Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 115 (2006) 283–287

CATALYSIS TODAY

www.elsevier.com/locate/cattod

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

Jae Hwan Jung [a], Moonhor Ree [a,*], Heesoo Kim [b,*]

[a] *Department of Chemistry, National Research Lab for Polymer Synthesis and Physics, and Polymer Research Institute,*
Pohang University of Science and Technology, Pohang 790-784, Republic of Korea
[b] *Department of Microbiology, Dongguk University College of Medicine, Gyongju 780-714, Republic of Korea*

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

---

* Corresponding authors. Tel.: +82 54 279 2120; fax: +82 54 279 3399.
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.2006.02.060

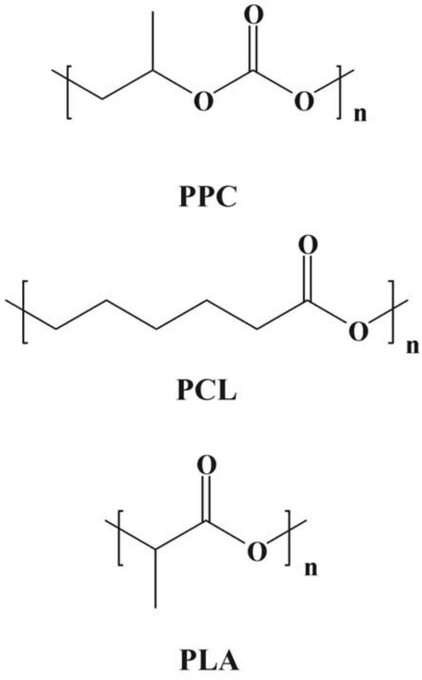

Fig. 1. Chemical structures of poly(propylene carbonate) (PPC), poly(ε-caprolactone) (PCL), and poly(D,L-lactic acid) (PLA).

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