Available online at www.sciencedirect.com
SCIENCE DIRECT
Catalysis Today 115 (2006) 288–294
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Enzymatic degradation of poly(propylene carbonate) and poly(propylene carbonate-co-ε-caprolactone) synthesized via CO_2 fixation

Yongtaek Hwang [a], Moonhor Ree [a,*], Heesoo Kim [b,**]

[a] *National Research Lab for Polymer Synthesis and Physic, Department of Chemistry, Center for Integrated Molecular System, School of Environmental Science and Engineering, Polymer Research Institute, and Division of Molecular & Life Sciences (BK21 Program), Pohang University of Science & Technology, Pohang 790-784, Republic of Korea*

[b] *Department of Microbiology, Dongguk University College of Medicine, Gyeongju 780-714, Republic of Korea*

Available online 3 April 2006

Abstract

Poly(propylene carbonate) (PPC) and poly(propylene carbonate-co-ε-caprolactone) (PPCCL) were synthesized via the zinc glutarate catalyzed copolymerization of carbon dioxide (CO_2) and propylene oxide (PO) without and with ε-caprolactone (CL), respectively. In addition, poly(ε-caprolactone) (PCL) was prepared via the homopolymerization of CL with the aid of methyl triflate catalyst. The polymer products were characterized in terms of their chemical compositions, molecular weights, and thermal properties. Films of these polymers were tested with a series of enzymes (four different families and a total of 18 enzymes) in a phosphate buffer in order to characterize their enzymatic degradabilities. This is the first report demonstrating that PPC films exhibit positive enzymatic degradability with *Rhizopus arrhizus* lipase, esterase/lipase ColoneZyme A, and Proteinase K. Moreover, PPCCL films exhibited positive enzymatic degradability with most of the enzymes utilized in our study, and thus PPCCL has an enzymatic degradability comparable to that of PCL. In particular, the PPCCL films exhibit excellent enzymatic degradability with *Pseudomonas* lipase, *Rhizopus arrhizus* lipase, and esterase/lipase ColoneZyme A. Considering its excellent enzymatic degradability, the PPCCL terpolymer has potential biomedical applications. In conclusion, ZnGA-catalyzed copolymerizations of CO_2 and PO with or without CL are chemical fixation processes of CO_2 that can be used to produce enzyme-degradable aliphatic polymers.

Keywords: Chemical fixation of CO_2; Polycarbonate; Poly(carbonate-co-ester); Zinc glutarate catalyst; Enzymes; Enzymatic degradability

1. Introduction

Carbon dioxide (CO_2) is considered the greenhouse gas most responsible for global warming, which may result in climate change [1]. Thus, the reduction of CO_2 emissions is a high priority, and CO_2 capture and utilization (or disposal) are currently under active investigation.

In fact, CO_2 is the cheapest and most abundant raw material source of carbon. One possible utilization of CO_2 is in the production of polymeric materials that can be used in industry. A good example of such polymeric materials is poly(alkylene carbonate), which can be produced by the copolymerization of CO_2 with alkylene oxide [2–15]. However, the major drawback of this approach is the relatively high stability of CO_2, which means that its copolymerization with alkylene oxide requires a highly active catalyst.

Recently, we reported a highly efficient process for the copolymerization of CO_2 and propylene oxide (PO) using zinc glutarate (ZnGA) catalyst, which can produce PPC in a high yield [10]. In this new copolymerization process, PO is used both as a comonomer and as the reaction medium, so no organic solvent is involved in the copolymerization and the process does not produce organic solvent waste [10]. Thus this copolymerization process is a green polymerization process. This green copolymerization process was found to produce poly(propylene carbonate) (PPC) containing no ether linkages and does not generate any byproducts.

* Corresponding author. Tel.: +82 54 279 2120; fax: +82 54 279 3399.
** Corresponding author.
E-mail addresses: ree@postech.edu (M. Ree), hskim@dongguk.ac.kr (H. Kim).

0920-5861/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2006.02.061

On the other hand, aliphatic polyesters are presently thought to be the most attractive class of artificial polymers from the environmental standpoint, in that they degrade in contact with living tissues and in outdoor conditions [16,17]. In particular, poly(ε-caprolactone) (PCL) is biodegradable and of commercial interest because of its remarkable compatibility with a number of polymers [16,17].

