Polymerization of Poly(ϵ -caprolactone) Using Yttrium Triflate

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ABSTRACT: The ring-opening polymerization of ϵ -caprolactone (CL) has been initiated by yttrium triflate (trifluoromethanesulfonate) in air using simple glass vials at 60 °C without desiccation steps and stirring. The number averaged molecular weight and molecular weight distribution of the obtained poly(ϵ -caprolactone) (PCL) was 5000–12000 and about 1.2, respectively. It was found that this polymerization reaction of CL was activated by the addition such as little water or 2-propanol. The copolymerization activities of comonomers such as L-lactide, γ -butyrolactone, δ -octanolactone, δ -decanolactone, or ω -pentadecalactone with CL by yttrium triflate were very low at 60 °C. Direct molding method during polymerization of PCL at 40 °C by yttrium triflate was developed. It was found that this direct molding PCL ($M_n = 2000$, $M_w/M_n = 3.07$) was biodegraded very slowly in a buffer (pH 7.0) with a lipase produced by *Rhizopus arrhizus*.

KEY WORDS Biodegradation / Polycaprolactone / ϵ -Caprolactone / ω -Pentadecalactone / Yttrium Triflate / Ring-Opening Polymerization /

Poly(ϵ -caprolactone) (PCL) has recently become well-known biodegradable polymer which is polymerized ring-opening of a cyclic ester, ϵ -caprolactone (CL). PCL can be biodegraded in compost,^{1,2} activate sludge,³ natural water,⁴ by the many kinds of microorganisms found in these environments. In addition, PCL can be degraded by purified enzymes.^{5,6} These degradations involve scission of the ester bonds in the PCL polymer chain forming 6-hydroxycaproic acid as the monomer unit by a hydrolysis enzyme such as a lipase excreted from the microorganisms that exist in these environments. Finally, 6-hydroxycaproic acid is metabolized to CO₂, CH₄, H₂O, and bacteria bodies by many microorganisms. Based on these points, PCL is an environmentally-friendly polymer. The degradation of the PCL films was examined in soil found in many places around Japan that was organized by the Biodegradable Plastics Society, Japan.⁷ The results of the biodegradation rate of the PCL film were different depending on the location. On the average, a 60% weight loss was observed after 2 years of soil burial. One PCL film that was almost degraded within 3 months had the fastest biodegradation rate. Within 4 days, the PCL film was completely degraded in a purified lipase solution.⁸ It was reported that the mechanism of these degradations was surface erosion. The molecular weight of the remaining film was maintained at its initial value which was different from the bulk degradation. In Japan, some companies were permitted by the Biodegradable Plastics Society, Japan,⁹ to use the symbol “GreenPla”, which means that only authorized biodegradable components were used in its prod-

uct.

PCL can be easily ring-opening polymerized from CL by heating or using a suitable catalyst. CL will readily polymerize to PCL at temperatures in the range from 110 to 200 °C. Suitable catalysts include dibutyltin dilaurate, stannous octanoate, and zinc octanoate. In alkoxides such as aluminum isopropoxide, this catalytic system provides a method of preparing polylactones with a controlled molecular weight and narrow molecular weight distribution (living polymerization) as well as specific random or block copolymers.¹⁰ Aluminum porphyrin in the presence of alcohol provides “immortal” polymerization (one kind of living polymerization) of CL. This system also gives a PCL polymer with a narrow molecular weight distribution.¹¹ In addition, it was found that the CL polymerization system using dialkyltin dialkoxides could occur in supercritical carbon dioxide.¹² Recently, the enzymatic ring-opening polymerizations of lactones by lipase, which is the hydrolysis enzyme of esters, have been studied.^{13,14} Lactones of the various ring-sizes including CL were polymerized in bulk by a lipase. Moreover, CL could be polymerized to PCL with high molecular weight (over 50000) under high pressure (over 800 MPa).¹⁵

Recently, the ring-opening polymerization of CL and other lactones has been successfully initiated by rare earth alkoxides.^{16–18} These system was found to be a very fast polymerization indicating that a 100% conversion of the monomer to polymer (M_n , 10000) was observed for the very short reaction time of 2 min.¹⁸ These yttrium compounds showed exceptionally high

