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Acid- and base-catalyzed hydrolyses of aliphatic polycarbonates and polyesters

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Abstract

Poly(propylene carbonate) (PPC) was synthesized by the zinc glutarate catalyzed copolymerization of carbon dioxide and propylene oxide (PO). Hydrolytic degradability of the PPC polymer was examined in tetrahydrofuran solutions containing 10 wt.% acidic or basic aqueous solutions of varying pH using viscometry and GPC analysis. Further, the hydrolysis behaviors of all PPC solutions were compared with those of poly(ε-caprolactone) (PCL) and poly(D,L-lactic acid) (PLA). All polymers studied show higher degradability in strong basic conditions than in strong acidic conditions, but very low degradability in moderate acidic, basic and neutral conditions. Moreover, PPC is degraded less in strong acidic conditions than the polyesters, while in strong basic conditions, the polycarbonate is more easily degraded. The difference in degradabilities of these polymers in acidic conditions is associated with the different nucleophilicities of their carbonyl oxygen atoms, while in basic conditions the differences are associated with the different electrophilicities of the corresponding carbonyl carbon atoms. With regard to the hydrolysis results and the structural and chemical nature of the polymer backbones, degradation mechanisms are proposed for the acid- and base-catalyzed hydrolyses of PPC, PCL and PLA.

Keywords: CO_2 copolymerization; Poly(propylene carbonate); Poly(ε-caprolactone); Poly(D,L-lactic acid); Acid-catalyzed hydrolysis; Base-catalyzed hydrolysis

1. Introduction

In recent years, the development of water-, enzyme-, and microbe-assisted degradable polymers has been extensively promoted in the chemical industry, finding applications in medicine, pharmacy, and agriculture, such as sutures, implants, drug release agents, mulches, and food packaging, as well as improving polymer waste disposal and maintaining the purity of the surrounding environment [1]. Certain microbial strains have been reported to degrade naturally occurring poly(β-hydroxybutyrate), as well as man-made polymers such as poly(ε-caprolactone), poly(ethylene adipate), poly(tetramethylene succinate), and poly(lactic acid) [1–4]. In addition, reports confirm that a number of enzymes are also able to degrade these same polyesters [1,5]. Due to their high susceptibility towards these particular enzymes and microorganisms, aliphatic polyesters are currently considered the most promising materials for the production of biodegradable plastics [1–5].

Aliphatic polycarbonates bearing no side group substituents such as poly(ethylene carbonate), poly(1,3-trimethylene carbonate), poly(1,4-tetramethylene carbonate), and poly(hexamethylene carbonate), have also been reported to exhibit a reasonably high susceptibility towards a number of enzymes and bacteria [6–9]. However, poly(propylene carbonate) (PPC) was reported to be impervious to attack by these same enzymes and bacteria [10,11]. It has been suggested that this poor susceptibility is due to the steric inhibition imparted by the methyl side substituents in the polymer backbone, as well as to the relatively high glass transition temperature T_g (=38.6 °C) and high modulus (=3.0 MPa) of the polymer [10,11]. However, we have recently reported for the first time that PPC shows positive enzymatic degradability towards *Rhizopus arrhizus* lipase, esterase/lipase ColoneZyme A, and Proteinase K [12].

The aliphatic polycarbonates with no side group substituents listed above are typically synthesized by ring-opening polymerizations of their cyclic monomers [6–9], and poly(ethylene carbonate) is often prepared from the copolymerization of

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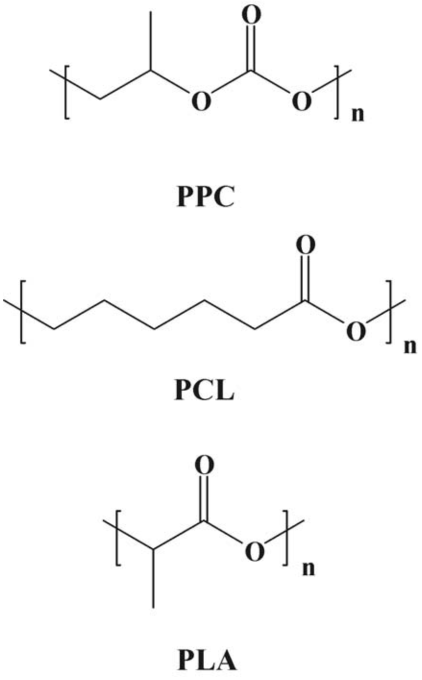

Fig. 1. Chemical structures of poly(propylene carbonate) (PPC), poly(ε-caprolactone) (PCL), and poly(D,L-lactic acid) (PLA).