Taking these considerations into account, we attempted to extend the proposed green polymerization process to the synthesis of a terpolymer of CO_2 and PO with ε-caprolactone (CL) [18]. The terpolymer poly(propylene carbonate-co-ε-caprolactone) (PPCCL) was successfully produced with various CO_2, PO, and CL compositions via the green polymerization process with the aid of a ZnGA catalyst. The PPCCL products were found to be highly soluble in PO and CL. The success of this green terpolymerization process is attributed to the high solubility of the terpolymer products in the comonomers. The ZnGA catalyst was found to exhibit catalytic activity in this terpolymerization process that is as good as that observed in the copolymerization of CO_2 and PO. However, the ZnGA catalyst was found to have no catalytic activity with respect to the polymerization of CL monomer. The synthesized PPCCL terpolymers were found to consist of propylene carbonate (PC) and CL blocks, i.e. they were not random in composition.

In this study, we investigated the enzymatic degradabilities of PPC copolymer and PPCCL terpolymers, which are very much attractive from the environmental standpoint and, on the other hand, necessarily as potential candidate materials for biomedical applications. The enzymatic degradations of films of PPC and PPCCL in the presence of various enzymes were studied in a phosphate buffer solution; the weight losses, crystallinities, thermal properties, and surface morphologies of the films that arose as a result of the enzymatic degradations were also determined. All results of these polymers were compared with those of PCL polymer in films investigated in the same conditions.

2. Experimental

2.1. Polymer syntheses

PPC copolymer was synthesized via the ZnGA-catalyzed copolymerization of CO_2 and PO, and PPCCL terpolymer was prepared via the ZnGA-catalyzed terpolymerization of CO_2 with PO and CL (Fig. 1 and Table 1) [10,18]. CO_2 (>99.8% purity) was obtained from the BOC Gases Company (Korea) and PO was obtained from SK Oxichemical Company (Korea). CL was purchased from the TCI Company (Japan). All other chemicals used in this study were purchased from Aldrich. PO was further purified by distillation over calcium hydride under dry nitrogen gas before use. Toluene and CL were purified with the usual methods before use. All the other chemicals were used as received without further purification. The ZnGA catalyst used in the polymerizations was synthesized from zinc oxide and glutaric acid, as described elsewhere [10]. In addition, PCL polymer was prepared via the homopolymerization of CL monomer in nitrobenzene with methyl triflate as a catalyst [18].

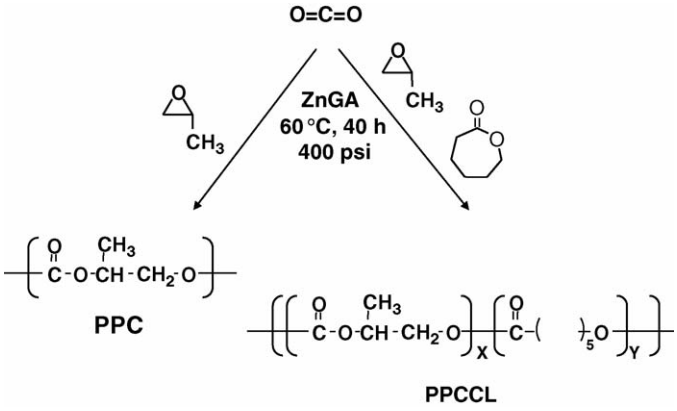

Fig. 1. Synthetic schemes of PPC and PPCCL from CO_2.

2.2. Film preparation

Films of the polymers were prepared for the enzymatic degradation studies by compression molding. The compression molding was carried out at 120 °C for 5 min at a pressure of 100 kg/cm^2, and then the films were cooled with liquid nitrogen. The thicknesses of the films were around 0.30 mm. For the enzymatic degradation tests, all the polymer films were cut into 10 mm × 10 mm pieces, which were dried in vacuum at room temperature for 2 days before use.

Table 1
Compositions, molecular weights, and thermal properties of the synthesized polymers

Polymer film	Composition (mol%)[a]		Molecular weight[b]	Phase transition temperature[c]	Crystallinity[d]
	PC	CL	$\bar{M}_w/\bar{M}_n$/PDI	T_g (°C)/T_m (°C)	X_c (%)
PPC	100	–	673k/226k/2.97	38.6/–	–
PPCCL	67	33	441k/165k/2.67	(−63.2)[e]/33.3/53.9	10.2
PCL	–	100	70k/53k/1.32	−63.2/57.9	49.5

[a] Determined by ^{1}H and ^{13}C NMR spectroscopy.
[b] Measured by GPC calibrated with polystyrene standards: $\bar{M}_w$, weight-average molecular weight; $\bar{M}_n$, number-average molecular weight; PDI, polydispersity.
[c] Measured with a rate of 10.0 °C/min under nitrogen atmosphere by differential scanning calorimetry (DSC).
[d] Bulk crystallinity from the DSC measurements.
[e] T_g expected for the CL blocks in DSC run but could not easily be measurable due to the inherently weak signal.

