

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 ¹³C-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 in 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 2 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. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1840–1846, 2004

Key words: degradation; polycarbonates; biodegradable; synthesis

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 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 rays.^{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 an 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 this 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) (PEG) comprising PCL (A) and PEG (B) segments by copolycondensation of ϵ -caprolactone (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.

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More recently, we have successfully synthesized high molecular weight poly(propylene carbonate) (PPC) from carbon dioxide and propylene oxide by using supported catalysts.^{10,11} The production cost of PPC is much lower than PCL or PCL/PCE copolymers because of 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 aliphatic ester linkages within the new polymer, and its amorphous microstructure, the PPC is considered to exhibit reasonable degradation properties. Because PPC is a newly synthesized polymer, very little information is available about its degradability in the literature. In this regard, we attempt to prepare degradable PPC thin-film specimens via the solution-casting method. The degradation behavior of PPC is examined by the soil burial and buffer solution immersion.

EXPERIMENTAL

Materials

Propylene oxide (PO) (Yueyang Petrochemical Co., Ltd., Nanjing, China) with a purity of 99.5% was further purified by distillation for 2 h over calcium hydride. 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 (from Shanghai Gas Co. Ltd., Shanghai, China). Toluene and acetone were of analytical reagent grade; methanol and 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 PPC film specimens by the solution-casting method. Glutaric acid (GA) (Jiangling Petrochemical Co. Ltd., Nanjing, China) of 98.0% purity, zinc oxide of 99.99% purity, and perfluorinated compounds were also used without further treatment.

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-necked 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 perfluorinated compound, and the mixture was slowly heated up to 55°C for 6 to 8 h under vigorous stirring. Upon cooling, the resulting mixture was filtered. The resulting solids were continuously washed with acetone several times, followed by drying overnight in a vacuum oven at 100°C. The supported zinc glutarate was obtained as a white

fine powder and at a yield greater than 99.5%. The copolymerization of CO₂ with PO was performed in a 500-mL autoclave equipped with a mechanical stirrer. Supported zinc glutarate was further dried at 100°C for 24 h prior to being used for the polymerization process. The detailed process was reported in previous work.¹⁰

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 5 wt % 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 rectangular box (50 × 25 × 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. The soil was watered every 3 days to make it wet. 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 0.2M potassium benzene dicarbonic acid and a small amount of NaOH. The container was then placed in a thermobath regulated at 45°C. 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, from both soil burial and buffer solution experiments, were dried with filter paper after washing with distilled water and weighed (W_1). The film specimens were dried in a vacuum oven to a constant weight (W_2). The amounts of water absorbed by the specimens were determined from the equation:

$$\text{Water sorption (\%)} = [(W_1 - W_2)/W_2] * 100$$

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 400MHz) and were listed in parts per mil-

TABLE I
Effect of Catalyst/PO Ratio on the Yield and Molecular Weight of PPC

PO (mL)	Catalyst (g)	PO/catalyst (mL/g)	Yield (g/g cat.)	M_n (k)
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

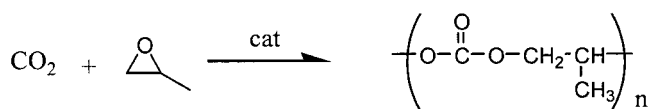
Copolymerization conditions: pressure of CO₂, 5.0 MPa, stirred at 100 rpm in a 500 mL autoclave at 60°C for 40 h.

lion (ppm) downfield from tetramethylsilane (TMS). Chloroform-d₁ (CDCl₃) was used as the solvent. The molar fraction of CO₂ units in the copolymer products was determined by ¹H-NMR spectroscopy. The surface morphologies of degraded membranes were examined in a scanning electron microscope (JEOL JSM 820). In addition, intrinsic viscosity [η] measurements were carried out in benzene at 35.0°C by using a Ubbelohde suspended-level capillary viscometer. The molecular weight (M_n) can be calculated from the equation: [η] $\times 10^{-2} = 1.11 \times 10^{-4} M_n^{0.8}$ (ml/g).

