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Ring-opening copolymerization of succinic anhydride with ethylene oxide initiated by magnesium diethoxide

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The ring-opening copolymerization of succinic anhydride (SA) with ethylene oxide (EO) was carried out by using mainly magnesium diethoxide (ME) as an initiator. ME was superior with respect to polymerization yield and number-average molecular weight (M_n) of the copolymers obtained. The copolymers were found to be alternating copolymers independent of feed monomer molar ratio. The yield and the M_n of the copolymers increased with the polymerization temperature and the time within 48 h. There was a maximum of M_n at a time of 48 h, at 100°C. The M_n of the alternating copolymers was as high as 1.3×10^4. The M_n of the copolymers increased proportionally with the increase of monomer/initiator molar ratio (M/I) up to M/I = 400. From analysis of the end-groups of low M_n of copolymers by ^{1}H n.m.r., these copolymers were a mixture of two copolymers having different end groups. One had ethyl ester group connecting with SA at either end group, the other had ethyl ester group connecting with SA and hydroxyl group connecting with EO. © 1997 Elsevier Science Ltd.

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INTRODUCTION

Pollution caused by wasted synthetic polymer products is nowadays one of the most serious ecological problems, because they do not spontaneously degrade in the environment. Therefore, it is urgently needed to develop environmentally friendly biodegradable polymers which can be substituted for conventional polymeric materials.

Aliphatic polyesters expected to be biodegradable have been studied by many researchers.

The polyesters were prepared by biosynthesis[1] and chemosynthesis such as a polycondensation method and a ring-opening polymerization method. The best known example of polycondensation methods is the synthesis of poly(ethylene succinate) and poly(butylene succinate) reported by Takiyama and Fujimaki[2]. On the other hand, the ring-opening polymerization method has the advantage of preparing easily various kinds of higher molecular weight polymers. Therefore, ring-opening polymerization of cyclic esters such as lactones, lactide, and glycolide have been reported. These aliphatic polyesters showed a wide range of biodegradability and mechanical or thermal propeties[3–16].

Polyesters are also synthesized by the ring-opening copolymerization of acid anhydride with oxirane[17,18]. This method had been investigated for the purpose of synthesizing aromatic polyesters in the 1960s. However, there are not many reports using aliphatic acid anhydride. Ishii *et al.* and Fisher conducted the ring-opening copolymerization of succinic anhydride with oxirane using dimethyltin dichloride and tertiary amine, respectively, as a initiator[19,20]. The ring-opening copolymerization of aliphatic acid anhydride with oxirane has recently been paid much attention owing to development of biodegradable polymers.

In order to obtain useful biodegradable materials, we have recently investigated the biodegradation of polyesters and polyesterethers synthesized by the ring-opening copolymerization of succinic anhydride (SA) with oxiranes, for example, ethylene oxide (EO), propylene oxide (PO) or styrene oxide, using diethylzinc, aluminium isopropoxide and bimetallic (Al, Zn) μ-oxobutoxide (AZ)[21–23] as initiators. Copoly(SA/EO)s and copoly-(SA/PO)s up to $M_n = 10\,000$ were completely hydrolysed by lipase from *Rhizopus arrhizus*. Further, it became apparent that the chain-extension reaction using $\mathrm{Ti[OCH(CH_3)_2]_4}$ as a catalyst between the copolymers leads to the useful biodegradable polymer having higher molecular weight[24]. Therefore, the copolymers synthesized by the ring-opening copolymerization have been expected as a starting material for a polycondensation with other biodegradable polymers such as polyesters, polyethers and polyamides. For

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practical uses of these polymers, it is necessary to take into account how the diffusion of the residue of metallic compounds used as an initiator in these copolymers influence environment before and after their biodegradation.

This paper reports on the controlled synthesis of high molecular weight poly(ethylene succinate), which, to our best knowledge, has not been published until now. The initiator is a common and nontoxic metal compound such as magnesium diethoxide (ME) and magnesium chloride (MC). Furthermore, the end-group of the copolymers are analysed by ^{1}H n.m.r.

EXPERIMENTAL

Materials

SA (from Wako Pure Chemical Co., Japan) was recrystallized from chloroform. EO (from Sumitomo Seika Co., Japan) was distilled over CaH_2 under reduced pressure. AZ was prepared and used as toluene solution according to the literature[25]. Other initiators were used as purchased from Wako Pure Chemical Co., Japan. Toluene was refluxed over CaH_2 and distilled.