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Scheme 1. Poly(ϵ -caprolactone) polymerized from ϵ -caprolactone using yttrium triflate.

reactivity, and some of them give “living polymerization”. Samarium (II) aryloxide also showed a very high reactivity for the CL ring-opening polymerization.¹⁹

Many reported polymerization systems of CL by a catalyst require complete desiccation involving equipments and chemicals using many steps such as flame-drying, distillation, and purging with dry nitrogen gas. In addition, the chemical impurities need to be removed, because the presence of a little water or impurity dramatically deactivates the catalyst for polymerization. These complicated steps prevent the mass production and application using the polymerization system of CL. We found that yttrium triflate could polymerize CL to PCL in air using the simple glass apparatus as indicated in Scheme 1. Recently, yttrium triflate was used to promote glycosyl fluorides as a catalyst for the preparation of pyridine and quinoline derivatives.^{20,21} It was found that triflate compounds with rare earth metals such as Y, Ln or Sm were stable and are active as a Lewis acids in water. In addition, it was reported that triflate compounds were used as the catalyst for cationic polymerization of isobutyl vinyl ether and *p*-methoxystyrene^{22,23} or radical polymerization of acrylamide²⁴ in water. For lactone monomers, scandium triflate was reported to catalyze cationic ring-opening polymerization in organic solvent such as toluene or pyridine.^{25,26}

This paper deals with the bulk polymerization of CL initiated by a novel system based on yttrium triflate (trifluoromethanesulfonate). This catalyst is actually stable in water and air. We developed the simple polymerization system of CL by yttrium triflate in air without desiccation steps for purification. We studied the polymerization conditions of CL and the copolymerization of other lactones with CL using this system. In addition, we discuss the activation with the addition of a little water or alcohol for this CL polymerization by NMR analysis. To develop the applicable usage of PCL, direct molding of PCL from CL monomer liquid during polymerization as simple molding system was studied. The biodegradation of direct molding PCL rod was studied by a lipase produced by *Rhizopus arrhizus*.

EXPERIMENTAL

Materials

ϵ -Caprolactone (CL, 2-oxepanone, Tokyo Kasei, Japan) was dried over CaH₂ at room temperature for 48 h and distilled under reduced pressure (< 10 mmHg) at 110 °C in the case using purified CL. Unpurified CL and 2-propanol were used as received. Yttrium triflate (trifluoromethanesulfonate) (Aldrich, 98%) was dried at 130 °C for 5 h under reduced pressure. Other lactones were used as received.

Polymerization Procedures

The CL, other lactone and catalyst (2–20 mg) were transferred to the glass vial (10 mL) with a plastic cap in air. The glass vial was capped, mixed well by a touch mixer and placed in an incubator at 60 °C without stirring for a specified period. At the end of the reaction period, the contents of the vial were dissolved in chloroform (10 mL). The chloroform solution was added to methanol (300 mL) to precipitate the polymer, the precipitate was washed with several portions of methanol and then the volatiles were removed in a vacuum oven (< 3 mmHg, r.t., 12 h). The obtained dry polymer was weighed and characterized.

Direct Molding of PCL Rods during Polymerization

The rods of PCL were prepared by direct molding during polymerization from CL monomer solution by yttrium catalyst in polyethylene tube. Yttrium trifluoromethanesulfonate (20 mg) and H₂O (20 μ L) were dissolved to CL monomer (2 mL) in 10 mL glass vial. This mixture was mixed well using touch mixer and transferred to the polyethylene (PE) tube (inside diameter 2 mm). The both terminal sides of PE tube were closed by melt press. This tube was incubated in an incubator at 40 °C for 48 h. After incubation, this PE tube was cut to pieces (5 mm length). PCL rods were taken out from cut PE tubes. The size of PCL rod was diameter 2 mm $\times$ length 5 mm (*ca.* 30 mg).

