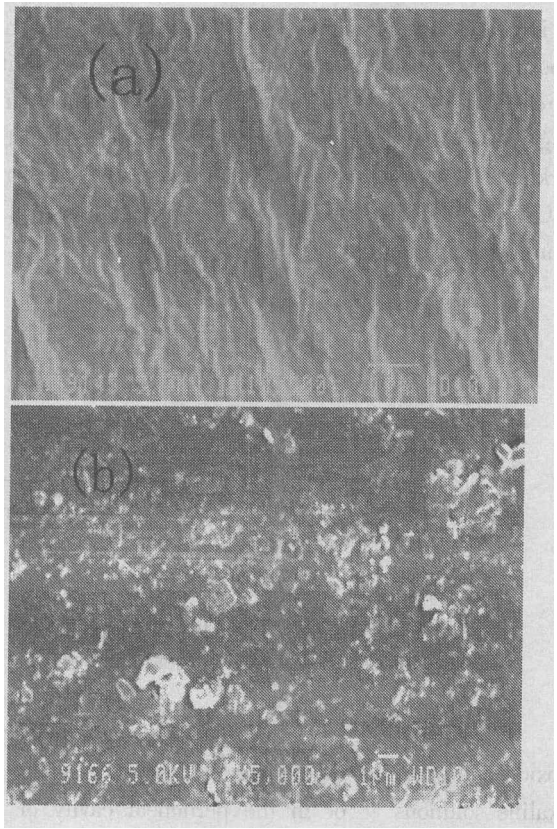


Fig.3 SEM micrographs of PPC thin film after soil burial degradation for (a) one month and (b) 6 months

No obvious degradation evidence can be seen from the morphology change of PPC as shown in Fig.3(a) due to a very low degree of degradation. The sample subjecting to 6 months burial shows a rough surface (Fig. 3(b)). This implies that the degradation indeed takes place, although it is not obvious from the weight loss experimental. It is considered that the degraded materials adhere firmly on the specimen surface. The degraded segments cannot be thoroughly washed away like immersing test. Fig.4(a) and Fig.4(b) show the surface morphologies of PPC specimens immersed in the buffer solution for two-month and five-month, respectively. Apparently, numerous large cavities can be observed in both samples. This is in good accordance with the weight loss results as discussed above (Fig.2). These micrographs with cavities evince that the degradation begins from the surface, and where have been degraded favors further degradation, therefore produces cavities in the surface of thin-films.

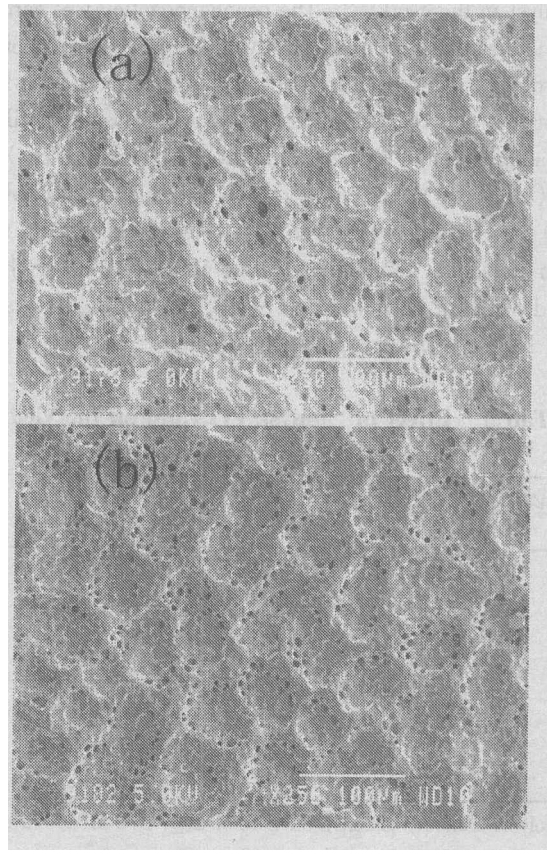


Fig.4 SEM micrographs of PPC thin film after soil burial degradation for (a) two month and (b) five months

Fig.5 is the IR spectra of original and degraded PPC specimens. No difference in the absorbance peaks can be observed for the samples both exposed to the soil and buffer solution for 6 months. From the ^1H NMR spectra (Fig.6) of these PPC specimens, and there is no difference between the original and degraded specimens. These results demonstrate that there is no chemical structural change occurrence during the degradation. The result is similar to that reported by other re-

searchers[21,22].