Ring-opening copolymerization

The ring-opening copolymerization was carried out in a glass ampoule. Unless otherwise noted, SA (0.25 mol) was placed in the polymerization ampoule and then an initiator (0.05–0.5 mol% for the total of two monomers) was added. After EO (0.025 mol) was transferred into the ampoule by trap to trap method, toluene (2 ml) was added by a syringe. The ampoule was sealed and kept at 100°C for 2–150 h. The crude product was dissolved on chloroform. The chloroform solution was concentrated *in vacuo* after filtration of insoluble materials. The polymers were precipitated with petroleum ether from chloroform solution and dried for 24 h at 80°C under reduced pressure.

Characterization of copolymers

^{1}H n.m.r. spectra were recorded on a JEOL JNM A-500 spectrometer (500 MHz) or a Varian UNITY plus-400 spectrometer (400 MHz). All spectra were obtained from chloroform-*d* solutions at room temperature with TMS as an internal standard. I.r. spectra were recorded on a Perkin-Elmer 1600 *FT*i.r. spectrometer, for film samples cast on a potassium bromide plate from chloroform solutions. Differential scanning calorimetry (d.s.c.) studies were conducted with a Seiko Denshi DSC120 for the sample from 4 to 8 mg. After the first run, the sample was cooled to −60°C at a rate of *ca.* 10°C min^{-1}, followed by the second run under the same conditions. Molecular weights (M_n) and molecular weight distributions (M_w/M_n) were determined by g.p.c. (TOSOH, HCL-8020). The columns were a TSKgel G4000HXL and a TSKgel G3000HXL with limited exclusion molecular weight of 4×10^5. Chloroform was used as an eluent at a flow rate of 0.6 ml min^{-1}. Polystyrene standards with low polydispersities were used to generate a calibration curve. Residual magnesium contents in copolymers were analysed according to JIS K0101 using atomic absorption and flame emission spectrophotometer (AA-8200F, Nippon Jarrell-Ash Co.).

RESULTS AND DISCUSSION

Ring-opening copolymerization of SA with EO by using several initiators

The ring-opening copolymerization of SA with EO was carried out by various initiators (*Table 1*) at feed monomer molar ratio of SA/EO = 50/50. *Figure 1* shows ^{1}H n.m.r. spectra of the typical copoly(SA/EO)s

Table 1 Ring-opening copolymerization of succinic anhydride (SA) with ethylene oxide (EO) by various initiators[a]

Initiator		Yield[c]			Polym. comp.[e]
Formula	M/I[b]	(%)	$M_n{}^d/10^4$	$M_w/M_n{}^d$	SA/EO (mol%)
LiCl	400	23	0.24	1.3	49/51
NaCl	400	91	0.51	1.9	49/51
KCl	400	89	0.46	1.4	49/51
$ZnCl_2$	100	80	1.04	1.8	46/54
$MgCl_2$	400	93	1.32	1.7	49/51
$FeCl_3$	100	91	1.07	1.6	49/51
$AlCl_3$	100	68	1.03	1.8	49/51
$SnCl_4$	400	0	–	–	–
$SnCl_2$	400	56	0.26	1.8	40/60
$SbCl_5$	400	0	–	–	–
$Zn(CH_2CH_3)_2$	400	85	0.80	1.5	45/55
$Al(CH_2CH_3)_3$	100	84	0.65	1.6	49/51
$Mg(OCH_2CH_3)_2$	400	95	1.32	1.7	49/51
$Al[OCH(CH_3)_2]_3$	400	90	0.55	1.4	49/51
$(n\text{-}C_4H_9O)_4Al_2O_2Zn$	400	88	0.75	1.6	46/54
$(n\text{-}C_4H_9)_3SnOCH_3$	400	0	–	–	–
$Ti[OCH(CH_3)_2]_4$	400	66	0.54	1.5	49/51

[a] Feed monomer ratio; SA/EO = 50/50 in toluene at 100°C for 48 h

[b] Monomer/initiator molar ratio

[c] Product precipitated with petroleum ether from chloroform solution including copolymers

[d] Determined by g.p.c. Solvent: chloroform, standard: polystyrene

[e] Determined by ^{1}H n.m.r.

