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Ring-Opening Polymerization of Cyclic Monomers with Aluminum Triflate

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Summary: A green method for the controlled synthesis of aliphatic polymers is presented. The ring-opening polymerizations of cyclic monomers including several lactones, such as caprolactone (CL) or pentadecalactone (PDL), and cyclic anhydride monomers, such as succinic anhydride (SUC) and tetrahydrofuran (THF), catalyzed by a series of metal triflates (trifluoromethanesulfonate) were studied. Aluminum triflate was found to be an advantageous candidate to catalyze the ring-opening polymerization of cyclic monomers. The details of the ring-opening polymerization of CL catalyzed by aluminum triflate were studied. The maximum number average molecular weight (M_n), polydispersity (M_w/ M_n) and yield of the obtained poly(-caprolactone) (PCL) at 60 °C for 6 hours were 18,400, 1.94 and 89 wt%, respectively. Those of poly(pentadecalactone) (PPDL) at 100 °C for 6 hours were 12,400, 2.24 and 49 wt%, respectively. The M_n, M_w /$M_n$and yield of the obtained poly(butylene succinate) (PBS) from SUC and THF at 100 °C for 48 hours were 4,900, 2.03 and 84 wt%, respectively. Furthermore, the mechanism of the polymerization was discussed based on the relationship between the conversion of CL and time. The molecular weight buildup of PCL was linear with a conversion in 50 min before the conversion reached 100 % and with M_w/M_n stabilized at about 1.5. The M_w/M_n of PCL then gradually increased. From these data, a living polymerization with a small transesterification was suggested from the PCL polymerization by aluminum triflate.

Keywords: aluminum triflate; catalyst; poly(butylene succinate); polycaprolactone; ring-opening polymerization

Introduction

Aliphatic polymers such as polycaprolactone (PCL) and poly(butylene succinate) (PBS) have received great interest in industrial applications such as agricultural mulch-films, ropes or cups utilizing its biodegradability in an agricultural area or in composting facilities[1]. Mulch-film was used to cover plants in vegetable fields to protect them and to stop weeds growing. While it is very hard to recover the non-biodegradable mulch-films from the vegetable fields and treat its waste after use, biodegradable mulch-film does not need to be recovered and thus lowers costs. PCL and PBS have been produced by some

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companies on a commercial scale and used as agricultural mulch-films in some countries, especially in Japan.

PCL is usually synthesized by the ring-opening polymerization of caprolactone (CL) with anionic, cationic, or free radical initiators[2,3] by many methods, such as heating or using a suitable catalyst[4], using lipase[5,6], or under high pressure [7] and so on. Many organometallic compounds, such as oxides, carboxylates, and alkoxides are effective initiators for the controlled synthesis of polymers[8-10]. PBS is condensation polymerized from succinic acid and 1,4-butanediol by a catalyst such as titanium tetraisopropoxide, tin 2-ethylhexanoate, etc.[11] Although a high selectivity with minimal side reactions has been demonstrated, polymerization systems of CL using such catalysts must be conducted under an absolutely dry atmosphere using many steps such as flame-drying, distillation, and purging with dry nitrogen gas. In addition, chemical impurities need to be completely removed, because any trace amount of water or impurity dramatically deactivates the catalysts. On the other hand, environmental concerns about current chemical research and industries are continually increasing. The challenge for a sustainable environment demands clean reaction processes that avoid the use of hazardous and harmful organic solvents. Recently, we found that yttrium triflate (trifluoromethanesulfonate) could polymerize CL to PCL without solvent (bulk) using a simple glass tube[12,13] . Triflate compounds with rare earth metals such as Y, Ln or Sm are stable and active as Lewis acids in water. It was reported that triflate compounds were used as the catalysts for the cationic polymerization of isobutyl vinyl ether and *p*-methoxystyrene[14,15] or the radical polymerization of acrylamide in water[16]. For lactone monomers, scandium triflate was reported to catalyze the cationic ring-opening polymerization in an organic solvent such as toluene or pyridine[17,18]. Using the catalytic system we reported, the PCL composite with a cellulose fiber could be prepared[19]. Easy homogeneous mixing of the cellulose fiber in the monomer liquid with a low viscosity at 60 °C reduces the production energy of the PCL composites.