Polymer Characterization

The molecular weight and molecular weight distribu-

Table I. Poly(ϵ -caprolactone) (PCL) polymerized from ϵ -caprolactone (CL) using aluminum isopropoxide or yttrium triflate at 60 °C

entry	catalyst	initiator	reaction time (h)	yield ^a (%)	molecular weight, M_n^b	M_w/M_n^b
1	Al(O- <i>i</i> Pr) ₃ in toluene ^c	2-propanol ^d	48	94.0	12400	1.11
2	Al(O- <i>i</i> Pr) ₃ in bulk ^e	None	24	16.9	17600	1.71
3	Y(OSO ₂ CF ₃) ₃ in bulk ^e	None	24	0	—	—
4	Y(OSO ₂ CF ₃) ₃ in bulk ^e	None	49	2.1	—	—
5	Y(OSO ₂ CF ₃) ₃ in bulk ^e	2-propanol ^f	28	80.2	7960	1.25
6	Y(OSO ₂ CF ₃) ₃ in bulk ^e	2-propanol ^f	50	78.3	9100	1.33
7	Y(OSO ₂ CF ₃) ₃ in bulk ^e	H ₂ O ^g	27	73.3	6980	1.29
8	Y(OSO ₂ CF ₃) ₃ in bulk ^e	H ₂ O ^g	48	82.8	9490	1.25
9	Y(OSO ₂ CF ₃) ₃ in bulk ^h	None	24	9.8	5420	1.44
10	Y(OSO ₂ CF ₃) ₃ in bulk ^h	None	49	16.6	4340	1.33

^aYield was determined using the weight of monomer and isolated dry polymer. ^bNumber average molecular weight and molecular weight distribution were determined by GPC. ^cPolymerization conditions: 1 g CL monomer, 13.8 mg catalyst, 10 mL toluene as solvent, under nitrogen with stirring at room temperature. ^d34 mg 2-Propanol was added under nitrogen. ^ePolymerization conditions; 1 g CL monomer, 10 mg catalyst in 10 mL glass vial with a plastic cap in air at 60 °C without stirring. ^f10 mg 2-Propanol was added in air to CL monomer liquid with catalyst. ^g2.5 mg H₂O was added in air to CL monomer liquid with catalyst. ^hUnpurified CL (as received) was used.

tion were determined by gel permeation chromatography (GPC) using a Tosoh 8000 GPC system with a refractive index detector. A combination of two TSK GMH_{XL} columns (Tosoh, Japan, 7.8 mm × 30 cm) with molecular weight ranges of 1000 ~ 1 × 10⁷ g mol⁻¹ was used. The columns were eluted by chloroform (flow rate of 1 mL min⁻¹ at 40 °C) and calibrated with polystyrene standards.

The NMR spectra were recorded at 25 °C using a Varian 400 spectrometer in CDCl₃. The Chemical shifts were relative to TMS.

Differential scanning calorimetry (DSC) studies were conducted on a SEIKO DSC5200 equipped with a EXSTAR6000 PC data station. Experiments were carried out with 5–10 mg of sample, a heating rate of 20 °C min⁻¹ and a heating of samples from -80 °C to 200 °C. Data reported for the melting temperature (T_m) and enthalpy of fusion (ΔH_m) were taken from the first heating scan. The reported T_m was the peak melting temperature of the largest endotherm transition. ΔH_m values were taken as the cumulative value over the entire melting transition range. T_g was defined as the midpoint of the transition from the second heating scan (20 °C min⁻¹) of the rapidly quenched samples from melt.

Biodegradation Studies

Weight loss of PCL rods were carried out in 1/15 phosphate buffer (pH 7.0) with a lipase (EC 3. 1. 1. 3) produced by *Rhizopus arrhizus* (Sigma). Ten mL buffer solution (pH 7.0) with a lipase included in a lipase (11800 units) and 0.01 wt% Plysurf A210G (Dai-ichi kogyo, Japan). For a given experiment, three replicate rods in separate vials were used for the measurements of weight loss at specified incubation time. The

rod incubators were carried out at 37 °C in an incubator without shaking. Phosphate buffer solution with a lipase was changed after 26 d to get fresh enzyme activity. At sampling times, three PCL rods were taken out from buffer solution, wiped gently and weighed. Then PCL rods were returned to buffer solutions and incubated continuously.