Table 2
PPC, PPCCL, and PCL degradation activities of various enzymes

Enzyme preparation	PPC (weight loss %)	PPCCL (weight loss %)	PCL (weight loss %)
Lipase (*Pseudomonas* spp.)[a]	0.6	65.3	78.2
Lipase (*Rhizopus arrhizus*)[b]	2.4	10.0	13.2
Esterase/lipase ColoneZyme A (ESL001-07™)[c]	9.2	22.6	16.4
Esterase/lipase ColoneZyme B (ESL001-06™)[d]	0.0	4.1	2.3
Esterase/lipase ColoneZyme C (ESL001-05™)[d]	0.0	4.1	2.2
Esterase/lipase ColoneZyme D (ESL001-04™)[d]	0.7	3.0	2.3
Esterase/lipase ColoneZyme D (ESL001-03™)[d]	0.7	4.4	3.7
Esterase/lipase ColoneZyme D (ESL001-02™)[d]	0.0	3.7	1.7
Esterase/lipase ColoneZyme D (ESL001-01™)[d]	0.8	3.9	2.5
Proteinase K[e]	4.2	5.0	5.3
Staphylococcal serine protease[b]	1.2	3.4	4.2
Trypsin (porcine pancreas)[b]	1.3	4.9	4.5
α-Amylase (bacillus)[f]	0.9	4.8	4.2
α-Amylase (porcine pancreas)[g]	0.5	1.6	1.5
α-Amylase (human saliva)[h]	0.2	1.6	1.7
α-Amylase (barley malt)[g]	0.4	2.5	2.3
β-Amylase (barley)[i]	0.8	5.2	4.9
β-Amylase (sweet potato)[j]	0.1	2.4	2.6

[a] 0.50 mg/1.0 mL buffer; 37 °C; 3 days.
[b] 2.00 mg/1.0 mL buffer; 37 °C; 3 days.
[c] 0.25 mg/1.0 mL buffer; 37 °C; 10 days.
[d] 0.25 mg/1.0 mL buffer; 60 °C; 10 days.
[e] 0.25 mg/1.0 mL buffer; 37 °C; 10 days.
[f] 1.20 mg/1.5 mL buffer; 37 °C; 7 days.
[g] 0.50 mg/1.0 mL buffer; 37 °C; 7 days.
[h] 50 unit/1.5 mL buffer; 37 °C; 7 days.
[i] 50 unit/1.0 mL buffer; 37 °C; 7 days.
[j] 500 unit/1.5 mL buffer; 37 °C; 7 days.

2.3. Enzymatic degradation tests

Eighteen different enzymes were purchased from Sigma Corporation and used in the enzymatic degradation tests: two lipases, seven esterase/lipase ColoneZyme™ kits, three proteinases, and six amylases (Table 2). All enzymatic degradation tests were carried out in 0.02 M phosphate buffer solution (pH 7.0) containing 0.04 wt.% sodium azide to prevent microbial contamination. Each film specimen was incubated in the buffer solution of each enzyme with gentle shaking (see Table 2), rinsed with distilled water, and then dried in vacuum at 25 °C to a constant weight. The weight loss was then determined.

2.4. Characterization

The spectroscopic analysis of the polymer products was performed using a Bruker NMR spectrometer (Model: ASPECT 300 MHz) with ^{1}H and ^{13}C probes. In the NMR spectroscopic measurements, chemical shifts were calibrated with the chemical shifts of the solvent, i.e., chloroform-d_1. The weight average molecular weight ($\bar{M}_w$) and polydispersity index (PDI) of each polymer product were determined with a gel permeation chromatography (GPC) system (Polymer Labs Model PL-GPC 210). The GPC system was calibrated with a series of polystyrene standards. Tetrahydrofuran (THF, HPLC grade) was used as the eluent. The thermal properties of the polymers were measured at a heating rate of 10.0 °C/min using a Seiko differential scanning calorimeter (Model: DSC-220CU); dry nitrogen gas was purged at a flow rate of 100 mL/min. The compositions, molecular weights, and properties of the polymer products are summarized in Table 1. The crystallinities, thermal properties, and surface topographies of the polymer film specimens were examined before and after the enzymatic degradations. In particular, the films' surface topographies were examined with a scanning electron microscope (SEM, Hitachi S-570) after coating with gold.