In this investigation, the ring-opening polymerizations of cyclic monomers, including several lactones, such as CL or pentadecalactone (PDL), and cyclic anhydride monomers, such as succinic anhydride (SUC) and tetrahydrofuran (THF) catalyzed by a series of metal triflates (trifluoromethanesulfonate), were studied. The details of the ring-opening polymerization of CL catalyzed by aluminum triflate were reported. Furthermore, the polymerization mechanism was also discussed.

Experimental

Materials. Caprolactone (2-oxepanone, CL) (Tokyo Kasei, Japan), succinic anhydride (SUC), dehydrated tetrahydrofuran (THF) and dehydrated 2-propanol (Wako, Japan), and metal triflates (trifluoromethanesulfonate) (Aldrich) were used as received unless otherwise noted. To confirm the stability of aluminum triflate in water, the lyophilized aluminum triflate was dried in a vacuum oven (< 3 mmHg, R.T., 12 hours) from a frozen aluminum triflate aqueous solution. The purified CL was obtained by the following process: dried over CaH_2 at room temperature for 48 hours and distilled under reduced pressure (< 10 mmHg) at 110 °C.

Polymerization procedure. The monomer (e.g., CL 10 mmol), catalyst (aluminum triflate 0.02 mmol) and initiator (glycerol 0.067 mmol) were transferred to the glass vial with a plastic cap in air. The glass vial was capped, mixed well by a touch mixer and placed in an incubator at the designed temperature without stirring for a specified period. The solid polymer was produced as the glass vial was cooled to room temperature.

To characterize the obtained polymer, 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 hours). The obtained dry polymer was then weighed and characterized.

Characterization by Gel Permeation Chromatography (GPC). The molecular weight and molecular weight distribution were determined by 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 x 30 cm) was used. The columns were eluted by chloroform (flow rate of 1 $mLmin^{-1}$ at 40 °C) and calibrated with polystyrene standards.

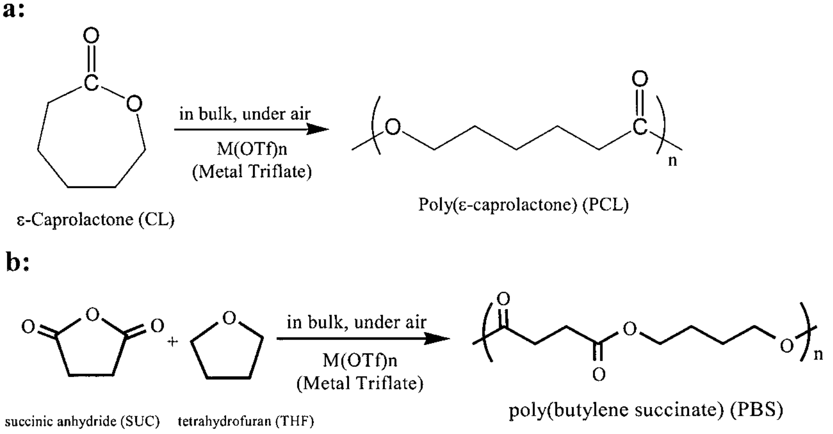
Differential Scanning Calorimetry (DSC). Calorimetric measurements of the polymers were carried out using a SEIKO DSC5200 equipped with an EXSTAR6000 PC data station. The sample (5-10 mg) was encapsulated in an aluminum pan. The DSC curve was obtained from the first heating scan from -80 to 200 °C with a scanning rate of 20 $^{\circ}Cmin^{-1}$, and quenched to -100 °C. The second heating scan was obtained at the same heating rate. The melting point (T_m) was taken from the first heating scan. The glass transition temperature (T_g) was defined as the top of the peak of the DDSC (the differentiated DSC) curve taken from the second heating scan (20 $^{o}Cmin^{-1}$).

Thermogravimetric Analysis (TGA). Thermogravimetric curves were obtained using a SEIKO TG/DTA220 assembled with a SSC/5200 thermal controller equipped with an EXSTAR6000 PC data station. The flow rate of the dry nitrogen gas was 100-150 $mlmin^{-1}$. The experiments were carried out with approximately 10 mg of samples and a heating rate of 10 $^{o}Cmin^{-1}$ in a temperature range from ambient to 300 °C.