RESULTS AND DISCUSSION

Molecular structure and properties of poly(propylene carbonate)

PPC derived from CO₂ and PO and catalyzed by perfluorine compound supporting zinc glutarate was previously reported in the literature.¹³ The reaction scheme is depicted as



PPC

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 a 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 (Table I). 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 ever been reported in the literature.

Figure 1 shows the ¹³C-NMR (CDCl₃) spectrum for the PPC: δ (ppm): 16.1 (CH₃), 69.0 (CH₂CH), 72.2 (CH₂CH), 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.

Degradation behavior

Weight loss

PPCs with molecular weights of 36.2 and 120.6K, respectively, were 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 1.69% in the first month and then continues to increase up to about 3.00% after 4 months exposure. Thereafter, the weight loss value shows little increase with further exposure in wet soil. Such small weight loss value is consistent with the results of other workers.¹⁴⁻¹⁶ According to their works, the copolymer of CO₂ and ethylene oxide exhibits better biological or natural degradation ability than PPC. However, there were no data reported for the degradability of PPC in buffer solution.

It was reported that the copolymers of carbon dioxide and epoxides can be degraded either in acidic and alkaline solutions¹⁷ or in the peritoneal cavity of rats without causing any visible inflammation reaction.¹⁵ Zhou et al.¹⁴ 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. 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. Figure 1 shows that the weight loss of PPC in buffer solution increases rapidly during the first 2 months and reaches 4.59%. After 4 months 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 resulted from the change of pH value in the degradation vessel.

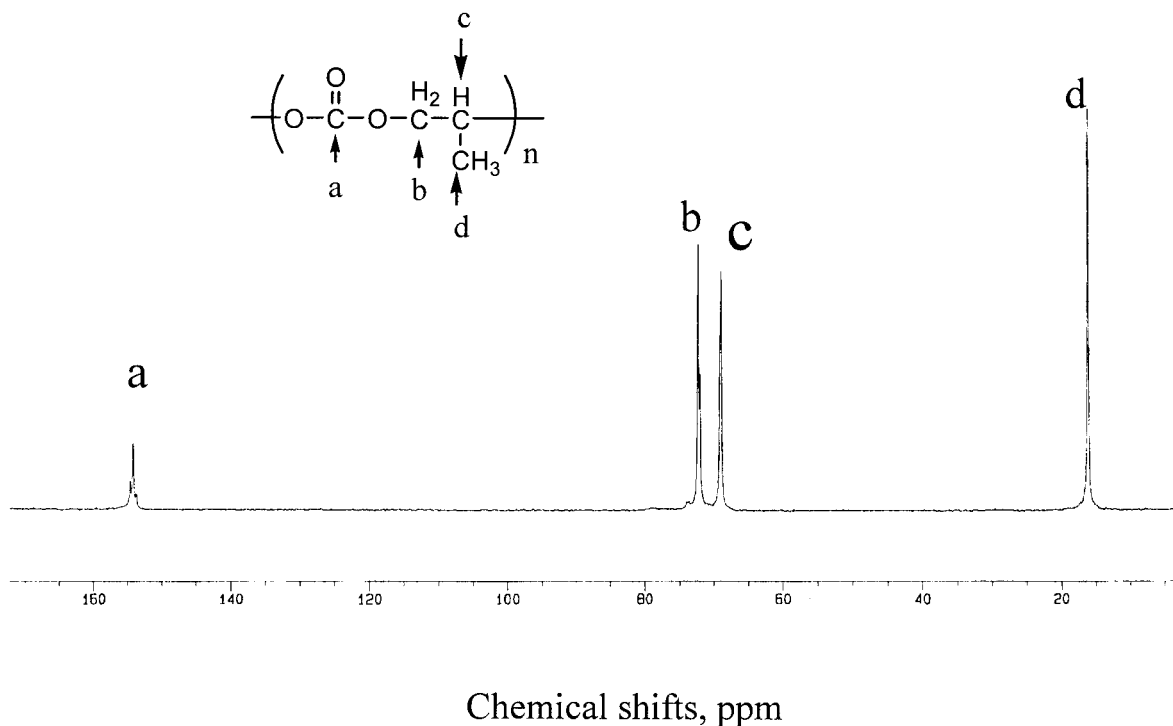


Figure 1 Typical ^{13}C -NMR spectrum of the alternating PPC copolymer derived from carbon dioxide and propylene dioxide.