RESULTS AND DISCUSSION

Polymerization of CL by Yttrium Triflate

It is known that many kinds of chemical catalysts could polymerize CL to PCL by ring-opening reactions. Quite recently, some lanthanide compounds such as yttrium alkoxide or samarium aryloxide were reported to polymerize CL with a very high reactivity. However, these catalysts should be deactivated by a little water or impurity included in the monomer or catalyst. Therefore, many complicated steps are required for removing the impurities. We have investigated some stable lanthanide compounds for the ring-opening polymerization of CL and found that yttrium triflate (trifluoromethanesulfonate) could polymerize CL in air using a simple glass vial.

Table I lists the results of the polymerization of CL by aluminum isopropoxide and yttrium triflate. For Al(O-*i*Pr)₃ in toluene in a nitrogen atmosphere with stirring (entry 1 in Table I), the yield was 94% indicating that the reactivity was very high as already reported by many other researchers. For this catalyst, air and water-sensitive handling techniques were required. For example, the polymerization ampule was treated with trimethylsilyl chloride, washed with methanol, dried at 150 °C in an oven and flame dried while purging with

dry nitrogen. The monomer and catalyst in toluene solution were transferred to this completely dried ampule under nitrogen. The polymerization was then started with stirring. However, if this catalyst was used in bulk in air using a simple glass vial without stirring (entry 2), the yield was dramatically decreased to only 16.9%. It was thought that some part of the Al catalyst was hydrodegraded by the water in the air and glass apparatus which was then deactivated by changing to an Al compound without polymerization activity. In this Al catalyst system, the molecular weight was increased by the increased $[CL]/[Al]$ due to the lower activity of the catalyst and the remaining CL monomer. However, deactivation of the Al catalysts occurred during the polymerization, so the catalysts with long and short activity times for polymerization were mixed. In this way, the molecular weight distribution of the obtained PCL polymer by the Al catalyst in bulk (entry 2) was increased to 1.71. In addition, this Al catalyst did not completely dissolve in the CL monomer liquid, so this catalyst precipitated in the liquid at the bottom (heterogeneous reaction) without stirring. From these points, the yield should dramatically decrease.

It was found that yttrium triflate could polymerize CL in bulk in air without stirring (entries 3–10). Upon the addition of the catalyst to the monomer liquid, the transparent color of the monomer liquid slowly changed to yellow then clear ruby red, suggesting that the yttrium catalyst was coordinated by the CL monomer. It was confirmed that the color of the yttrium triflate solution was not a clear ruby red in water or 2-propanol. Also, the yttrium catalyst could dissolve in the monomer liquid (homogeneous polymerization reaction), different from the Al catalyst. In the case of the addition with some H_2O or 2-propanol to the monomer (entries 5–8), the reactivity of the CL ring-opening polymerization was much higher than that using only purified CL (entries 3, 4). This means that the additive plays the role of an initiator for the CL ring-opening polymerization. It was interesting that the polymerization reactivity using unpurified CL (as received) by yttrium triflate (entries 9, 10) was higher than using purified CL (entries 3, 4). This is due to the impurities such as water or alcohol in the unpurified CL monomer liquid.

Figure 1 shows the time dependence of the CL ring-opening polymerization yield using yttrium triflate in bulk at 60 °C. It was found that the polymerization reactivity indicated the order; purified CL with H_2O , 2-propanol > unpurified CL > purified CL. About 80% in yield value was maximum, because the feeding of the monomer molecules to the catalyst active center was inhibited by the high viscosity of the monomer liquid

Figure 1. Time dependence on the yield of poly(ϵ -caprolactone) (PCL) polymerized from ϵ -caprolactone (CL, 1 g) using yttrium triflate (10 mg) in bulk at 60 °C in air without stirring. The yield was determined from the weight of monomer and isolated dry polymer. ○; purified CL, ●; unpurified CL, ▼; purified CL with H_2O (2.5 mg), ▽; purified CL with 2-propanol (10 mg).