Determination of time conversion of CL. The polymerization was performed under the following conditions: 20 mmol purified CL was ring-opening polymerized by 0.04 mmol as-received aluminum triflate with 0.4 mmol dehydrated 2-propanol as the initiator at 60 °C. Samples were removed from the reaction mixture during polymerization at 10, 20, 30, 40, 50, 60, 90, 120, 240, and 360 minutes. The molecular weights and conversion values of the samples were determined by GPC.

Results and Discussion

Ring-opening polymerization of cyclic monomers catalyzed by metal triflates. In a previous paper, we reported that yttrium triflate could catalyze the ring-opening polymerization reaction of CL in air at low temperatures (40-60 °C)[12,13]. On the other hand, the metal triflate is known as a Lewis acid and is stable and active in water[14,15].



Scheme I. Polymers polymerized from cyclic monomers using metal triflate. a: ring-opening polymerization of PCL from CL; b: ring-opening polymerization of PBS from SUC and THF.

Therefore, other metal triflates may exist with better catalytic activities; thus other kinds of metal triflates were investigated for CL polymerization (Scheme Ia).

The results are shown in Table 1. The reaction time was determined by the time that the reactant liquid became viscous, or was stopped in ten days. Most of the investigated metal triflates, except sodium triflate [Na(OTf)], magnesium triflate [$Mg(OTf)_2$], and ytterbium triflate [$Yb(OTf)_3$], have the ability of ring-opening polymerizing CL from the crude monomer with impurities such as oxygen or water in bulk. Among the metal triflates, lanthanum triflate [$La(OTf)_3$] and samarium triflate [$Sm(OTf)_3$] could only catalyze the monomer to an oligomer. yttrium triflate [$Y(OTf)_3$] and silver triflate [Ag(OTf)], needing 48 and 240 hours, respectively, to produce PCL with a lower yield (ca. 50%). Compared with copper(II) triflate [$Cu(OTf)_2$], scandium triflate [$Sc(OTf)_3$] and aluminum triflate [$Al(OTf)_3$] had higher catalytic activities. From these results, aluminum triflate should be the best catalyst in the investigated triflates for the ring-opening polymerization of CL in bulk in air. In order to clarify the ability of aluminum triflate for cyclic monomer ring-opening polymeri-zation, lactones with four to fifteen carbons and a mixture of succinic anhydride/tetrahydrofuran (SUC/THF) were used as the monomer.

Table 1. Effect of metal triflate on the ring-opening polymerization of CL[a]

Entry	M(OTf)n	Time /hour	Yield[b] /wt.%	Molecular weight[c]	
				M_n x10^{-3}	M_w / M_n
1	Na(OTf)	240	-[d]	-	-
2	$Mg(OTf)_2$	240	-[d]	-	-
3	$Yb(OTf)_3$	240	-[d]	-	-
4	$La(OTf)_3$	240	-[e]	0.3	2.90
5	$Sm(OTf)_3$	240	-[e]	0.3	3.50
6	Ag(OTf)	240	46	6.7	1.89
7	$Y(OTf)_3$	48	54	13.3	1.45
8	$Cu(OTf)_2$	24	86	16.4	1.97
9	$Sc(OTf)_3$	6	66	11.1	1.66
10	$Al(OTf)_3$	6	89	18.4	1.94

[a] Polymerization conditions: 10 mmol CL monomer (as received, 1.14g), 0.02 mmol catalyst, 0.067 mmol glycerol in air without stirring at 60 °C; [b] Determined using the weights of monomer and dry polymer; [c] Determined by GPC; [d] Unable to be determined; [e] The reactors became a slightly viscous at the end of the reaction.