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 Takanashi et al.,¹⁷ who reported a similar degradation behavior of aliphatic polycarbonate exposed in a strong acidic solution with pH = 1.

Morphology observation

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

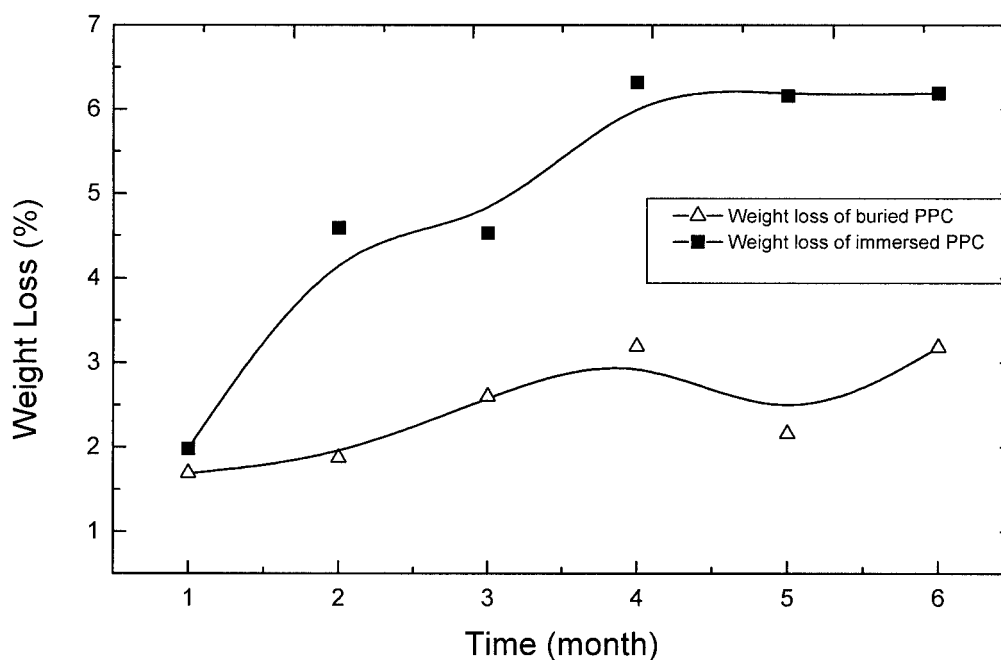


Figure 2 Weight loss versus time for poly(propylene carbonate) in soil burial and buffer solution.

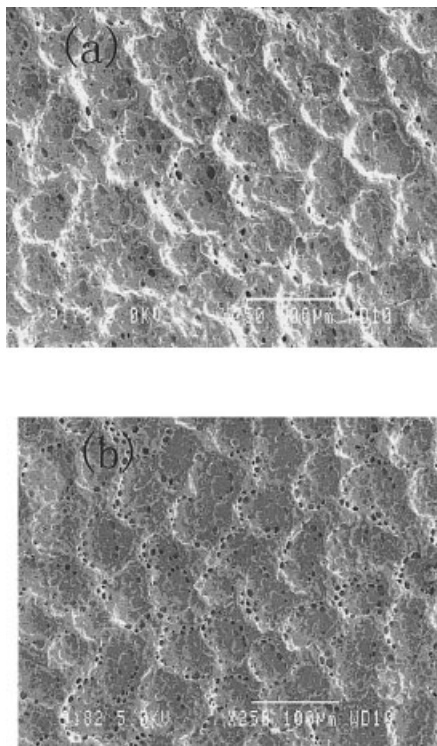


Figure 3 SEM micrographs of original PPC film (c) PPC thin film after soil burial degradation for (a) 1 month and (b) 6 months.

months, respectively. Compared with the morphology of original PPC film [Fig. 3(c)], no obvious degradation evidence can be seen from the morphology change of PPC, as shown in Figure 3(a) due to a very low degree of degradation. The sample subjected 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 experiment. It is considered that the degraded materials adhere firmly on the specimen surface due to the relative low glass transition temperature (about 40°C) of PPC. The degraded segments cannot be thoroughly washed away like the immersing test. Figure 4(a, b) shows the surface morphologies of PPC specimens immersed in the buffer solution for 2 and 5 months, 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 degradation favors further degradation, therefore, produces cavities in the surface of thin films.