3. Results and discussion

PPC polymer was synthesized via the ZnGA-catalyzed copolymerization of CO_2 with PO, and PPCCL polymer was prepared via the ZnGA-catalyzed terpolymerization of CO_2 with PO and CL in a 50/50 molar ratio. In addition, PCL polymer was synthesized. All the polymers were obtained with reasonably high molecular weights. These polymer products were characterized, and the results are summarized in Table 1. Note that the PPC polymer we obtained is completely amorphous, with a glass transition temperature T_g of 38.6 °C and that the PCL polymer is semicrystalline, with a T_g of −63.2 °C and a melting point T_m of 57.9 °C. The PPCCL polymer was found to be a terpolymer consisting of PC and CL blocks, with a T_g of 33.3 °C for the PC blocks and a T_m of 53.9 °C for the CL blocks. A glass transition was expected to appear for the CL blocks near −63.2 °C, but was not detected

due to its very weak signal. The glass transition of the PCL homopolymer could not be detected in the DSC measurements because of the high crystallinity of the polymer.

The PPC, PPCCL, and PCL films were treated with various enzymes in a phosphate buffer solution with pH 7.0 for a day at 37 or 60 °C. The weight losses of the films due to enzymatic degradation were monitored. Four different families of enzymes were tested. The results are shown in Table 2.

The first enzyme family consists of lipases. As can be seen in Table 2, *Pseudomonas* lipase, the most common lipase, exhibits very poor activity in the degradation of the PPC film. This result is consistent with the results of previous reports [19,20]. It has been suggested that this lack of enzymatic activity is due to either steric inhibition of the access of PPC to the active site of the enzyme by the methyl substituents in the polymer backbone, or to PPC's physical properties, i.e., its relatively high glass transition temperature T_g and high modulus, when compared to those of poly(ethylene carbonate) (PEC), which exhibits some enzymatic degradability with *Pseudomonas* lipase [19,20].

In contrast, the PPCCL polymer film surprisingly exhibits very high degradability with the *Pseudomonas* lipase (Table 2), even though the terpolymer is a semicrystalline polymer consisting of 67 mol% PC blocks and only 33 mol% CL blocks, with a high T_m (53.9 °C), a high T_g (33.3 °C), and a high modulus. In fact, this lipase has previously been reported to exhibit excellent activity in the degradation of PCL films [21,22]. The high activity of this lipase in the degradation of PCL films was also confirmed in the present study (Table 2). Taking these facts into account, the high enzymatic degradability of the PPCCL film found in our study is mainly attributed to the favorable high susceptibility of the CL blocks in the terpolymer to the enzymatic attacks of the lipase. This result also indicates that the chemical structural features of polymers are more influential than their physical properties (T_g, T_m, crystallinity, mechanical modulus, etc.) on their susceptibility to enzyme attack.

Interestingly, another lipase, *Rhizopus arrhizus* lipase, exhibits better activity in the degradation of PPC films than the *Pseudomonas* lipase (Table 2). This result indicates that the PPC chemical backbone has greater susceptibility to the attack of *Rhizopus arrhizus* lipase, and also suggests that *Rhizopus arrhizus* lipase is an enzyme with potential to mediate the degradation of PPC. On the other hand, the PPCCL and PCL films exhibit weight losses in the range 10–13.2 wt.% in treatments with this lipase. These weight losses are much lower than those observed in the treatments with *Pseudomonas* lipase, which indicates that the attack of the *Rhizopus arrhizus* lipase on the CL backbones in the PCL film and the CL blocks in the terpolymer is less favorable than that of the *Pseudomonas* lipase. However, the observed weight losses are still larger than that for the PPC film. Overall, these results are significantly different from those in a previous report, which claimed that *Rhizopus arrhizus* lipase has no activity in the degradation of aliphatic polyesters or of polycarbonates such as PEC and PPC [23]. Perhaps, these discrepancies are attributed to the catalytic activity of *Rhizopus arrhizus* lipase that depends on its production batch to batch and the test conditions; the test conditions of the present and the previous studies were somewhat different. However, the discrepancies in the catalytic activity are not clearly understood at this moment.

The second enzyme family is a series of esterase/lipase ColoneZymes. ColoneZyme A exhibits excellent activity in the degradation of PPC films (Table 2), and indeed the highest enzymatic activity reported so far for PPC polymers. This enzyme also exhibits reasonably high activity in the degradation of PPCCL and PCL films (Table 2). These catalytic activities are almost two times higher than those of *Rhizopus arrhizus* lipase, but lower than those of *Pseudomonas* lipase. However, the other ColoneZymes exhibited no catalytic degradation activity in the degradation of the PPC film, and only low, positive catalytic activities in the degradation of the PPCCL and PCL films.

