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Poly(lactic acid) Polymerized by Aluminum Triflate

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Summary: The ring-opening polymerization of L-lactide (LA) has been initiated by aluminum triflate (trifluoromethanesulfonate) in air using a simple glass tube at 100 °C without desiccation steps and stirring. It was found that the molecular weight of poly(lactic acid) (PLA) was increased by the addition of an alcohol as an initiator to the reaction mixture. The highest number averaged molecular weight, molecular weight distribution, and recovery of the obtained PLA at 100 °C for 6 h were 18,200, 1.20, and 73%, respectively. With the addition of a small percentage of alcohol and a long reaction time of the polymerization method with the re-addition of LA, PLA (ca. 80 wt%) with a higher molecular weight (ca. 30,000) initiated by the added alcohol was produced with PLA (ca. 20 wt%) with a lower molecular weight (ca. 2,000) initiated by impurities such as water, which exist in a monomer, initiator, or catalyst.

Keywords: aluminum triflate; biorenewable; L-lactide; poly(lactic acid); ring-opening polymerization

Introduction

Recently, biorenewable polymers have become more important for innovation regarding the sustainable development of a global society. Biorenewable materials are materials produced from biomass immobilized from carbon dioxide in the atmosphere. These materials have benefits independent of oil resources and consuming of materials, such as carbon dioxide, that are responsible for the greenhouse effect and global warming. In addition, many kinds of biorenewable materials are biodegradable. Composting, which utilizes the biodegradation of polymeric materials by microorganisims, is an effective management of waste materials for the reuse of waste. For example, biodegradable plates, forks and spoons contaminated by food after use will be altered in order to compost them in a composting facility. The obtained compost will be used in agricultural fields to enhance the growing of vegetables. Additionally, biodegradable mulch-films or ropes to support the growing of vegetables are very useful from the view point that these wastes can be biodegraded at the use site. The use of these products reduces the energy and cost of collecting, transporting and disposing of waste for the agricultural industry.

The production amount of poly(lactic acid) (PLA) is the highest of all biodegradable polymers in the present market. PLA is a biodegradable and bio-renewable polymer that is

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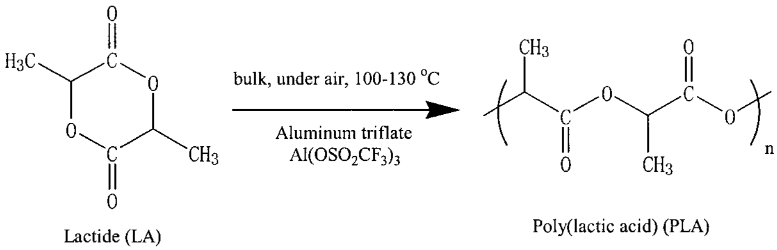
polymerized from lactic acid or lactide (LA).[1] Lactic acid is fermented from glucose or starch with high efficiency and recovery. Cargill-Dow (USA) is one of the PLA product companies that sell PLA synthesized from corn.[2] This company's plant, located in Nebraska, USA, has a capacity of 150,000 tons and sells PLA at a reasonable price, competitive with that of other commodity polymers, although the price of this PLA is slightly more expensive than that of other commodity polymers. However, many companies that use plastics select this PLA from the viewpoint of an environmentally-friendly concept for consumer acceptance. From the life cycle inventory assessment for PLA production from corn, PLA was reported to potentially contribute to reductions in energy use and greenhouse gases.[3] This PLA film was degraded in a compost at 58 °C.[4] After 7 days, the PLA film became hazy, and was degraded after 21 days.