Table 1
Variations in the molecular weights and polydispersity indices of the PPC, PCL, and PLA polymers before and after hydrolysis at various pH conditions[a]

Polymer	Hydrolysis for 20 days, pH value	GPC analysis[b]		
		$\bar{M}_n$	$\bar{M}_w$	PDI
PPC	– (virgin sample)	226400	673200	2.97
	1.0	86800	146900	1.69
	3.0	164600	276100	1.68
	11.0	83100	174200	2.10
	13.0	24200	43100	1.78
PCL	– (virgin sample)	122100	195300	1.60
	1.0	2200	7900	3.59
	2.0	9300	21200	2.28
	5.0	120000	150400	1.38
	11.0	91500	174200	1.64
	13.0	400	6300	15.75
PLA	– (virgin sample)	117200	259800	2.22
	1.0	12200	31900	2.61
	5.0	86400	150400	1.74
	11.0	85100	144400	1.70
	13.0	12000	22000	1.83

[a] Hydrolysis was conducted at 30 °C for 20 days. Each polymer solution in THF contained 0.5 wt.% polymer and 10 wt.% aqueous acid or base solution of a certain pH value.

[b] GPC was calibrated with polystyrene standards; the eluent was THF.

ethylene oxide and carbon dioxide. The use of carbon dioxide (CO_2) in the production of polymeric materials for application in industry represents an excellent source of this cheap and most abundant raw material. A good example of such polymeric materials is poly(alkylene carbonate), which can be produced by the copolymerization of CO_2 with alkylene oxide [13–27]. Recently, we reported a highly efficient process for the copolymerization of CO_2 and propylene oxide (PO) using a zinc glutarate (ZnGA) catalyst to produce PPC in high yield [21]. This new copolymerization process is considered a *green* process since no additional organic solvent is involved in the reaction [21].

In this work, we further investigate the hydrolytic degradability of PPC by assessing the effects of both acid and base catalysts (Fig. 1). In addition, the hydrolytic degradation measurements are extended to poly(ε-caprolactone) (PCL) and poly(D,L-lactic acid) (PLA) (Fig. 1), two remarkable biodegradable polymers [1,5]. The hydrolysis results of PPC are discussed with consideration to the structure of its polymer backbone and its degradation mechanism, and compared with the corresponding parameters of PCL and PLA.

2. Experimental

The PPC polymer was prepared from the ZnGA-catalyzed copolymerization of CO_2 and propylene oxide (PO) using the synthetic procedure reported previously [21]. PCL and PLA polymer samples were obtained from SK Yu Kong Company (Korea) and Aldrich Chemical Company (USA), respectively. Tetrahydrofuran (THF) and all other chemicals were purchased from Aldrich and used as received. In addition, water was purified by deionization and subsequent distillation, and then used immediately in the preparation of the acidic and basic aqueous solutions.

The weight average molecular weights ($\bar{M}_w$) and polydispersity indices (PDI) of the polymer samples were determined using a gel permeation chromatography (GPC) system (Polymer Labs Model PL-GPC 210), which was calibrated with a series of polystyrene standards using THF (HPLC grade) as an eluent. The characterized $\bar{M}_w$ and PDI results of the polymers are listed in Table 1.