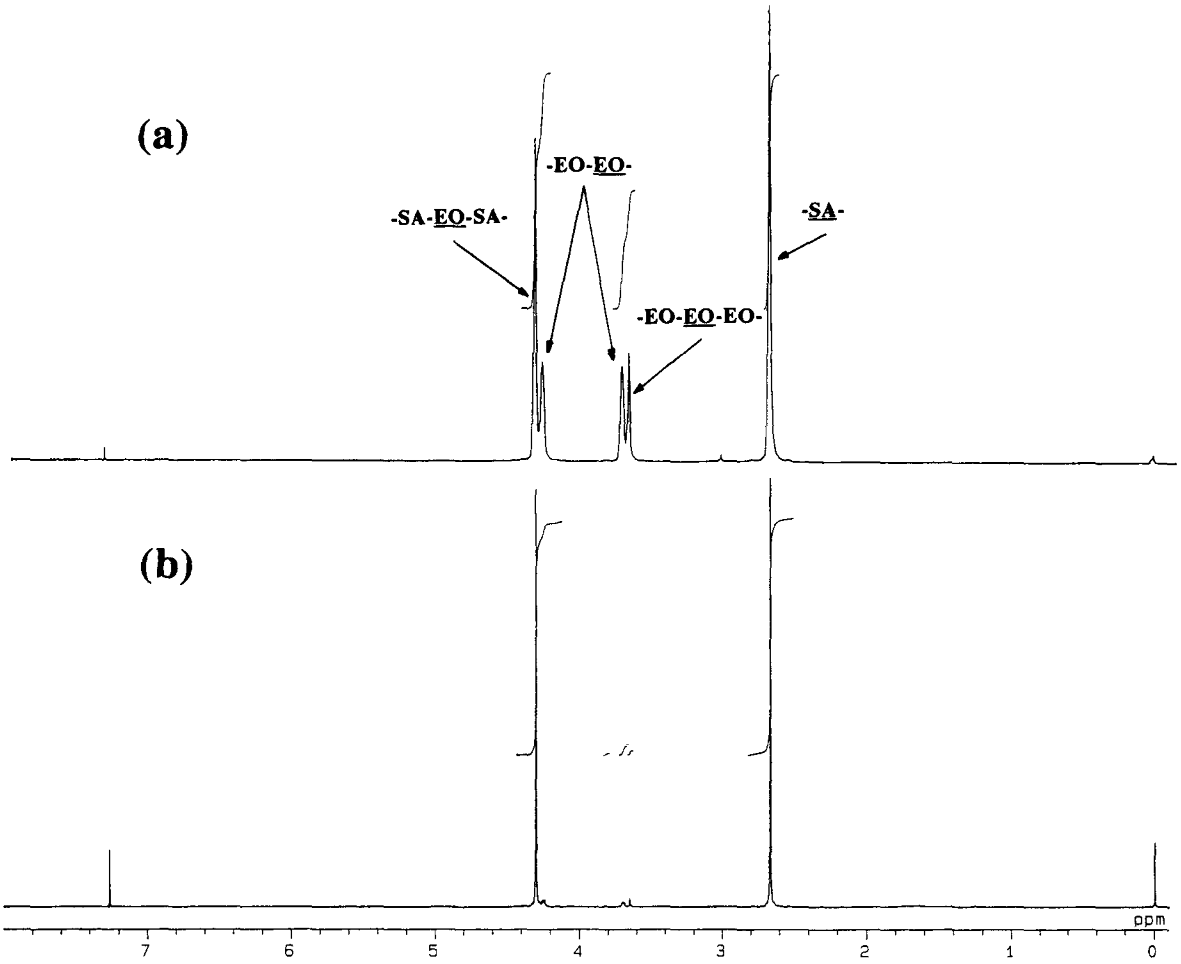
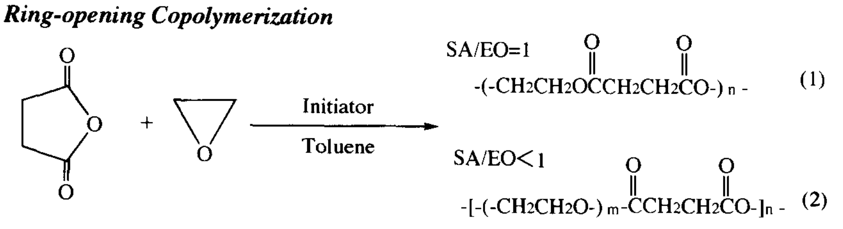