PLA was developed for medical utilities such as absorbable sutures, matrices for a drug delivery system (DDS), or bone fixation screws. Consequently, the catalyst used for the production of PLA was limited from a safety standpoint because of its use in the human body. In addition, fine products for medical use do not require the efficiency and economical properties of the catalyst for PLA production. Recently, the development of catalysts for PLA polymerization in the field of industrial plastic production has been restarted. A PLA homopolymer with a high molecular weight had been ring-opening polymerized from LA by stannous octanoate, $Sn(Oct)_2$, at 120 – 220 °C.[5] A PLA homopolymer with a high molecular weight could be directly produced from lactic acids using molecular sieves and a water-azeotropic solvent at 140 °C.[6,7] A PLA homopolymer with a narrow molecular weight distribution could be living-polymerized from LA by aluminum isopropoxide[8] and aluminum porphyrin.[9] Recently, we found that yttrium triflate (trifluoromethanesulfonate) could polymerize ε-caprolactone (CL) to poly(ε-caprolactone) (PCL) without solvent (bulk) using a simple glass tube.[10] Triflate compounds with rare earth metals such as Y, Ln or Sm are as stable and active as a Lewis acid in water. It was reported that triflate compounds were used as the catalyst for the cationic polymerization of isobutyl vinyl ether and *p*-methoxystyrene[11,12] or the radical polymerization of acrylamide[13] in water. For lactone monomers, scandium triflate was reported to catalyze the cationic ring-opening polymerization in an organic solvent such as toluene or pyridine.[14,15] Using this catalytic system, a PCL composite with cellulose fiber could be prepared.[16] Easy and homogeneous mixing of a cellulose fiber in the monomer liquid with a low viscosity at 60 °C reduces the production energy of the PCL composites. In addition, we found that this system could be applied to the preparation of the PLA composite with cellulose fiber. Previously, the preparation conditions and mechanical properties of the PLA composites with cellulose fiber have been studied. In addition, the biodegradation of these PLA composites in a compost at 58 °C has been studied in detail. We attempted to polymerize LA by many kinds of metal triflates and found that aluminum triflate could polymerize LA to PLA (M_n = ca. 18,000, recovery = ca. 80%) in 3-6 h without solvent (bulk) in air using a simple glass tube as shown in Scheme I.

This paper deals with a bulk polymerization of LA initiated by a novel system based on aluminum triflate. This catalyst is actually stable in water and air. We developed the simple polymerization system of LA by aluminum triflate in air without desiccation steps for purification. We studied the polymerization conditions with several kinds of alcohols as the initiator to obtain PLA with a high molecular weight.



Scheme I.

Experimental

Materials. L-Lactide (LA, (3S, 6S)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione, Tokyo Kasei, Japan), metal triflates (trifluoromethanesulfonate) (Aldrich) and alcohols were used as received.

Polymerization procedures. The L-LA (10 mmol, 1.44 g), an initiator (alcohol such as 2-propanol or glycerin) and triflate catalyst (0.01 mmol, ca. 5 mg, 4.7 mg in the case of $Al(OTf)_3$) were transferred to a glass tube (5 mL) without a cap in air. The glass tube was placed in an incubator at 100 °C. After melting the LA, the mixture in the glass tube was well mixed by a touch mixer and placed in an incubator at 100 °C without stirring for a specified period. At the end of the reaction period, the solid polymer was produced in the tube after cooling to room temperature.

Conversion measurement from LA to PLA by GPC. After solidification of the reaction mixture during polymerization at 100 °C, sampling from the reaction tube was impossible. Samples for every specific period were separately prepared. All samples included 10 mmol LA, 0.01 mmol Al triflate, and 0.1 mmol glycerol in a 5 mL glass tube without a cap. The polymerization temperature was 100 °C. At the end of the reaction period, the solid polymer was present in the tube after cooling to room temperature.

LA Monomer re-addition during polymerization. Samples for every specific period were separately prepared. All samples included 10 mmol LA, 0.01 mmol Al triflate, and 0.1 mmol glycerol in a 5 mL glass tube without a cap. The polymerization temperature was 100 °C. At 1 h of incubation, pre-heated dissolved LA (10 mmol, 1.44 g) was added to the reaction tube. Quenching was the same as explained in the above section.

Purification procedure for polymer characterization. The contents of the tube were dissolved in chloroform (4 mL). A portion of the chloroform solution was diluted for suitable concentration by adding chloroform for determination of the conversion of LA by GPC. The remaining chloroform solution was filtered, then added to methanol (300 mL) to precipitate the polymer; the precipitate was washed with several portions of methanol and then the volatiles were removed by a vacuum oven (< 3 mmHg, r.t., 6 h). The obtained dry polymer was weighed and characterized. The isolated recovery of PLA was calculated from the amounts of this polymer's weight and added lactide. The molecular weight and molecular weight distribution 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 x 30 cm) with molecular weight ranges of $1000 – 1 \times 10^7$ g mol^{-1} was used. The columns were eluted with chloroform (flow rate of 1 mL min^{-1} at 40 °C) and calibrated with polystyrene standards.