A series of acidic and basic aqueous solutions of varying pH were prepared from hydrochloric acid (HCl) and sodium hydroxide (NaOH), respectively. THF solutions of each polymer were prepared with 0.5 wt.% solid content and filtered using PTFE-membrane microfilters of pore size 0.20 μm. The various acidic or basic aqueous solutions were then added to the polymer solutions at 10 wt.% with respect to the total weights of the polymer solutions. The prepared solutions were poured into Ubbelohde viscometers immersed in a water bath at 30 °C, and the relative viscosities were measured as a function of time. The solutions were then dried over anhydrous magnesium sulfate and filtered. The solvent was removed by rotary evaporation, and the products washed with copious amounts of water to remove residual salts. After filtering, the products were dried in a vacuum oven at room temperature for 2 days, and their molecular weights determined.

3. Results and discussion

The hydrolytic degradation of PPC, dissolved in THF in the presence of 10 wt.% acidic or basic aqueous solutions, was performed for a range of pH values at 30 °C. For each PPC solution, viscosity changes due to the hydrolytic degradation of

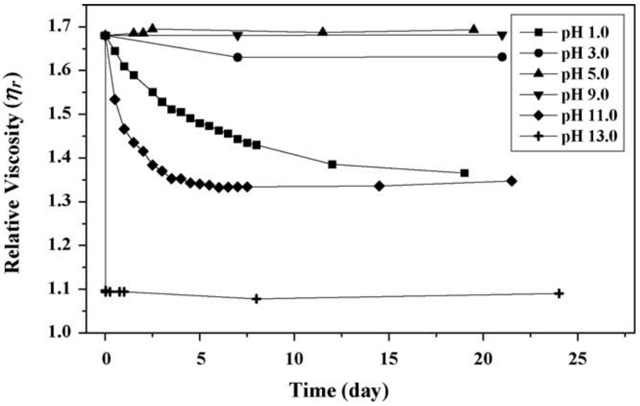

Fig. 2. Variations in the relative viscosities η_r of PPC solutions (0.5 wt.% polymer) at varying pH, as a function of time. Each polymer solution contained 10 wt.% aqueous acid or base solution of a certain pH value. Viscosity measurements were carried out at 30 °C.

Table 2
Rate constants for the acid- and base-catalyzed hydrolyses of the PPC, PCL, and PLA polymers[a]

Polymer	Rate constant of hydrolysis, k (day^{-1})[b]						
	pH 1.0	pH 2.0	pH 3.0	pH 5.0	pH 9.0	pH 11.0	pH 13.0
PPC	−0.05	–	~0	~0	~0	−0.21	−64.04
PCL	−0.31	−0.16	~0	~0	~0	~0	−19.72
PLA	−0.21	–	~0	~0	~0	~0	−110.12

[a] Each polymer solution in THF contained 0.5 wt.% polymer and 10 wt.% aqueous acid or base solution of a certain pH value. Viscosity measurements of each polymer solution were conducted at 30 °C using a capillary Ubbelohde viscometer.

[b] Each hydrolysis rate constant was estimated from the relative viscosity measured over the early stages of hydrolysis; here the estimation of rate constant k was made under the assumption that the hydrolysis follows a first order kinetics.

PPC were monitored as a function of time, and the results plotted in the graph shown in Fig. 2. This graph reveals that PPC polymer solutions in the pH range 5.0–9.0 show little or no viscosity changes up to around 20 days, indicating that PPC exhibits a high resistance towards hydrolytic degradation over this pH range. However, a discernible decrease in viscosity with time is detected for PPC solutions in acidic conditions of pH 3.0 and below. Moreover, viscosity decreases are also observed for PPC solutions in strong basic conditions (pH > 9.0), and these occur significantly more rapidly than those conducted in acidic solutions (Fig. 2). Overall, the decrease in PPC solution viscosity with time is highly dependent upon the pH of the solution.

Molecular weight variations in the PPC polymer due to hydrolytic degradation were examined using GPC analysis over a 20 days period in varying pH conditions. As listed in Table 1, the PPC molecular weight was typically reduced by hydrolytic degradation according to the pH condition, and was found to be more significant as the acidity or basicity of the solution was raised. Moreover, the molecular weight reduction was determined to be relatively more significant in strongly basic solutions than in strongly acidic solutions.