Table II. Effect of yttrium triflate catalyst amount on polymerization of CL with 2-propanol as initiator for 24 h at 60 °C^a

entry	catalyst amount (mg)	yield ^b (%)	molecular weight, M_n^c	M_w/M_n^c
11	1	0	—	—
12	5	34.4	5520	1.14
13	10	76.0	6720	1.14
14	20	77.1	8290	1.27

^aPolymerization conditions: 1 g CL monomer, 10 mg 2-propanol in 10 mL glass vial with a plastic cap in air at 60 °C without stirring. ^bYield was determined using the weight of monomer and isolated dry polymer. ^cNumber average molecular weight and molecular weight distribution were determined by GPC.

Table III. Effect of 2-propanol amount on polymerization of CL by yttrium triflate catalyst for 24 h at 60 °C^a

entry	2-propanol amount mg	yield ^b (%)	molecular weight, M_n^c	M_w/M_n^c
15	2	32.7	5200	1.14
16	5	45.8	6030	1.14
17	10	78.5	6150	1.28
18	20	45.2	5630	1.27

^aPolymerization conditions: 1 g CL monomer, 10 mg catalyst in 10 mL glass vial with a plastic cap in air at 60 °C without stirring. ^bYield was determined using the weight of monomer and isolated dry polymer. ^cNumber average molecular weight and molecular weight distribution were determined by GPC.

with prepared polymer. In this way, it was found that yttrium triflate could polymerize CL with little H_2O or 2-propanol in air without stirring at 60 °C for 24 h.

Tables II and III show the effect of the catalyst amount and the 2-propanol amount for this CL ring-opening polymerization in bulk, respectively. The optimal condition was a 10 mg catalyst (18.7×10^{-3} mM) and 10 mg 2-propanol (0.166 mM) for 1000 mg CL

(8.76 mM). The mole ratio [CL]/[Y] was 470 for the optimal conditions. The observed molecular weight distributions were narrow (1.14–1.28).

The end groups of the polyester chains, which polymerized from CL with 2-propanol (entry 18 in Table III), have been analyzed by ^1H NMR as shown in Figure 2, indicating the conclusion that the PCL chains are capped by an isopropoxy ester at one end and an alcohol at the other end. This structural feature agrees with the “coordination–insertion” mechanism reported for the aluminum alkoxide and yttrium alkoxide.^{10,16} For this catalyst such as yttrium alkoxide, if water was added to the polymerization solution, the catalyst was degraded to the inactive compound which could not polymerize CL. In addition, the bond between yttrium and the trifluoromethyl sulfonic acid of yttrium triflate used in this study is thought to be

Figure 2. ^1H NMR spectrum of PCL polymerized from CL with 2-propanol using yttrium triflate at 60 °C (entry 18 in Table III).

stable. It was postulated that the insertion of CL to this bond was difficult. For the emulsion polymerization of *p*-methoxystyrene in aqueous media, cationic polymerization mechanism was suggested for metal triflate catalyst.^{22,23} On the other hand, radical polymerization mechanism was suggested for the polymerization of acrylamide and its derivatives in water or alcohol.²⁴ More detailed experiments and characterization are required to confirm the mechanism of this catalytic system for CL ring-opening polymerization.

The molar ratio calculated from the intensity of peak **a** was same as that of peak **g** in the case of entry 18 as indicated in Figure 2 (peak intensity ratio was $\mathbf{a}/6 = \mathbf{g}/2$). This means all PCL chains were capped with an isopropoxy ester group at the end of the polymer chain. In the case of entry 17, the peak ratio of peak **a** was smaller than that of peak **g**. This indicated that some of the CL was ring-opened by the water included in the monomer liquid which was different from 2-propanol. In this way, 2-propanol existed at the terminal end of the PCL chain, indicating that 2-propanol played the role of initiator for the CL ring-opening polymerization of this system.