Figure 5 is the IR spectra of original and degraded PPC specimens. No difference in the absorbance peaks can be observed for the samples exposed to both the soil and the buffer solution for 6 months. From the $^1\text{H-NMR}$ spectra (Fig. 6) of these PPC specimens, there is no difference between the original and degraded

specimens. These results demonstrate, for the remaining and undegradable PPC film, that there is no chemical structural change on the backbone during the degradation. The result is similar to that reported by other researchers.^{16,17}

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. Figure 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

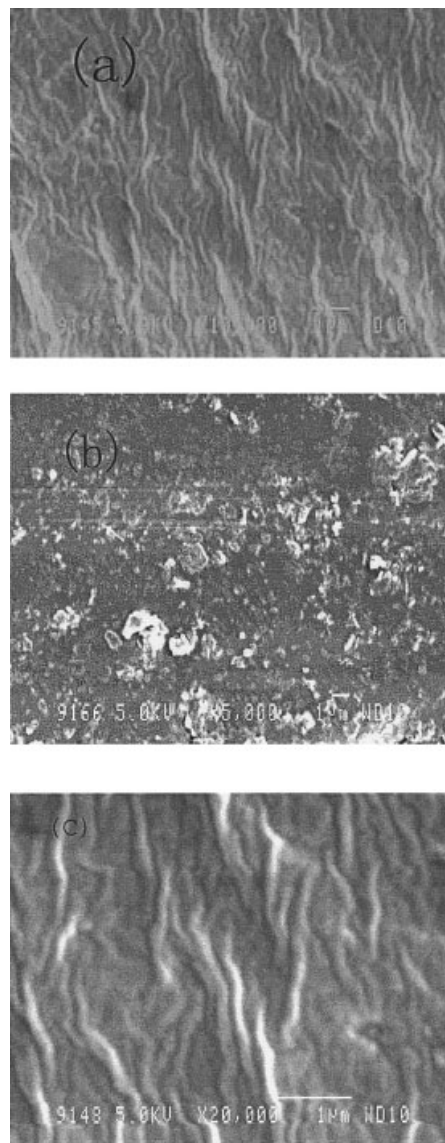


Figure 4 SEM micrographs of PPC thin film immersed in buffer solution for (a) 2 months and (b) 5 months.