Results and Discussion

Polymerization of LA by several kinds of metal triflates. To develop a process for PLA production based on efficiency and economics, we investigated several kinds of metal triflates as a catalyst that could work in air at a lower temperature. We found yttrium triflate could ring-opening polymerize caprolactone to polycaprolactone in air at a lower temperature. (60 °C) However, the activity of yttrium triflate for the ring-opening polymerization of LA was very low. Therefore, several kinds of metal triflates were investigated for LA polymerization. Metal triflates are known as a Lewis acid that is stable and active in water. These triflates have abilities that can be used for crude monomers with impurities such as oxygen or water and work in aqueous mediums for the polymerization of PLA. We have checked the catalytic activities of several kinds of metal triflate as indicated in Table 1 for ring-opening polymerization of LA to PLA without solvent (bulk) in air at 100 °C. To check polymerization ability in an aqueous medium, H_2O was added as an initiator to the LA monomer with a catalyst. The reaction time was determined by the time needed for solidification of the LA monomer liquid during polymerization. At 100 °C, the liquid of LA (T_m = 92 – 94 °C) was changing to a solid, according to the production of PLA (T_m = 180 °C). At 240 h into the polymerization, all remaining samples were quenched. All the metal triflates indicated in Table 1 had a catalytic activity for PLA polymerization. We did not check all the metal triflates that were purchased and more work with the other triflates is also needed. Aluminum (Al) and indium (In) triflates, which belong to group IIIB (13) in the periodic table, had the higher activities for PLA polymerization. At 24 h, the LA liquids changed to a solid for the scandium (Sc) and copper (Cu) triflates. However, these PLAs had lower molecular weights (under M_n = 1,000) and lower recoveries (under 50 %).

To check the polymerization activity of LA by Al triflate in an aqueous medium, we investigated the added amount of H_2O to the LA liquid. The addition of more H_2O (> 9

Table 1. Poly(L-lactic acid) (PLA) polymerized from L-lactide (LA) using metal triflate with H_2O as an initiator at 100 °C.[a]

entry	catalyst	reaction time / h	recovery[b] / %	molecular weight[c]	
				M_n	M_w/M_n
1	$Al(OTf)_3$	6	65	4,300	1.38
2	$In(OTf)_3$	6	39	3,500	1.12
3	$Sc(OTf)_3$	24	48	840	3.77
4	$Cu(OTf)_2$	24	46	800	2.76
5	AgOTf	240	13	580	2.19
6	$Mg(OTf)_2$	240	26	760	2.45
7	$Y(OTf)_3$	240	47	940	3.18
8	$La(OTf)_3$	240	31	900	2.57
9	$Sm(OTf)_3$	240	40	760	3.86
10	$Yb(OTf)_3$	240	45	1,160	2.94

[a] Polymerization conditions: 10 mmol LA monomer (1.44 g), 0.01 mmol metal triflate as a catalyst and 0.5 mmol H_2O (9 mg) in a 5 mL glass tube without a cap in air with no stirring at 100 °C.

[b] Recovery was determined using the weight of the monomer and isolated dry polymer.

[c] Number average molecular weight and molecular weight distribution were determined by GPC.

mg) dramatically inhibits PLA polymerization. In addition, the polymerization of LA (10 mmol) by Al triflate (0.01 mmol) did not occur in an aqueous medium (10 mL).

In this way, it was found that the ring-opening polymerization of LA was initiated by Al and In triflates without solvent (bulk) at 100 °C in 6 h. In triflate has the ability to polymerize LA to PLA with a high M_n but has lower activity with a slower LA polymerization reaction rate than that of Al triflate. From these results, we have studied the ring-opening polymerization of LA to PLA by Al triflate in detail.