Copolymerization of Other Lactones with CL

For polymer synthesis studies, copolymerization of comonomer with CL is very important method for control the thermal and mechanical properties such as melting point, crystallinity, tensile strength, and elongation at break of polymer materials. In addition, biodegradation speed is strongly dependent on the monomer composition of copolymers. Many kinds of lactones including lactide were copolymerized with CL by many cata-

Table IV. Copolymerization of various comonomer with CL by yttrium triflate catalyst for 48 h at 60 °C^a

entry	comonomer with CL	yield ^b %	comonomer in polymer ^c mol%	molecular weight ^d		melting point ^e	
				M_n	M_w/M_n	°C	ΔH_m , mJ mg ⁻¹
6	0	78.3	0	9100	1.33	61.6	157
19	L-lactide, 1 mM	0	—	—	—	—	—
20	γ -butyrolactone, 1 mM	0	—	—	—	—	—
21	δ -octanolactone, 1 mM	1.2	—	—	—	—	—
22	δ -decanolactone, 1 mM	3.7	trace	9700	1.31	59.9	157
23	ω -pentadecalactone, 1 mM	18.1	trace	8200	1.36	64.8	185

^aPolymerization conditions: 5 mM (0.57 g) CL monomer, 1 mM comonomer, 0.01 mM (5.4 mg) yttrium triflate catalyst in 10 mL glass vial with a plastic cap in air at 60 °C without stirring. ^bYield was determined using the weight of monomer and isolated dry polymer. ^cComonomer unit in polymer was determined by ^1H NMR. ^dNumber average molecular weight and molecular weight distribution were determined by GPC. ^eMelting point and enthalpy of fusion were determined by DSC.

lysts.

Table IV indicate the results of copolymerization with CL by yttrium catalyst at 60 °C. In the cases of 5 mM CL added with only 1 mM comonomer, polymer yields were decreased dramatically from 78.3% (entry 6) to 0 for L-lactide and γ -butyrolactone (entries 19, 20) or little for lactones which carbon number are bigger than CL (entries 21–23). In the cases of δ -decanolactone (entry 22) and ω -pentadecalactone (entry 23), small amount of polymers were given. However much amount of comonomer unit was not inserted to PCL polymer determined by the results of ^1H NMR analysis. Molecular weight and thermal analysis data of given polymers was almost same as the data of PCL homopolymer by yttrium catalyst (entry 6 in Table IV) due to the very small comonomer content ($< 1 \text{ mol}\%$) of sample polymer. In this way, the activities of copolymerization of comonomers with CL by yttrium triflate were very low at 60 °C. In addition, it was found that the lactone added as a comonomer deactivated the yttrium catalyst for CL ring-opening polymerization.

Direct Molding of PCL during Polymerization

The useful usage of biodegradable plastics is thought to be microspheres or small pieces as drug carrier matrix in medical fields. Many kinds of drugs or enzymes which are required into microspheres have weak heat resistance. The activities of these drugs or enzymes in microsphere must keep during preparing process without exposure of high temperature and harmful organic solvents. It was found that yttrium triflate in this study could polymerize CL monomer to PCL at 40 °C which is lower than melting point of PCL (61 °C). CL monomer liquid with yttrium triflate and H_2O changed to PCL solid at 40 °C for 48 h. Figure 3 shows the direct molding samples (PCL rods) during polymerization by yttrium triflate using polyethylene tube (inside diameter 2 mm) at 40 °C for 48 h. Table V indicates molecular weight and thermal analysis data of direct molding samples (PCL rods) compared with purified sample (PCL powder). Figure 4 shows the GPC curve of the

direct molding sample (PCL rod) during polymerization by yttrium triflate. It was found that about 20 % of molecular mass was oligomers of CL and there was trace of CL monomer in this GPC curve. It was thought that these oligomers could not insert or grow to polymer with high molecular weight due to the high viscosity and solidification of CL monomer liquid at final period of polymerization time. So molecular weight was lower and molecular weight distribution was wider as indicated in Table V. The molecular weight was higher in the case of purified PCL powder (Figure 4) because

Figure 3. Direct molding samples (PCL rods) during polymerization by yttrium triflate using polyethylene tube (inside diameter 2 mm) at 40 °C for 48 h (entry 24 in Table V).

Figure 4. GPC curves of direct molding sample (PCL rod) during polymerization by yttrium triflate using polyethylene tube (inside diameter 2 mm) at 40 °C for 48 h (entry 24 in Table V) and purified sample (PCL powder, entry 6 in Table I, V). — Direct molding sample (PCL rod); - - - Purified sample (PCL powder).