Table 2. Effect of aluminum triflate on the ring-opening polymerization reaction of cyclic monomers.[a]

Entry	Monomer (amount)	Time /h	Yield[b] /wt.%	Molecular weight[c]		T_m[d] /°C	T_g[e] /°C
				M_n x10^{-3}	M_w / M_n		
11	-butyrolactone(10mmol)	6	-[f]	-	-	-	-
10	CL(10mmol)	6	89	18.4	1.94	57.7	-60.2
12	-octanolactone(10mmol)	6	-[f]	-	-	-	-
13	-decanolactone(10mmol)	6	-[f]	-	-	-	-
14	PDL(10mmol)	6	49	12.4	2.24	90.6	-
15	Suc/THF (10mmol:10mmol)	48	84	4.9	2.03	105.1	-34.9
16	Suc/THF (10mmol:0mmol)	48	-[f]	-	-	-	-
17	Suc/THF (0mmol:10mmol)	48	-[f]	-	-	-	-

[a] Polymerization conditions: as-received monomer, 0.02 mmol aluminum triflate, 0.07 mmol glycerol at 100 °C in air without stirring;
[b] Determined using the weights of monomer and dry polymer;
[c] Determined by GPC;
[d] Melting point, determined by DSC during the first scan;
[e] Glass transition temperature, determined by DSC during the second scan;
[f] Unable to be determined.

As shown in Table 2, aluminum triflate failed to catalyze the ring-opening polymerization of single lactones with four (-butyrolactone), eight (-octanolactone) or ten (-decanolactone) carbons while it could initiate the ring-opening polymerization of the fifteen (-pentadecalactone, PDL). Poly(PDL) (PPDL) was polymerizaed at 100 °C in 6 hours with M_n, M_w /M_n and yielded 12,400, 2.24 and 49 wt.%, respectively.

On the other hand, poly(butylene succinate) (PBS) was obtained in entry 15 when the same amounts (10 mmol) of SUC and THF were used as monomers (Scheme 1b). PBS is a well-known biodegradable polymer developed by Showa High Polymer Co., Ltd. PBS is usually polymerized from succinic acid and 1,4-butanediol by a catalyst such as titanium tetra-isopropoxide and tin 2-ethylhexanoate, using a condensation method. The melting point (T_m) and glass transition temperature (T_g) of PBS were reported as 117 and -36 °C, respectively[1,11]. In entry 15, the T_m and T_g of PBS were 105.1 °C and -34.9 °C (Figure 1), respectively. In the DSC thermal diagram of the first heating scan of the PBS (Figure 1A), another melting peak at about 78.8 °C was observed. From the ^{1}H NMR spectra (not shown) of the obtained PBS, peaks from poly(tetrahydrofuran) (lower than 5 mol%) were also observed; therefore, the lower T_m was between the melting temperature of PBS and poly(tetrahydrofuran) (T_m ca. 43 °C [1,20]). On the other hand, aluminum triflate could not polymerize THF to poly(THF) and SUC to poly(SUC) as shown in Table 2, entries 16 and

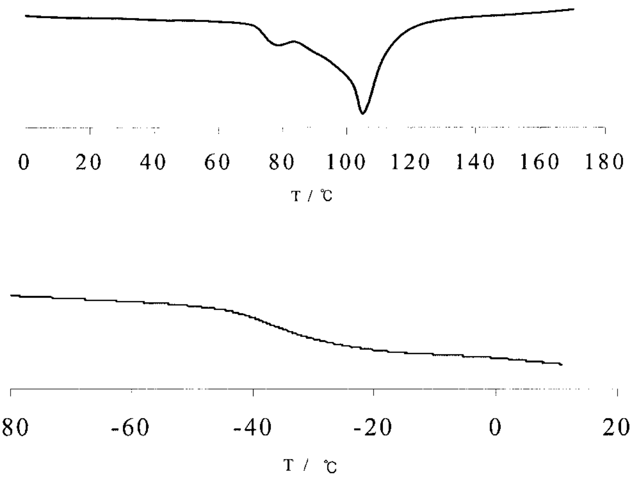


Figure 1. DSC thermal diagrams of PBS obtained in entry 15 by the first (A) and the second scans (B).