The third family consists of proteinases. As can be seen in Table 2, all three proteinases tested in our study exhibit positive catalytic activities in the degradation of the PPCCL and PCL films. They all exhibited almost the same level of catalytic activity, regardless of their origin. For the PPC films, however, only Proteinase K exhibited positive catalytic activity, while the other two proteinases exhibited no catalytic activity. The enzymatic activity of Proteinase K in the degradation of the PPC films is comparable with those of the proteinases for the PPCCL and PCL films. Moreover, the catalytic activity of this enzyme is better than that of *Rhizopus arrhizus* lipase, but worse than that of ColoneZyme A.

In addition, it is noteworthy that the catalytic activity observed in our study of Proteinase K in the degradation of the PCL films is significantly lower than that observed previously for polylactides (PLAs) [24]. In fact, PLAs have been reported to exhibit very high enzymatic degradability with Proteinase K, regardless of their stereoregularity and crystallinity: the T_m of L-PLA is 180 °C with a T_g of 67 °C; copolymers of L- and D-lactides have glass transition temperatures near 58 °C [24]. Thus PCL, a polyester analogue, is thus expected to exhibit very high enzymatic degradability with Proteinase K. However, this was not observed in our study.

The last family consists of amylases. Only the bacillus α-amylase and barley β-amylase exhibit positive catalytic activities in the degradation of the PPCCL and PCL films. The other amylases exhibited no catalytic activity in the degradation of the PPCCL and PCL films. Moreover, the PPC films exhibited no degradability with all the amylases.

As described above, *Pseudomonas* in particular exhibited excellent catalytic activity in the degradation of the PPCCL films. Therefore, the degradability of PPCCL films with this lipase was further investigated as a function of concentration and mediation time of the enzyme. The results are shown in Fig. 2. As can be seen in this figure, the overall degradation of the polymer film is greater for higher enzyme loadings. Moreover, the PPCCL films are almost completely degraded within 4 days for enzyme loadings in the range 0.5–2.0 mg/mL.

The enzymatic degradability of the PPCCL film was also compared to that of the PCL film in order to investigate the mechanism of enzymatic degradation. As shown in Fig. 3,

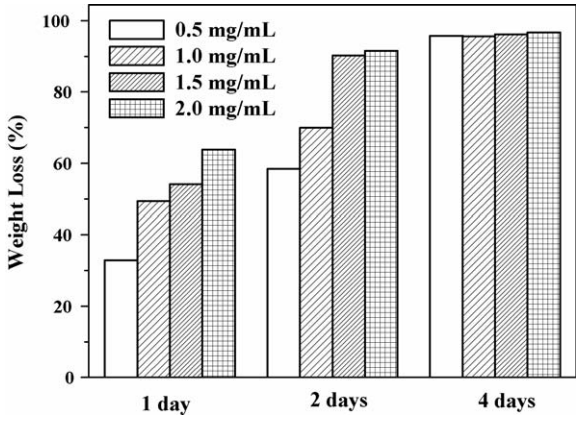

Fig. 2. Enzymatic degradations of the PPCCL films in phosphate buffer solutions (0.02 M; pH 7.0) with various loadings of *Pseudomonas* lipase for given times over 1–4 days.

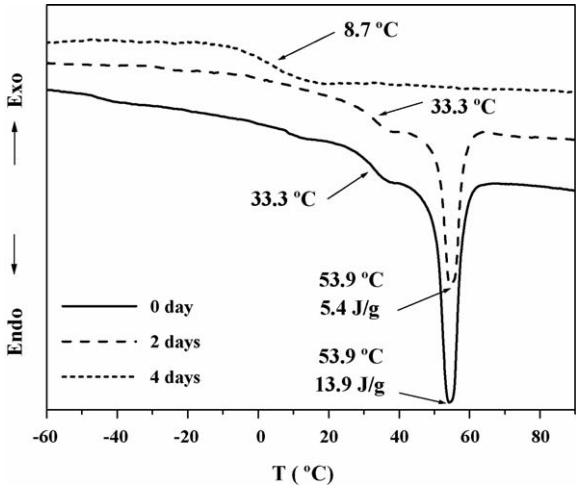

Fig. 4. DSC thermograms of the PPCCL films before and after enzymatic degradation in a phosphate buffer solution (0.02 M; pH 7.0) containing *Pseudomonas* lipase (0.5 mg/mL) at 37 °C for given times.