Taking the reductions in PPC molecular weight into account, the observed viscosity decreases in these polymer solutions are considered to be due to the acid- or base-catalyzed hydrolysis of the polymer chains. Indeed, for those PPC solutions showing a discernible or significant viscosity fall, it is possible to estimate a rate constant of hydrolytic degradation of the PPC polymer from the initial stage of viscosity decrease (Fig. 2). The corresponding rate constants are summarized in Table 2. In comparison, the hydrolytic degradation of PPC polymer chains in strongly basic conditions is significantly more rapid than in strongly acidic conditions; for example, hydrolysis at pH 13.0 occurs 3820 times faster than that at pH 1.0.

The hydrolytic degradation behavior of poly(ε-caprolactone) (PCL) was investigated under the same conditions used to examine PPC. The viscosity differences of PCL solutions measured in various pH conditions are presented in Fig. 3. As shown in Fig. 3, the PCL solutions exhibit little or no viscosity changes over the pH range of 3.0–11.0. However, the PCL solution viscosity is observed to decrease significantly over time in strongly acidic (pH 1.0–2.0), and strongly basic (pH 13.0) conditions. These viscosity changes are directly reflected in the accompanying molecular weight variations of the PCL polymer (Table 1), which are due to hydrolytic degradation, depending on the pH condition. Here, the PCL polymer chains are hydrolytically degraded more readily in strongly acidic and basic solutions; the degradation is more significant in the strongly basic solutions, as observed for PPC. The rates of hydrolytic degradation in the PCL solutions were determined from the initial viscosity decreases over time (Fig. 3). These results are compared with the rate constants obtained for the PPC solutions in Table 2. In comparison, the hydrolytic degradation rate of the PCL polymer at pH 1.0 is faster than that of PPC at the same acidic pH. However at pH 13.0, the PCL polymer degrades at a much slower rate compared to PPC at the same strongly basic pH.

Fig. 4 shows the viscosity variations in poly(D,L-lactic acid) (PLA) solutions at various pH conditions. In the pH range of 3.0–11.0, no appreciable viscosity changes in the PLA solutions are observed with time, in accordance with the PCL solutions at the same pH conditions. However, the PLA solution viscosity

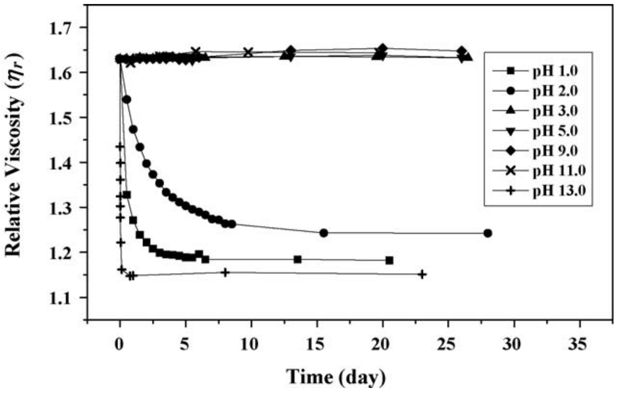

Fig. 3. Variations in the relative viscosities η_r of PCL solutions (0.5 wt.% polymer) at varying pH, as a function of time. Each polymer solution contained 10 wt.% aqueous acid or base solution of a certain pH value. Viscosity measurements were carried out at 30 °C.

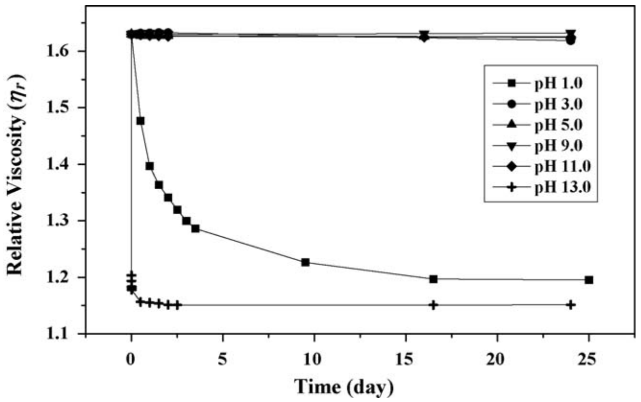

Fig. 4. Variations in the relative viscosities η_r of PLA solutions (0.5 wt.% polymer) at varying pH, as a function of time. Each polymer solution contained 10 wt.% aqueous acid or base solution of a certain pH value. Viscosity measurements were carried out at 30 °C.