Table V. Molecular weight and thermal analysis data of direct molding sample (PCL rod) during polymerization using polyethylene tube (inside diameter 2 mm) at 40 °C for 48 h and purified sample^a (PCL powder) after polymerization of CL by yttrium triflate catalyst

entry	method	molecular weight ^b		melting point ^c		T_g^c , °C
		M_n	M_w/M_n	°C	ΔH_m , mJ mg^{-1}	
6	purified PCL powder ^a	9100	1.33	61.6	157	-54.7
24	direct molding PCL rod	2000	3.07	64.4	169	-65.5

^aIsolated dry polymer powder after purification of precipitation by adding the polymer chloroform solution to methanol. ^bNumber average molecular weight and molecular weight distribution were determined by GPC. ^cMelting point, enthalpy of fusion, and glass transition temperature were determined by DSC.

Figure 5. Enzymatic degradation of direct molding sample (PCL rod, entry 24 in Table V) in buffer solution with a lipase produced by *Rhizopus arrhizus*. ● PCL rods in buffer solution (pH 7.0); ○ PCL rods in buffer solution (pH 7.0) with a lipase.

of the higher activity of catalyst at 60°C and the removing of lower molecular weight moiety (under 1000) by purification process.

It was known that PCL polymer had fast crystallization rate from the melt. Thermal analysis was done after one month from preparation of PCL samples. So equilibrium crystallinity may be given. In spite of the presence of additive such as unreacted monomer, dimer, oligomer, and yttrium catalyst in PCL polymer, ΔH_m of the direct molding PCL rods was almost same as that of purified PCL powder. This result indicates the crystallization of PCL is not inhibited in this direct molding during polymerization by this catalyst at 40°C. T_g of PCL rod (−65.5 °C) was lower than that of purified PCL powder (−54.7 °C). This may be due to the presence of oligomers which play a role as plasticizer with good compatibility to PCL polymer.

Biodegradation of PCL Rod by Yttrium Triflate

PCL polymer is biodegradable plastics. To confirm the biodegradability of the direct molding PCL rods during polymerization (entry 24 in Table V and Figure 3), the biodegradation of PCL rods was measured using a lipase which was known as PCL degraded enzyme. Figure 5 shows the enzymatic degradation of the direct molding PCL rods in buffer solutions (pH 7.0) with a lipase produced by *Rhizopus arrhizus*. In this biodegradation conditions, cast film of commercial PCL (M_n , 42500) was well degraded, 10 wt% of this PCL cast film was degraded for 3 d in buffer with this lipase, then this film was degraded to many pieces for 5 d. The direct molding PCL rod (○ in Figure 5) was biodegraded much slower than that of commercial cast film by this lipase. Two wt% of PCL rod was degraded for 15 d, then degradation was stopped as observed plateau of relative weight change. This may be due to the deactivation of the lipase. By changing buffer

solution with the lipase, degradation was restarted then additional 2 wt% of PCL rod was degraded for another 15 d. The surface of the direct molding PCL rod was very smooth as observed by optical microscopy. The surface of the commercial cast film was porous and rough. It was thought that biodegradation speed of this direct molding PCL rod was very slow due to the small surface area and there was no effect for biodegradation of this PCL rod by the crystallinity and the presence of remaining oligomers and yttrium catalyst.

CONCLUSION

The biodegradable PCL polymer could be polymerized by a yttrium catalyst stable in water and air. Using this yttrium catalyst, PCL could be prepared at 60°C using a simple glass vial without air-sensitive handling. Adding a little H₂O or 2-propanol, the activity of the polymerization by this catalyst was increased. This simple polymerization method can be applied for the direct molding during polymerization of PCL by yttrium triflate at near room temperature without harmful organic solvent. Using this method, many drugs or enzymes which are unstable for high temperature and organic solvent can be incorporated to biodegradable polymer materials. However it is fact that there are technical problems such as low molecular weight and slow polymerization speed in this method. In the near future, much more optimization of the polymerization conditions and characterization of the polymerization mechanism will be done.

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