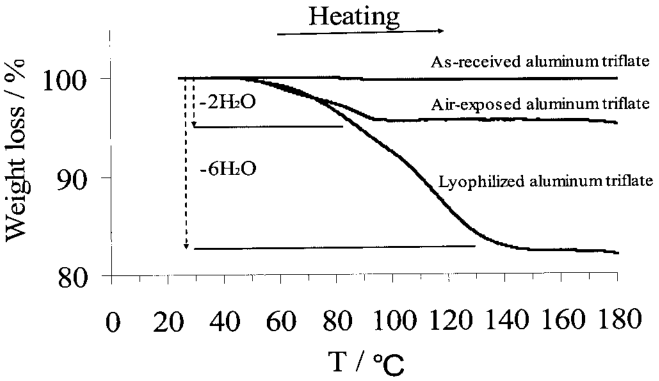


Figure 2. Thermogravimetric analysis (TGA, the increasing temperature rate was 10 °Cmin^{-1}) of the as-received, air-exposed and lyophilized aluminum triflates.

17. These data indicate the existence of repeating units of THF in the PBS polymer chains; PBS was the main product when the same amount of SUC and THF were used as monomers. On the other hand, it was also confirmed that lactide could be ring-opening polymerized by metal triflates, including aluminum triflate, to form poly(lactide) (PLA) [21]. The high activity of the metal triflates, especially aluminum triflate, on the ring-opening polymerization of cyclic monomers offered a simple way to obtain polymers with controlled thermal characteristics.

Ring-opening polymerization of CL by aluminum triflate. To confirm the stability of aluminum triflate in water, the as-received aluminum triflate was dissolved in water and then lyophilized. It is known that metal triflate can be coordinated by water molecules. The number of coordinated waters to metal triflate varied depending on the drying method, such as heating in an oven, laying at room temperature under a vacuum, exposure to air, or being lyophilized from an aqueous solution[13]. The lyophilized aluminum triflate contains more coordinated water than the as-received one. Therefore, the coordinated water of the as-received, air-exposed (the as-received sample exposed to air for 15 min), and the lyophilized aluminum triflates were determined by a thermogravimetric analysis (TGA). The results (Figure 2) showed that the as-received aluminum triflate rarely contained any water, while it absorbed two moles of water per mole aluminum when exposed to air for just 15 min. Furthermore, one molar of the lyophilized one contained six moles of coordinated water.

The catalytic activities of the as-received and lyophilized aluminum triflates were compared. Both of the two aluminum triflates could catalyze the ring-opening polymerization of CL to form similar results (Table 3, entries 18 and 20). The lyophilized aluminum triflate could catalyze the ring-opening polymerization reaction from either the as-received or purified CL (Table 3, entries 18 and 19). The results indicated that aluminum triflate is very stable in water; therefore, the water existing in monomers or air will not influence the polymerization. In a previous study[13], we investigated the role of water coordinated to yttrium triflate in the polymerization of CL, and found that water is necessary for the polymerization system because the dry yttrium triflate had no catalytic activity in the pure polymerization system. In the case of aluminum triflate, a similar result could be suggested, though we did not test this because the aluminum triflate quickly absorbs water from the air. Therefore, a more critical experiment is needed to eliminate water. From the purified CL, PCL with a slightly higher molecular weight was obtained, which indicated that the existence of water or impurities would somewhat influence the polymerization.

Table 3. Effect of the state of monomer and catalyst on the ring-opening polymerization reaction of CL[a]

Entry	Monomer	Catalyst	Yield[b] /wt.%	Molecular weight[c]	
				M_n x10^{-3}	M_w / M_n
18	as-received	lyophilized	71	9.9	1.40
19	purified [d]	lyophilized	75	13.8	1.30
20	as-received	as-received	79	10.7	1.47

[a] Polymerization conditions: 10 mmol CL monomer (1.14g), 0.02 mmol aluminum triflate, 0.2mmol dehydrated 2-propanol in air without stirring at 60 °C for 6 h; [b] Determined using the weights of monomer and dry polymer; [c] Determined by GPC; [d] Dried over CaH_2 at room temperature for 48 hours and distilled under reduced pressure (<10 mmHg) at 110 °C.