Polymerization conditions of LA by Al triflate. PLA with a higher M_n could not be obtained by Al triflate with or without water as the initiator. We found that the ring-opening polymerization of caprolactone was accelerated by the addition of alcohol as an initiator.[17] In the case of polycaprolactone (PCL) polymerized by yttrium triflate, without an additive to the monomer liquid with a catalyst the PCL polymer could not be produced. PCL with M_n = 6,600 (recovery = 49 %) was obtained by Y triflate with methanol. PCL with M_n = 12,300 (recovery = 70 %) was obtained with 1,3-propanediol. In this way, we found that alcohol addition to the PCL polymerization system was very effective for improving the M_n and recovery. The effects of alcohol addition as an initiator for LA polymerization by Al triflate were investigated as indicated in Table 2. The recoveries of PLA were independent of the addition of any alcohol. In the case of no additive (entry 11), the M_n of the obtained PLA was 5,500. The increase in the M_n of the obtained PLA was observed with the addition of an alcohol. The M_n of PLA with 1,3-propanediol (entry 14) was higher than that with a mono-alcohol (entries 12, 13). In the cases with tri-ol (glycerol,

Table 2. Effects of addition of alcohol as an initiator on ring-opening polymerization of LA by Al triflate for 6 h at 100 °C[a]

entry	initiator	initiator amount / mmol	monomer /initiator	recovery / %	molecular weight	
					M_n	M_w/M_n
11	none	-	-	72	5,500	1.65
12	1-propanol	0.2	50	77	7,700	1.24
13	2-propanol	0.2	50	74	8,400	1.21
14	1,3-propanediol	0.1	100	76	13,820	1.19
15	glycerol	0.07	143	80	6,100[b]	3.43
16	pentaerythritol	0.05	200	77	6,300[c]	3.45

[a] Polymerization conditions: initiator, 10 mmol LA monomer (1.44 g), and 0.01 mmol Al triflate (4.7 mg) as a catalyst in a 5 mL glass tube without a cap in air with no stirring for 6 h at 100 °C.

[b] Peak with double tops as shown in Fig.1 was observed. Main peak indicated M_n = 30,800, M_w/M_n = 1.08, and area = 51 %.

[c] Peak with double tops was observed. Main peak indicated M_n = 32,400, M_w/M_n = 1.08, and area = 68 %.

entry 15) and tetra-ol (pentaerythritol, entry 16), the total M_n calculated from the higher and lower PLA peaks in the GPC chart were not very high but the peak for a higher M_n was observed. The values of M_n at the higher peak were 30,800 and 32,400 for glycerol and pentaerythritol, respectively. In these cases, there were PLAs with a lower M_n initiated by impurities. In this way, the alcohol added to the reaction mixture could work as an initiator and improve the M_n of the obtained PLA. First, a possible reason for the increase in the M_n was that increasing the initiation's reaction rate by alcohol with an Al catalyst caused an acceleration of the entire polymerization rate of CL to PCL by Al triflate. A second possible reason was due to the polymerization being initiated from more than one hydroxyl group of the alcohol. However, only one kind of initiation reaction was expected in the glycerol molecule because of the narrow M_w/M_n value. We need more detailed investigations for clarifying the mechanism of this system. In this way, the addition of an alcohol with di-hydroxyl or more hydroxyl groups as an initiator caused the production of PLA with a higher M_n.

We investigated the effect of the catalyst amount to clarify the optimal polymerization conditions. The recovery and M_n of the obtained PLA with the increasing Al triflate from 0.01 mmol with 10 mmol LA monomer and 0.1 mmol glycerol were not changed.

The effects of the glycerol amount on the polymerization of LA by Al triflate as a catalyst for 6 h at 100 °C were investigated as shown in Table 3 and Fig. 1. The recoveries were independent of the amount of initiator. The optimal glycerol amount for the total M_n was determined. The M_n of the obtained PLA increased to 18,200 with the increase in the glycerol amount to 0.1 mmol (entry 20). For a 0.2 mmol glycerol amount (entry 21), the M_n decreased to 11,600. As shown in Fig. 1, there were two peaks in PLA obtained by Al triflate. One was the broad peak of PLA with a lower M_n independent of the glycerol