falls significantly over time in strongly acidic (pH 1.0) and strongly basic (pH 13.0) solutions. These viscosity changes in the PCL solutions at various pH conditions are also evident in the molecular weight variations determined for PCL (Table 1). Overall, like PPC and PCL, the PLA polymer chains are more easily degraded in strongly acidic and basic solutions, whereas hydrolytic degradation is more significant in basic conditions. The rates of hydrolytic degradation in the PLA solutions have been determined from the initial viscosity decreases over time (Fig. 4), and compared with the rates obtained for the PPC and PCL solutions at the same pH (Table 2). At pH 1.0, the hydrolytic degradation rate for PLA is slightly slower than that for PCL, but much faster than that found for PPC. On the other hand, in stronger basic conditions (pH 13.0), the hydrolytic degradation rate for PLA is much faster than that for PCL, but slightly slower than that for PPC.

As discussed above, all the polymers in our study show hydrolytic degradability, depending on the acidic and basic pH conditions. Overall, the three polymers studied exhibit very slow degradability in moderate acidic and basic conditions, as well as in neutral conditions. However, all of these polymers reveal higher degradability in strongly basic rather than strongly acidic conditions. In comparison, PPC is less susceptible to degradation in strong acidic conditions than PCL and PLA, the order of increasing susceptibility being PPC $\ll$ PLA $<$ PCL. In contrast, PPC is more readily degraded in strong basic conditions than both PCL and PLA, the order of increasing susceptibility in strong basic conditions being PCL $\ll$ PLA $<$ PPC.

Here, it is worth considering the chemical characteristics of each polymer backbone, and then correlating these with the observed acid- and base-catalyzed hydrolysis behaviors. The PPC polymer is composed of a carbonate (i.e., one carbonyl and two oxygen atoms) and a propylenyl linkage per repeat unit (Fig. 1). The propylenyl linkage is non-polar compared to the other components, and is thus able to act as an electron donor group. The electron donor ability of this propylenyl unit is comparable to that of the propylenyl linkage in PLA, but relatively weaker than that of the *n*-pentylenyl linkage in PCL. Taking into account the electronegativity differences in the carbon and the three oxygen atoms, as well as the electron donor ability of the propylenyl linkage, the PPC carbonyl carbon is more electrophilic, compared to the carbonyl carbon atoms of PCL and PLA. Due to these chemical characteristics, the carbonyl carbon atoms in the PPC polymer chains have higher susceptibility to attack by hydroxide ions in basic conditions, particularly strong basic conditions (e.g., pH $\geq$ 13.0). Therefore, the much faster hydrolysis of PPC in strong basic conditions is attributed to the high electrophilicity of the carbonyl carbon atoms in the polymer backbone.

In the case of the two polyesters, the carbonyl carbon atoms in PCL are less electrophilic than those in the PLA polymer backbone, because the *n*-pentylenyl linkage in PCL possesses a larger electron donor ability than the propylenyl linkage in PLA. Thus, the slower hydrolytic degradation of PCL in basic conditions compared to PLA is attributed to the lower susceptibility of the PCL carbonyl carbon atoms to attack by hydroxide ions.