Table 4. Effect of initiator (glycerol) amount on ring-opening polymerization of CL initiated by aluminum triflate.[a]

Entry	Initiator Amount /mmol	M/I ratio[b]	DP[c]	Yield[d] /wt.%	Molecular Weight[e]	
					M_n x10^{-3}	M_w / M_n
21	0.050	200	132	91	15.1	2.35
10	0.067	150	160	89	18.4	1.94
22	0.100	100	120	87	13.8	2.00
23	0.200	50	78	76	9.0	1.74
24	0.400	25	64	51	7.4	1.33

[a] Polymerization conditions: as-received CL 10 mmol, 0.02 mmol catalyst at 60 °C for 6 h in air without stirring; [b] M/I: the molar ratio of monomer and initiator; [c] DP: degree of polymerization, calculated from *M*n (DP=(*M*n-91)/114); [d] Determined using the weights of monomer and dry polymer; [e] Determined by GPC.

The amount of initiator and catalyst, and the reaction conditions such as temperature and time, will influence the molecular weight of the obtained polymer. Therefore, we investigated these factors and summarized the results in Table 4 and Table 5.

Table 4 shows the effect of the initiator (glycerol) amount on the ring-opening polymerization of CL catalyzed by aluminum triflate. As can be seen from the table, when the monomer/initiator molar feed ratio (M/I) decreased from 150 to 25 (entries 10, 22 to 24) by increasing the initiator amount from 0.067 mmol to 0.4 mmol, both the yield and degree of polymerization (DP) of the obtained PCL decreased. Furthermore, in entries 22 to 24, the DP values were larger than the M/I ratios. In Table 4, only when the M/I ratio was 150, that is, when 0.067 mmol glycerol was used to initiate 10 mmol of the CL monomer, was the DP value similar to the related M/I ratio. When the M/I ratio reached

200 (entry 21), the DP decreased with a broader molecular weight distribution. The observed DP values were higher than the calculated M/I, though the yields were lower than 80% at M/I values from 25 to 150. This may suggest that not all of the initiator participates in the polymerization of CL catalyzed by aluminum triflate in bulk without stirring. On the other hand, in the case of M/I=200, the observed DP was 132. From Table 4 an M/I ratio near 150 should be favorable to obtain PCL with a high yield and molecular weight (under the condition of 60 °C, 6 h, in air without stirring) for the CL polymerization catalyzed by aluminum triflate due to the high viscosity of the reaction mixture.

Table 5. Summary of ring-opening polymerization of CL[a] catalyzed by aluminum triflate using 0.067 mmol glycerol as initiator in air without stirring.

Entry	Catalyst amount /mmol	Temperatue /°C	Time /h	Yield[b] /wt.%	Molecular Weight[c]	
					M_n x10^{-3}	M_w / M_n
25	0.02	40	6	82	8.5	1.64
10	0.02	60	6	89	18.4	1.94
26	0.02	80	6	84	12.6	1.73
27	0.02	60	3	83	10.6	1.54
28	0.02	60	8	86	16.1	2.04
29	0.02	60	12	85	17.0	1.93
30	0.02	60	24	86	16.5	2.06
31	0.01	60	6	88	19.3	2.03
32	0.04	60	6	88	18.6	1.61
33	0.06	60	6	82	16.6	1.69

[a]. As received CL 10 mmol; [b]. Determined using the weights of monomer and dry polymer; [c]. Determined by GPC.

Table 5 summarizes the effects of temperature (entries 25, 10 and 26), reaction time (entries 27-30), and catalyst amount (entries 31-33) on the ring-opening polymerization of CL by aluminum triflate initiated by glycerol. Comparing the PCL polymerized at 40-80 °C, 60 °C was found to be the optimum temperature for polymerization. After 6 h, a similar PCL would be obtained in 24 hours. Furthermore, the amount of catalyst ranged from 0.01 to 0.06 mmol corresponding to 10 mmol CL, and PCL with a similar yield and molecular weight was obtained. Not requiring a strict control of the catalyst amount made it easy to reproduce PCL or other polymers with the same characteristics.