Figure 1 ^{1}H n.m.r. spectra of the copoly(succinic unhydride/ethylene oxide)s, copoly(SA/EO)s, synthesized by the ring-opening copolymerization of SA with EO using bimetallic (Al, Zn) μ-oxobutoxide, AZ (a) or magnesium diethoxide, ME (b) as an initiator



$$-(-CH_2CH_2O\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}O-)_n- \quad (1)$$

$$-[-(-CH_2CH_2O-)_m-\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}O-]_n- \quad (2)$$

Scheme 1

synthesized using ME or AZ at feed monomer molar ratio of SA/EO = 50/50. Various metallic chlorides except tin(IV) chloride and antimony(V) chloride were effective for the copolymerization. In the case of metallic chlorides such as iron(III) chloride, aluminium chloride, zinc chloride, and MC, the M_ns of the copolymers increased compared to the case of the chlorides of the alkali metal such as potassium and sodium. The copolymerization was initiated by various metallic alkoxides and metal alkyl compounds except for $(n\text{-}C_4H_9)_3SnOCH_3$. The copolymers obtained had the composition of SA/EO = 49/51 and scarcely contained the diad homo sequences of EO from ^{1}H n.m.r. except for ones produced by zinc compounds or tin(II) chloride as an initiator. The diad homo sequences of SA was not observed by ^{1}H n.m.r. On the other hand, using zinc compounds, unreacted SA was recovered and the diad homo sequences of EO was observed. These facts indicated that the copolymers synthesized using other initiators except for zinc compounds and tin(II) chloride are alternating copolymers of SA and EO, namely poly(ethylene succinate) [*Scheme 1*, equation (1)]. The composition of the copolymers produced by zinc compounds or tin(II) chloride was SA/EO = 45/55 (or 46/54), 40/60, respectively [*Scheme 1*, equation (2)]. These facts suggest that the mechanism of the ring-opening copolymerization initiated by zinc compounds or tin(II) chloride is different from that by other initiators. It can be thought that zinc compound or tin(II) chloride promote the ring-opening polymerization of EO in the absence of SA, on the other hand, other initiators cannot accelerate both this copolymerization and EO homopolymerization without SA.

ME and MC were superior to other initiators with respect to the yield and the M_n of copolymers obtained. We finally focused on ME as an initiator in the following studies because ME has the advantage of easier handling and nontoxicity.

Ring-opening copolymerization of SA with EO by using ME

Figure 2 shows the relationships between the yield or the M_n of the polymers synthesized at 100°C for 48 h and monomer/initiator molar ratio, M/I. Below M/I = 400, the yield was constant over 80% and a linear relationship existed between the M_n and M/I. On the contrary, above M/I = 400, the yield and the M_n decreased with an increase of M/I. These results could be explained by the fact that the polymerization proceeds as a living polymerization mechanism below M/I = 400 and termination is predominant over polymerization with the decrease of the initiator above M/I = 400 because the polymerization rate is suppressed due to a small amount of initiator concentration. On the point of M/I = 400, these two opposite parameters are balanced and the M_n had a maximum. On the basis of these results, subsequent polymerizations were carried out at M/I = 400.

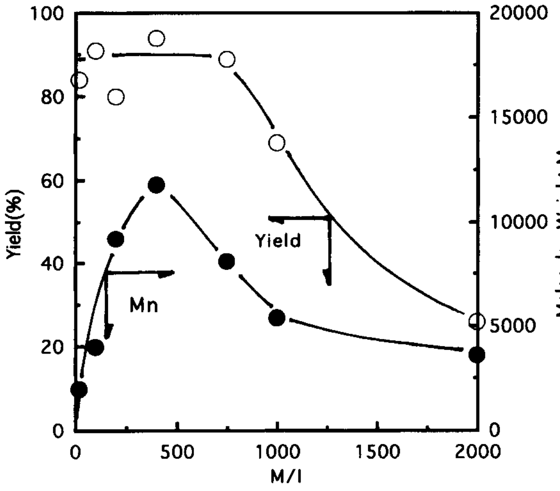


Figure 2 Relationship between the yield or the number-averaged molecular weight, M_n and monomers/initiator molar ratio, M/I with SA of 0.025 mol, EO of 0.025 mol by ME as an initiator in toluene at 100°C for 48 h