the enzymatic degradation rate of the PPCCL film is slower than that of the PCL film. DSC analyses were carried out on PPCCL films immediately after enzymatic treatment for various lengths of time. The resulting DSC thermograms are presented in Fig. 4. As can be seen in the figure, a PPCCL film with 58.4% weight loss after 1 day has a T_g (corresponding to the glass transition of the PC blocks) and a T_m (corresponding to the melting of the crystalline CL blocks) that are identical to those of the film before enzymatic degradation. However, this degraded film has a heat of fusion (ΔH_f) of only 5.4 J/g (corresponding to a crystallinity, X_c, of 4.0%), which is much lower than that (13.9 J/g; 10.2%) of the film before enzymatic degradation. After 4 days of enzyme-mediated degradation, the film suffered a weight loss of 95.8%, and had a T_g of 8.7 °C, but no melting transition was detected. The detected glass transition, which is associated with the glass transition of the PC blocks, is at a much lower temperature than that of the PC blocks before the enzymatic degradation. This lower T_g is attributed to the decrease in the PPC blocks' molecular weight that results from the enzymatic degradation. This is a good indication that the PC blocks also undergo degradation in the presence of *Pseudomonas* lipase. Overall, the films of the PPCCL polymer containing only 33 mol% CL blocks in the backbone exhibit significant weight losses within 4 days of enzymatic degradation. These results provide important information about the enzymatic degradation of the PPCCL film as follows. First, in the PPCCL film the crystalline CL block phases favorably undergo enzymatic degradation, in addition to the enzymatic degradation of the amorphous CL block phases. Second, the CL blocks undergo enzymatic degradation more favorably than the PC blocks. Finally, the PPCCL polymer chains are at first fragmented by the more favorable enzymatic degradation of the CL blocks, and then the enzymatic degradation of the fragmented PC blocks is accelerated.

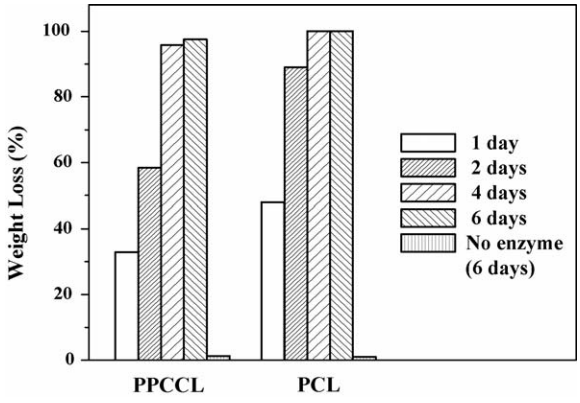

Fig. 3. Enzymatic degradations of the PPCCL and PCL films in a phosphate buffer solution (0.02 M; pH 7.0) containing *Pseudomonas* lipase (0.5 mg/mL) at 37 °C as a function of treatment time.

The surfaces of the PPCCL films were investigated with scanning electron microscopy (SEM) before and after degradation with *Pseudomonas* lipase. Some SEM results are presented in Fig. 5. As can be seen in Fig. 5a, the PPCCL film has a smooth surface before enzymatic degradation. Similar smooth surfaces were observed on the PCL films (data not shown). Fig. 5b shows a SEM image taken after enzyme treatment of the PCL film for 1 day. The surface of the PCL film appears blemished and very rough, which is indicative of surface erosion due to enzymatic degradation. Moreover, the boundaries of spherulitic crystals are discernible. Within these spherulitic boundaries, bundles of lamellar crystals in the radial direction are also clearly discernible. These observations indicate that the enzymatic degradation of the PCL film proceeds via surface erosion processes, which attack the amorphous phases before the crystalline phases.