Table 3. Effect of glycerol amount on polymerization of LA by Al triflate catalyst for 6 h at 100 °C[a)]

entry	initiator amount / mmol	monomer/initiator	recovery / %	peak at higher Mn			peak at lower Mn			Total	
				M_n	M_w/M_n	area / %	M_n	M_w/M_n	area / %	M_n	M_w/M_n
17	0	-	69	-	-	-		-	-	3,400	2.60
18	0.025	400	80	32,200	1.09	65	2,400	2.40	35	5,700	4.32
19	0.05	200	76	28,700	1.10	77	2,300	2.37	23	9,400	2.79
20	0.1	100	73	-	-	-	-	-	-	18,200	1.20
21	0.2	50	79	-	-	-	-	-	-	11,600	1.15

[a)] Polymerization conditions: 10 mmol LA monomer (1.44 g) and 0.01 mmol Al triflate (4.7 mg) as a catalyst in a 5 mL glass tube without a cap in air with no stirring at 100 °C.

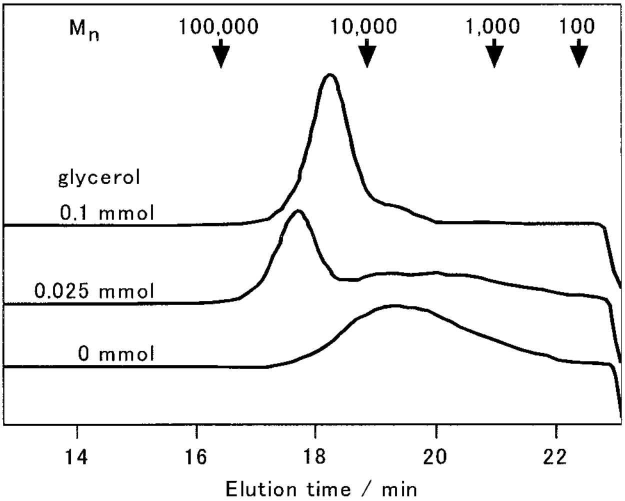


Figure 1. GPC curves of purified poly(L-lactic acid) (PLA) polymerized by aluminum (Al) triflate and glycerol as an initiator with different amounts (entries 17, 18 and 20 in Table 3) from L-lactide (LA) at 100 °C for 6 h.

amount (entry 21, 23). These may be due to initiation by impurities such as water existing in the crude monomer, initiator or catalyst. Another was the narrow peak of PLA with a higher M_n initiated by Al triflate with glycerol. Similar to the general initiation mechanism of polymerization, the M_n of PLA at a higher M_n was decreasing, and the area (concentration) of this PLA was increasing with the increasing initiator amount. Table 4 indicates the effect of the reaction temperature. PLA with a lower M_n was obtained at a reaction temperature higher than 120 °C for 6 h.

Table 4. Effect of polymerization temperature of LA by Al triflate catalyst[a]

Entry	temperature / °C	recovery / %	molecular weight	
			M_n	M_w/M_n
22	100	85	8,700	1.88
23	120	79	9,000	2.02
24	140	63	3,200	2.29

[a] Polymerization conditions: 10 mmol LA monomer (1.44 g), 0.02 mmol Al triflate as a catalyst and 0.067 mmol glycerol in a 5 mL glass tube without a cap in air with no stirring for 6 h.

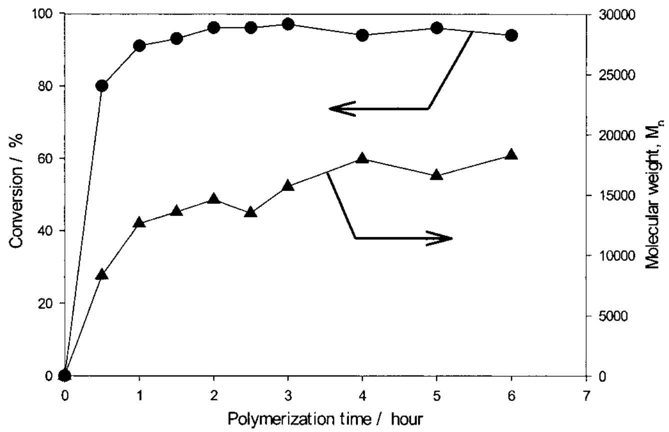


Figure 2. Time dependence of the conversion of LA and molecular weight (M_n) of PLA polymerized from LA by Al triflate without solvent (bulk) at 100 °C under air with no stirring. (●) conversion of LA determined by the peak area in GPC chart, (▲) M_n of PLA determined by GPC.