Mechanism of aluminum triflate catalyzed CL ring-opening polymerization. To examine the extent of polymerization in terms of M_n as a function of conversion, 20 mmol

CL was polymerized by 0.04 mmol of the as-received aluminum triflate with 0.4 mmol of dehydrated 2-propanol as the initiator at 60 °C, while the polymerization time was varied to affect the monomer conversion. The polymerization results are plotted in Figure 3 and Figure 4. As shown in Figure 3, the conversion of CL increased to 100 % in 60 min. During this initial period, the molecular weight distribution (M_w/M_n) of the PCL ranged between 1.4 and 1.6. In the catalytic system, the molar ratio of catalyst/initiator was 1/10. In this bulk system without stirring, it was thought that not all of the initiator could react with the CL monomer by a catalyst for a short time, and propagation of CL at the activated position of the initiator was very fast. In this way, the M_w/M_n of PCL at 10 min

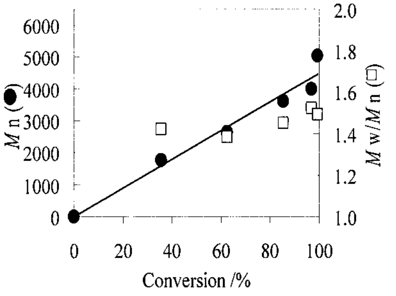


Figure 3. Time-conversion relationship for the ring-opening polymerization of CL using 0.04 mmol aluminum triflate with 0.4 mmol dehydrated 2-propanol as initiator at 60 °C. The initial monomer amount was 20 mmol.

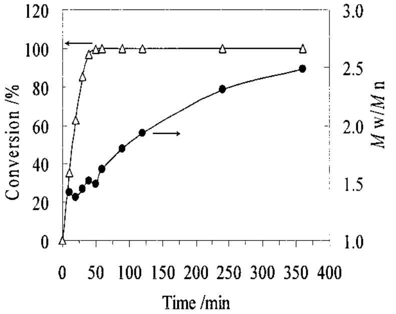


Figure 4. Plots of number-averaged molecular weight (*M*n) versus conversion for the polymerization of purified CL using 0.04 mmol aluminum triflate with 0.4 mmol dehydrated 2-propanol as initiator at 60 °C. The initial monomer amount was 20 mmol.

was already broad (ca. 1.5). After this initial period, polymerization was performed with a living characteristic because the M_w/M_n was maintained around 1.5 and the relationship between the conversion of CL and M_n was linear, as shown in Figure 4, for a polymerization time less then 50 min[19]. A similar living characteristic was also demonstrated during the ring-opening polymerization of lactide to form PLA with a high conversion by aluminum triflate[21]. That is, aluminum triflate can ring-opening polymerize CL, lactide and perhaps more cyclic monomers with a living characteristic. After 50 min of polymerization, the M_w/M_n gradually increased from 1.5 to 2.5 up to 360 min though the conversion reached 100% as shown in Figure 3. These data indicated the existence of a transesterification reaction between the PCL polymer chains by aluminum triflate. The polydispersity values were somewhat broad. Many reports have shown that, particularly for the higher monomer-to-initiator ratios, a competition between propagation and transesterification occurs and elimination takes place[23]. Considering that the M_w/M_n values did not change during the propagation reaction for the initial period of 50 min of polymerization, the propagation speed of CL was much faster than the transeterification speed. Briefly, a living polymerization with a small transesterification reaction could be suggested for the ring-opening polymerization reaction of CL catalyzed by aluminum triflate.

Conclusion

The ring-opening polymerization of cyclic monomers, including several lactones and succinic anhydride (SUC) with tetrahydrofuran (THF), was found to be catalyzed by a series of metal triflates (trifluoromethanesulfonate). Among the metal triflates, aluminum triflate can be an excellent candidate to catalyze the ring-opening polymerization of cyclic monomers. Furthermore, a living polymerization with a small transesterification reaction was suggested for the ring-opening polymerization reaction of CL catalyzed by aluminum triflate. The active ring-opening polymerization of different kinds of cyclic monomers with good control of the molecular weight made it possible to obtain biodegradable polymers with different thermal characteristics in a green way. Furthermore, because the polymerization could be performed in bulk without solvent, it could be applied for direct molding to produce a composite material containing cellulose fibers during polymerization to obtain materials with better mechanical characteristics.

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