The enzyme-degraded PPCCL film has a significantly different surface morphology to that of the enzyme-degraded PCL film. As can be seen in Fig. 5c, surface erosion due to enzymatic degradation is clearly evident in the PPCCL film after exposure for just 1 day; as a result of this exposure, 32.9% weight loss occurred in the film. The film surface is very rough and has a morphological texture consisting of large bowls, with some small size bowls present in the large bowls. However,

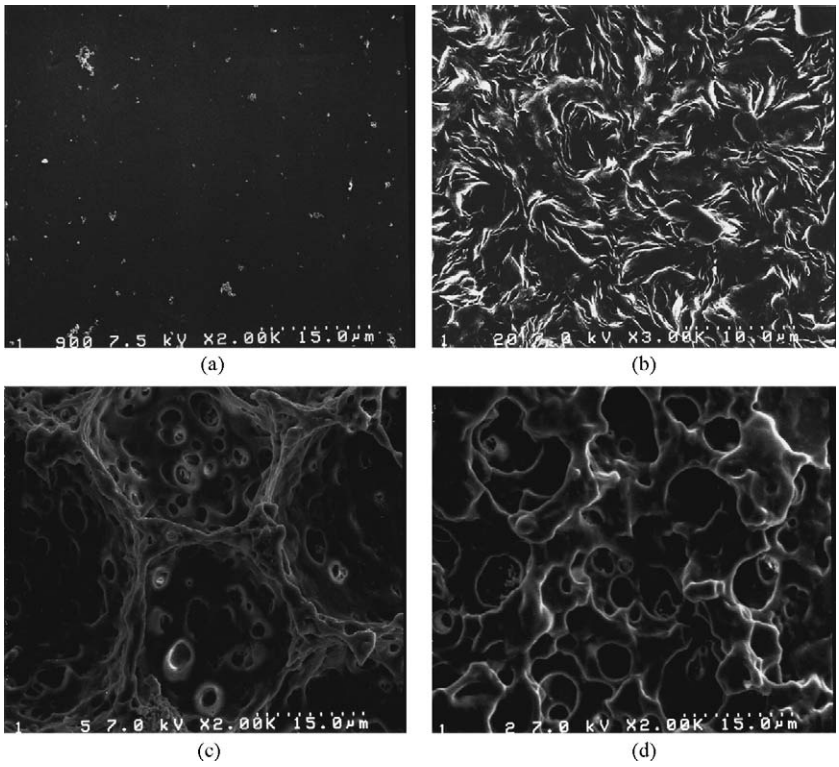

Fig. 5. SEM images of the surfaces of PPCCL and PCL films enzyme-mediated with *Pseudomonas* lipase (0.5 mg/mL) in a phosphate buffer solution (0.02 M; pH 7.0) at 37 °C: (a) PPCCL film before enzyme-mediation; (b) PCL film enzyme-mediated for 1 day (48% weight loss); (c) PPCCL film enzyme-mediated for 1 day (32.9% weight loss); (d) PPCCL film enzyme-mediated for 2 days (58.4% weight loss).

there is no evidence of bundles of lamellar and spherulitic crystals on the film surface. Fig. 5d shows that the enzymatic degradation of the film is more severe after an additional day of exposure, exhibiting significant weight loss (58.4%).

As discussed above, this PPCCL film is composed of 67 mol% PC blocks and 33 mol% CL blocks in the polymer backbone and exhibits relatively low crystallinity (10.2%), which is associated with the crystallizable CL blocks. In this study we also found that the PPC polymer is not miscible with the PCL polymer in binary blends. Taking into account these considerations and the PCL film's higher degradability with *Pseudomonas* lipase, the surface morphologies of the enzyme-degraded PPCCL films can be understood as follows. Because of the CL blocks' tendency to crystallize and their immiscibility with the PC blocks, the CL blocks are favorably phase-separated from the PC blocks, ultimately forming CL-rich phases in the film. Such CL-rich phases appear as coarsened spherulitic domains, which are evident in the SEM image in Fig. 5c. These CL blocks' coarsened spherulitic domains undergo enzymatic degradation first due to their higher susceptibility to *Pseudomonas* lipase, resulting in significant changes to the film surface. Then, the phases composed of fewer CL blocks undergo enzymatic degradation that is slower than that of the CL-rich phases, i.e. the PC-rich phases undergo enzymatic degradation much more slowly. However, the CL and PC blocks are linked with each other in the polymer backbone. Thus, the favorable enzymatic degradation of the CL blocks in the PPCCL film leads to the fragmentation of the polymer chains, resulting in significant reduction in the molecular weight. The polymer chain fragments are more likely to be attacked by the enzyme, so their enzymatic degradation is accelerated.

4. Conclusions

In this study, PPC and PPCCL polymers were synthesized via the ZnGA-catalyzed copolymerization of CO_2 and PO without and with CL, respectively. In addition, PCL polymer was prepared. These polymer products were characterized in terms of their chemical compositions, molecular weights, and thermal properties.