Conversion of LA by Al triflate. To clarify the ring-opening polymerization mechanism, we investigated the conversion of LA by GPC measurement of the reaction mixtures as shown in Fig. 2. During the initial period of polymerization, the viscosity of the reaction mixture quickly increased due to the production of PLA with a high M_n. For 2 h after starting, the reaction mixture had a lower fluidity with a high viscosity. At 2.5 h, solidification of the reaction mixture was observed. For only 1 h, the conversion quickly increased to 90 %, and the M_n increased to 12,300 as shown in Fig. 2. After 2 h, the conversion reached 96 %. After 3 h, the conversion and Mn were almost stable due to the solidification of the reaction mixture. The relationship between the Mn and conversion in the range 80 –96 % did not follow the theoretical zero order line. However, the M_n (M_w/M_n) values of PLA were 8,300 (1.09) at 0.5 h, and 13,600 (1.10) at 1 h. The values of M_w/M_n are very narrow during polymerization so that these data suggest a living polymerization for this catalytic system. We have to investigate over a wide range of conversion of LA in this catalytic system as described in the next section. In this way, the polymerization speed of LA to PLA by Al triflate was very fast and polymerization was stopped by the solidification of the reaction mixture after only 3 h of polymerization at 100 °C.

LA Monomer re-addition during polymerization. To obtain PLA with a higher M_n by solidification inhibition of the reaction mixture, which included 10 mmol LA, 0.01 mmol Al triflate and 0.1 mmol glycrerol, melted LA monomer (10 mol) was re-added to the reaction mixture at 100 °C during polymerization before the solidification of the reaction mixture. Fig. 3 shows the conversion of LA and M_n of PLA with the second addition of LA at 1 h during polymerization. The conversion of LA was 53 % at 1 h before the LA re-addition as shown in Fig. 4. After the LA re-addition at 1 h, the total added LA was increased to 20 mmol and then conversion at 1 h became 27 % as indicated in Fig. 3. The solidification time was delayed to 5 h of polymerization by adding the LA monomer at 1 h during the polymerization. Additional monomer could work as a solvent. The produced PLA could dissolve the reaction mixture with the re-added LA monomer. By keeping the reaction mixture fluid, the conversion and M_n increased to 78 % and the M_n was 27,200 continuously for 7 h. However, PLA (17 %) with a lower M_n (1,300) was produced in the reaction mixture at 7 h as shown in Fig. 4. The total M_n of the obtained PLA at 7 h was only 6,100 (M_w/M_n = 4.14). Fig. 5 shows the relationship between the conversion vs. M_n and M_w/M_n of the PLA obtained by the LA monomer re-addition system with Al triflate

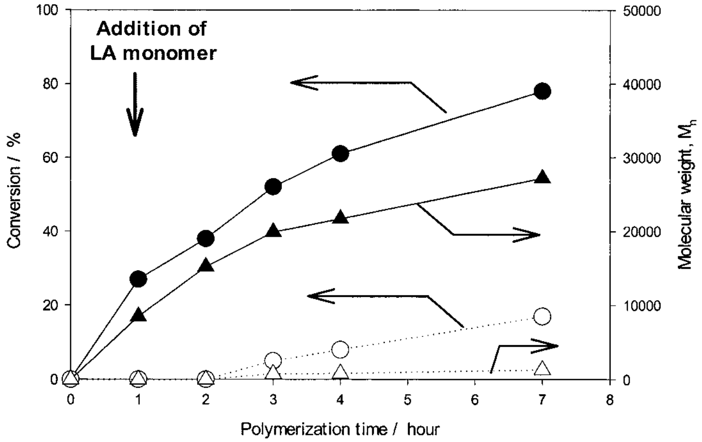


Figure 3. Time dependence of the conversion and M_n of PLA polymerized by Al triflate with re-addition of LA at 1 h under 100 °C. (●) conversion of LA with higher M_n, (▲) M_n of PLA with higher M_n, (○) conversion of LA with lower M_n, (△) M_n of PLA with lower M_n.