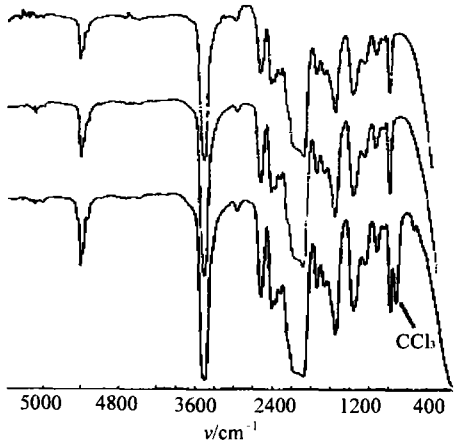


Fig.5 IR spectra of various PPC specimens
(a) original specimen,
(b) the specimen degraded in buffer solution for 6 months;
(c) the sample degraded in soil for 6 months

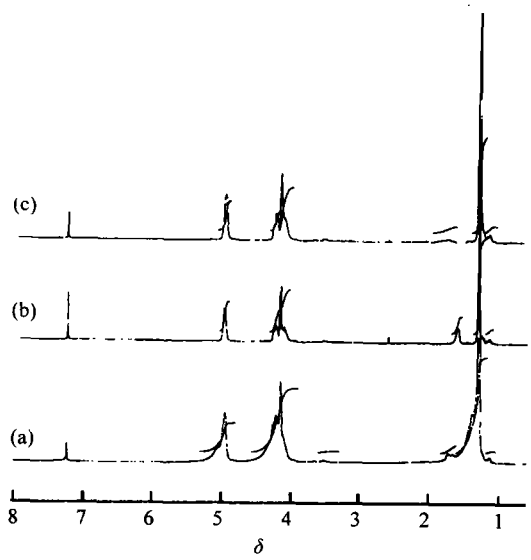


Fig.6 1H NMR spectra of various PPC samples
(a) original specimen,
(b) the sample degraded in soil for 6 months,
(c) the specimen degraded in buffer solution for 6 months

3.2.3 Hydrophilicity

The amount of water absorbed by aliphatic polyesters during burial and immersion plays a key role in enhancing their degradation rate. Water content is generally used to evaluate the hydrophilicity of examined samples. Fig. 7 shows the water sorption as a function of time for the PPC film specimens after soil burial and buffer solution degradation, respectively. The water absorption for the PPC film immersed in buffer solution changes very little over the six months period. But it is still higher than that of the sample buried in soil for the first three months. This arises from that the weight loss of PPC thin film in buffer solution is higher than that exposed in soil burial.

Fig. 7 reveals that a water absorption of the soil burial sample increases rapidly up to 10.4% after 4 ~ 6 months. Considering a small weight loss of the buried samples, it is believed that the degraded segments on the sample surface can absorb considerable amount of water. This is consistent with the SEM observation. On the basis of experimental results, it appears that the difference in the degradation rate between the samples exposed to the soil burial and buffer solution immersion is not so significant as shown in Fig. 2. We conclude that the synthesized PPC can degrade in either soil burial or buffer solution immersion.

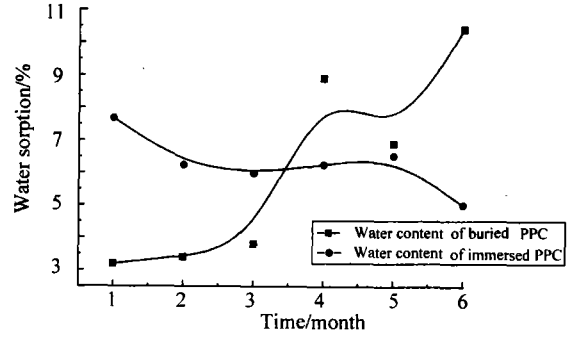


Fig.7 Water sorption versus time for the PPC specimens degraded in soil burial and buffer solution, respectively

4 Conclusions

High molecular weight and regular molecular structure poly(propylene carbonate) with an alternating molecular structure was successfully synthesized from the carbon dioxide and propylene oxide. Degradation behavior of the PPC was examined by the soil burial and buffer solution immersion tests, respectively. The results showed that the weight loss of PPC membranes exposed to the soil burial increased more slowly than that immersed in buffer solution. For the PPC films in buffer solution with low acid concentration (pH = 6), the weight loss tended to increase rapidly during the first two months and reached a maximum value of 6.32% after 6 months exposure. The water sorption test results revealed that the sample immersed in the buffer solution was more hydrophilic than that exposed to the soil burial. SEM morphologies of the degraded samples were consistent with the results of weight loss and water sorption measurements. Finally, PPC showed poorer degradability exposed to the soil burial compared with that immersed in buffer solution.

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由二氧化碳和环氧丙烷生成的聚碳酸亚丙酯的合成与降解行为

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摘 要: 由二氧化碳和环氧丙烷成功合成了高分子量、规则分子链结构的聚碳酸亚丙酯(PPC)。^{13}C NMR 谱证明所得 PPC 共聚物具有交替结构。PPC 的降解行为通过土壤埋藏法和溶液沉浸法来研究。结果表明在 6 个月后土壤埋藏的 PPC 膜比沉浸在缓冲溶液中的膜质量损失增加得更慢。而在缓冲溶液中沉浸的膜在最初的两个月中质量损失增加的很快,达到 4.59%。吸水实验也同样显示在缓冲溶液中的 PPC 膜比土壤埋藏测试中吸水性更强。PPC 膜的降解机理和样品的形态、红外光谱以及 ^1H NMR 谱相一致。扫描电镜形态和质量损失以及吸水测量的结果一致。

关键词: 降解;聚碳酸亚丙酯;二氧化碳;环氧丙烷

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