A series of enzymes (four different families and a total of 18 enzymes) were selected and then their degradation of the synthesized polymers was tested in a phosphate buffer. PPC films were found to exhibit positive enzymatic degradabilities with *Rhizopus arrhizus* lipase, esterase/lipase ColoneZyme A, and Proteinase K. These results indicate that the PPC copolymer has a reasonable level of susceptibility to the attacks of the enzymes even though it consists of methyl side group and reveals relatively high T_g and high modulus. This is the first report of the enzymatic degradability of PPC polymer. Moreover, PPCCL films were found to exhibit positive enzymatic degradabilities with most of the enzymes investigated in our study. In particular, excellent enzymatic degradation of the PPCCL film was achieved with *Pseudomonas* lipase, *Rhizopus arrhizus* lipase, and esterase/lipase ColoneZyme A. Overall the enzymatic degradabilities of the PPCCL films with various enzymes in our study are comparable

to those of the PCL homopolymer film. These enzymatic degradations were found to occur via an erosion processes.

In conclusion, ZnGA-catalyzed copolymerizations of CO_2 and PO with and without CL are beneficial chemical fixation processes for CO_2 that can produce enzyme-degradable aliphatic polymers. The PPC and PPCCL products are potential candidate materials for biomedical applications.

Acknowledgements

This study was supported by the Korea Science and Engineering Foundation (National Research Lab Program: Contract No. 2005-01385), by the Ministry of Education (BK21 Program), and by POSCO.

References

[1] J. Paul, C.M. Pradier (Eds.), Carbon Dioxide Chemistry: Environmental Issues, Royal Society of Chemistry, Cambridge, 1994.
[2] J.H. Jung, M. Ree, T. Chang, J. Polym, Sci.: Part A: Polym. Chem. Ed. 37 (1999) 3329.
[3] J.-S. Kim, H. Kim, M. Ree, Chem. Mater. 16 (2004) 2981.
[4] S. Inoue, H. Koinuma, T. Tsuruta, Makromol. Chem. 130 (1969) 210.
[5] K. Soga, E. Imai, I. Hattori, Polym. J. 13 (1981) 407.
[6] D.J. Darensbourg, J.R. Wildeson, J.C. Yarbrough, J.H. Reibenspies, J. Am. Chem. Soc. 122 (2000) 12487.
[7] M. Super, E. Berluche, C. Costello, E. Beckman, Macromolecules 30 (1997) 368.
[8] C.-S. Tan, T.-J. Hsu, Macromolecules 30 (1997) 3147.
[9] M. Cheng, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 120 (1998) 11018.
[10] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, J. Polym, Sci.: Part A: Polym. Chem. Ed. 37 (1999) 1863.
[11] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, Kor. Polym. J. 7 (1999) 333.
[12] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, Y.-T. Hwang, T. Chang, Polym. Eng. Sci. 40 (40) (2000) 1542.
[13] J.-S. Kim, M. Ree, T.J. Shin, O.H. Han, S.J. Cho, Y.T. Hwang, J.Y. Bae, J.M. Lee, R. Ryoo, H. Kim, J. Catal. 218 (2003) 209.
[14] J.-S. Kim, M. Ree, S.W. Lee, Y.-T. Hwang, S. Baek, B. Lee, B.T.J. Shin, H.C. Kim, K.J. Kim, B. Kim, J. Luning, J. Catal. 218 (2003) 386.
[15] B. Lee, J.H. Jung, M. Ree, Macromol. Chem. Phys. 201 (2000) 831.
[16] I. Arvanitoyannis, Rev. Macromol. Chem. Phys. C 39 (1999) 205.
[17] G. Scott, D. Gilead, Degradable Polymer, Chapman & Hall, London, 1995 .
[18] Y. Hwang, J. Jung, M. Ree, H. Kim, Macromolecules 36 (2003) 8210.
[19] T. Kawaguchi, M. Nakano, K. Juni, S. Inoue, Y. Yoshida, Chem. Pharm. Bull. 31 (1983) 1400.
[20] S. Inoue, T. Tsuruta, T. Takada, N. Miyazaki, M. Kambe, T. Takaoka, Appl. Polym. Symp. 26 (1975) 257.
[21] C. Wu, Z.H. Gan, Polymer 39 (1998) 4429.
[22] A. Iwamoto, Y. Tokiwa, J. Appl. Polym. Sci. 52 (1994) 1357.
[23] M. Zhou, M. Takayanagi, Y. Yoshida, S. Ishii, H. Noguchi, Polym. Bull. 42 (1999) 419.
[24] R.T. MacDonald, S.P. McCarthy, R.A. Gross, Macromolecules 29 (1996) 7356.