and glycerol at 100 °C. These M_n values of the obtained PLA were calculated from peaks located at the higher M_n as shown in Fig. 4. A linear relationship exists between the conversion and M_n. The values of M_w/M_n were stable in the range from 1.05 to 1.08. From these data, it was found that this catalytic system performed under living polymerization without a transesterification reaction. Thus, the second addition of the LA monomer caused the production of PLA with a higher M_n by keeping the reaction mixture fluid and the production of PLA with a lower M_n at the same time. We must search for better conditions such that only PLA with a higher M_n is produced.

The polymerization mechanism for this Al triflate catalytic system of an LA is unknown. For the emulsion polymerization of *p*-methoxystyrene in aqueous media, a cationic polymerization mechanism was suggested for the metal triflate catalyst.[11,12] On the other hand, a radical polymerization mechanism was suggested for the polymerization of acrylamide and its derivatives in water or alcohol.[13] More detailed experiments and characterization are required to confirm the mechanism of this catalytic system for the LA ring-opening polymerization.

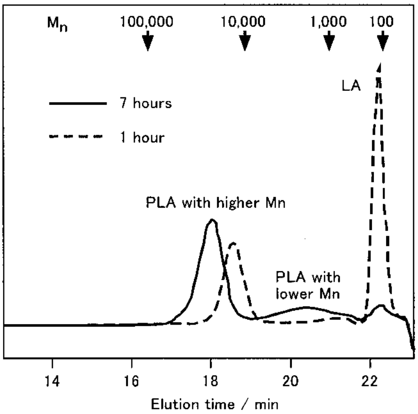


Figure 4. GPC curves of PLA polymerized by Al triflate with glycerol at 100 °C. Dotted line: at 1 h before re-addition of LA; solid line: at 7 h with re-addition of LA at 1 h.

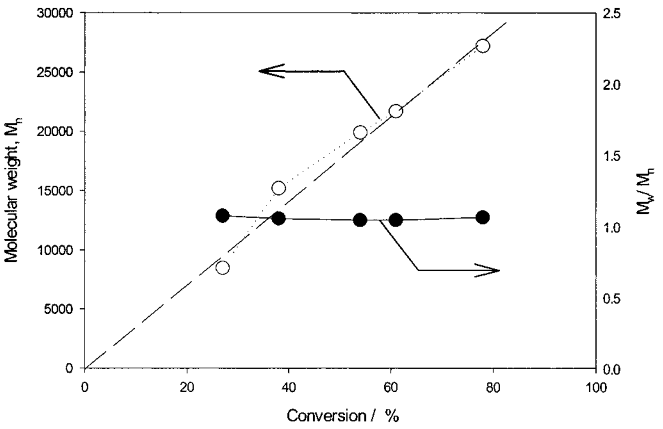


Figure 5. Relationship between conversion vs. M_n and M_w/M_n of PLA polymerized from LA by Al triflate with re-addition of LA at 1 h under 100 °C. (○) M_n of PLA with higher M_n, (●) M_w/M_n of PLA with higher M_n.

Conclusion

The biodegradable and biorenewable PLA polymer could be polymerized by aluminum triflate as a catalyst. This aluminum (Al) triflate is a Lewis acid stable in water and air. Using this Al catalyst, PLA could be prepared at 100 °C using a simple glass tube without air-sensitive handling. Adding a little alcohol as an initiator, the molecular weight (M_n) of the PLA polymerized by Al triflate increased. For a lower amount of alcohol and long reaction time, PLA with a lower M_n was co-produced in PLA with a higher M_n. Thus the total M_n of these samples was lower. In the near future, we must develop optimal conditions without producing PLA with a lower M_n. This simple polymerization method can be applied for the direct molding of a PLA composite with cellulose fibers during polymerization by Al triflate without harmful organic solvents at a lower temperature than the melting temperature of PLA. However, it is a fact that there are technical problems such as coloring to deep brown and remaining catalytic activity after polymerization. In the near future, much more optimization of the polymerization conditions and characterization of the polymerization mechanism will be studied.

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