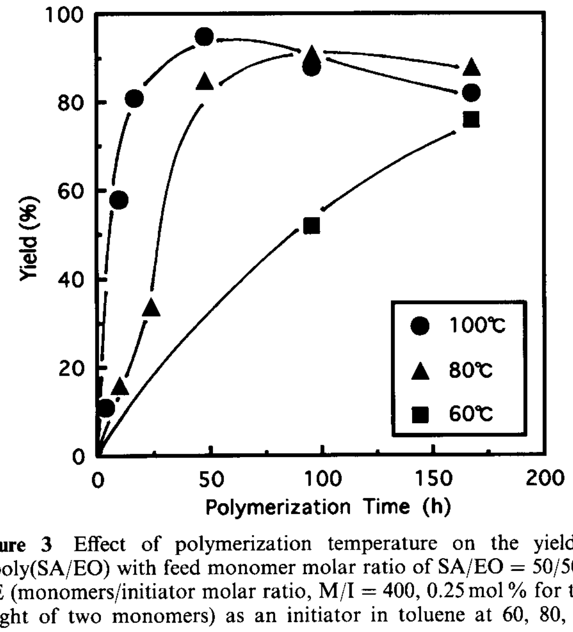


Figure 3 Effect of polymerization temperature on the yield of copoly(SA/EO) with feed monomer molar ratio of SA/EO = 50/50 by ME (monomers/initiator molar ratio, M/I = 400, 0.25 mol % for total weight of two monomers) as an initiator in toluene at 60, 80, and 100°C

Figure 3 shows the relationships between the yield and the polymerization time at 60, 80 and 100°C (M/I = 400), respectively. The yield increased with the polymerization time. The rate of polymerization increased with rising polymerization temperature. The yield was levelled off after 48 h at 80°C and 100°C. The relationships between the M_n of copolymers and polymerization time at 60, 80 and 100°C (M/I = 400) are shown in *Figure 4*. The M_n of copolymers increased with polymerization time and reached a maximum after 48 h at 100°C. It can be seen that the reaction of SA with EO completes in 48 h at 100°C. At 100°C, the yield and the M_n of the copolymers decreased after 48 h. These results suggest that intermolecular transesterification may cause a decrease of the M_n of produced polymers.

The effects of feed monomer molar ratio (SA/EO) on the copolymerization are shown in *Table 2* under polymerization conditions; M/I = 400, at 100°C, for 48 h. EO was not homopolymerized by ME. The yield

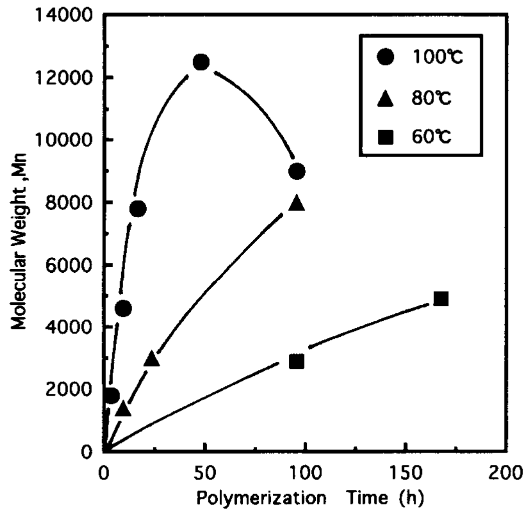


Figure 4 Effect of polymerization temperature on the M_n of copoly(SA/EO) with feed monomer ratio, SA/EO = 50/50, by ME (monomers/initiator molar ratio, M/I = 400) as an initiator in toluene at 60, 80, and 100°C

Table 2 Results of the ring-opening copolymerization of SA with EO by magnesium diethoxide as an initiator[a] at various feed monomer ratios

Feed monomer ratio, SA/EO (mol%)	Yield (%)	$M_n{}^b/10^4$	$M_w/M_n{}^b$	Polym. comp.[c] SA/EO (mol%)
0/100	0	–	–	–
25/75	54	0.94	1.6	43/57
33/67	59	1.15	1.6	47/75
50/50	95	1.32	1.7	49/51
67/33	51	0.40	1.5	51/49

[a] Monomer/initiator molar ratio, M/I = 400, in toluene at 100°C for 48 h

[b] Determined by g.p.c. Solvent: chloroform, standard: polystyrene

[c] Determined by ^{1}H n.m.r.

was the best when SA/EO was 50/50. The M_n of the copolymers increased with the increase in SA feed content up to 50 mol%. Even if EO was added in excess relative to SA, the EO content in the copolymers was smaller than the feed EO content. At the feed monomer molar ratio of SA/EO = 67/33, large amounts of unreacted SA were recovered and the copolymer composition of produced copolymer, SA/EO, was 51/49. SA content over 50% is enabled by the presence of SA unit at both ends of the relatively low molecular weight copolymer.