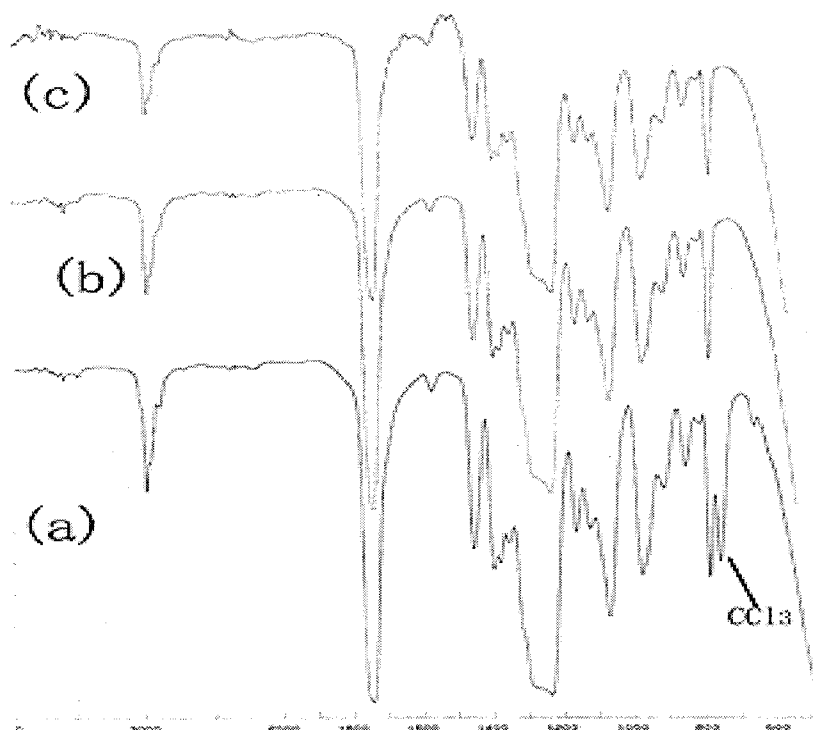


Figure 5 IR spectra of various PPC specimens. (a) Original specimen, (b) the specimen degraded in buffer solution for 6 months, and (c) the sample degraded in soil for 6 months.

solution changes very little over the 6-month period. However, it is still higher than that of the sample buried in soil for the first 3 months. This arises from the finding that the weight loss of PPC thin film in buffer solution is higher than that exposed in soil burial. Figure 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 a 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 to the buffer solution immersion is not so significant, as shown in Figure 2. We conclude that the synthesized PPC can degrade in either soil burial or buffer solution immersion.

CONCLUSION

High molecular weight and regular molecular structure PPC 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 ($\text{pH} = 6$), the weight loss tended to increase rapidly during the first 2 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 consis-

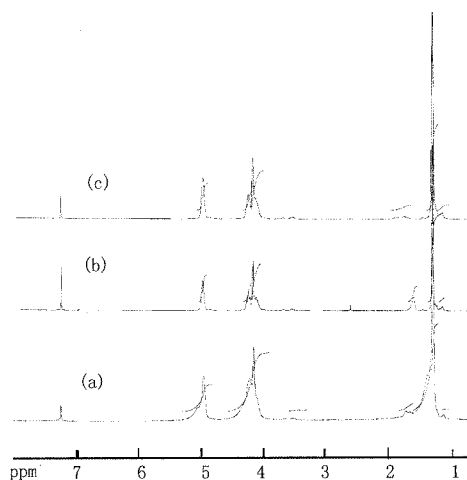


Figure 6 $^1\text{H-NMR}$ spectra of various PPC samples. (a) Original specimen, (b) the sample degraded in soil for 6 months, and (c) the specimen degraded in buffer solution for 6 months.

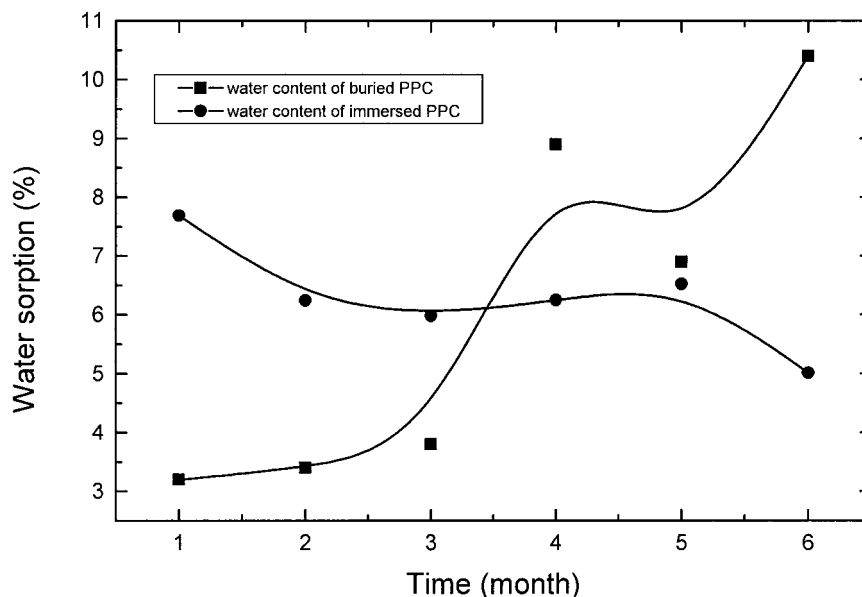


Figure 7 Water sorption versus time for the PPC specimens degraded in soil burial and buffer solution, respectively.

tent 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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