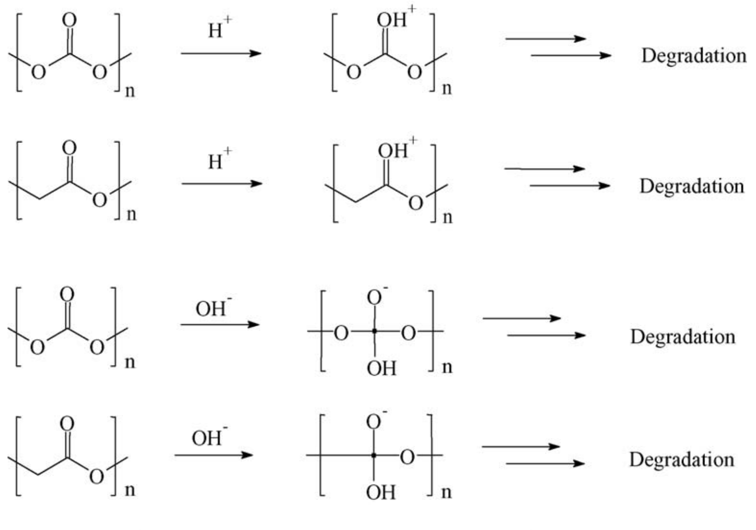

Fig. 5. Schematic diagrams for the acid- and base-catalyzed hydrolysis of aliphatic polycarbonate and polyester.

On the other hand, the carbonyl oxygen atom in PPC competes with the other two oxygen atoms to share electrons with the chemically bonded carbonyl carbon atom (Fig. 1). In comparison, the carbonyl oxygen atoms in PCL and PLA compete with only one oxygen atom (Fig. 1). Considering these facts, as well as the electron donor abilities of the propylenyl and *n*-pentenyl linkages, the nucleophilicity of the carbonyl oxygen atom in the polymers studied increase in the order PPC $\ll$ PLA $<$ PCL. These nucleophilicity differences in the carbonyl oxygen atoms are directly reflected in the acid-catalyzed hydrolyses of the three polymers: PPC shows a much lower activity towards acid-catalyzed hydrolysis compared to the polyesters, where PCL reveals a slightly higher activity than PLA.

Taking these facts, and the observed hydrolytic degradation results, into account, mechanisms for the acid- and base-catalyzed hydrolyses of PPC are proposed (Fig. 5). These mechanistic approaches are also extended to account for the acid- and base-catalyzed hydrolyses of PCL and PLA with respect to their chemical and structural nature. The hydrolytic degradation mechanisms of these polyesters are also illustrated in Fig. 5, and are typical for acid- and base-catalyzed cleavage of an ester.

4. Conclusions

PPC was synthesized using the ZnGA-catalyzed copolymerization of CO_2 and PO. The hydrolytic degradability of the synthesized PPC polymer was examined in THF solutions containing 10 wt.% acidic or basic aqueous solutions of varying pH using viscometry and GPC analysis. In comparison, the hydrolytic degradabilities of the polyesters PCL and PLA were also determined at the same conditions described for PPC.

All three polymers studied reveal excellent hydrolytic degradability, depending on the acidic and basic conditions of the THF solution. All the polymers show much higher degradability in strongly basic ($pH \geq 13.0$) conditions than in strongly acidic ($pH \leq 1.0$) conditions. Here, the degradability in strongly acidic pH occurs in the increasing order PPC $\ll$ PLA $<$ PCL, while in strongly basic pH, degradability increases in the order PCL $\ll$ PLA $<$ PPC. However, all these polymers show very slow degradation in moderate acidic and basic conditions, as well as in neutral conditions.

The differences between the acidic hydrolytic degradabilities of the three polymers are attributed to the different nucleophilicities of their respective carbonyl oxygen atoms; carbonyl oxygen atoms with higher nucleophilicity show a greater susceptibility to attack by hydrogen ions, leading to higher degradability. On the other hand, the differences between the basic hydrolytic degradabilities of the polymers are attributed to the different electrophilicities of their respective carbonyl carbon atoms; carbonyl carbon atoms with higher electrophilicity exhibit a greater susceptibility to attack by hydroxide ions, leading to higher degradability.

Considering the observed degradation results and the chemical nature of the three polymer backbones, degradation mechanisms are proposed for the acid- and base-catalyzed hydrolyses of PPC and the two polyesters (PCL and PLA).

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