Figure 5 shows the ^{1}H n.m.r. spectrum of the copoly(SA/EO) of $M_n = 2600$, and assignment of its proton signals. One of the end groups is $-COOCH_2CH_3$ [$-COO\underline{H}_2CH_3$, q, J = 7.2 Hz, δ 4.15 ppm, $-COOCH_2C\underline{H}_3$, *t*, J = 7.2 Hz, δ 1.26 ppm]. Another end group is $-OCH_2CH_2OH$ [$-COOCH_2C\underline{H}_2OH$, *t*, J = 4.4 Hz. δ 3.82 ppm, $-COOC\underline{H}_2CH_2OH$, *t*, J = 4.4 Hz, δ 4.25 ppm]. From the integrated intensity of the protons of $-COOC\underline{H}_2CH_3$ and $-COOCH_2C\underline{H}_2OH$, the ratio of [$-COOCH_2CH_3$]/[$-COOCH_2CH_2OH$], was around 2.5. From this ratio and the fact that EO homopolymerization does not proceed by ME, it is presumed that the ring-opening copolymerization is initiated by the reaction between SA and ME. Furthermore, in order to clarify the mechanism of the initiation of the copolymerization, equimolar reaction of SA and ME were performed in toluene at 100°C. The reaction was followed by ^{1}H n.m.r. analyses of the reaction mixture. ^{1}H n.m.r. spectra of the reaction mixtures for 1 h and 2 h are shown in *Figures 6a* and *6b*, respectively. According to ^{1}H n.m.r. (*Figure 6a*), it can be presumed that the reaction product comprises a mixture of two compounds. One is $CH_3CH_2OCOCH_2CH_2COMgOCH_2CH_3$ (**2** in *Scheme 2*), the other is diethyl succinate (**3** in *Scheme 2*). These reasons are as follows: (1) the methyl proton signals (1, 1′, and 6) of $-OCOCH_2C\underline{H}_3$ were observed; (2) three methylene proton signals (3, 4, and 7) of $-OCOC\underline{H}_2C\underline{H}_2COO-$ existed; (3) the methylene proton signals (2, 2′, and 5) of $-COOC\underline{H}_2CH_3$ and $-OCOMgOC\underline{H}_2CH_3$ were observed. These proton signals were assigned on the basis of the proton signals of commercial SA, ME, diethyl succinate, mono ethylsuccinate, and succinic acid. **3** was identified by liquid chromatography[26] by a solvent system of methanol/H_2O = 84/16 v/v using commercial diethyl succinate. After 2 h (*Figure 6b*), the proton signals of 3, 4 and 5 of **2** in *Figure 6a* were small. It is thought that **2** in *Scheme 2* were mainly produced by equimolar reaction of SA and ME by considering the poor solubility of **2** in toluene and **2** changes to **3** with the passage of time.

From these results, it is considered that the ring-opening copolymerization of SA and EO initiated by ME proceeds in the following manner[3,7,27–29]. By cleavage of acyl-oxygen bond of SA, **2** in *Scheme 2* is produced, followed by insertion of EO to O–Mg bond in $OCO-MgOCH_2CH_3$ of **2**. Further, the insertion of SA to O–Mg bond after the one of EO is performed. In this manner, such insertions of monomers are alternately repeated. By this mechanism, one of the end-groups of the copolymers must be ethyl ester group connecting with SA. This finding is in agreement with the fact that the above ratio of [$-COOCH_2CH_3$]/[$-COOCH_2CH_2OH$] is *ca.* 2.5. After polymerization, the copolymerization is stopped by a trace amount of water or ethyl alcohol containing solvents used at the work-up of the polymerization by equation (3) in *Scheme 3*.

Release of magnesium from the copolymers at the work-up step was confirmed by the results of atomic absorption spectrum of magnesium in copolymers. As a result, magnesium contents in the copolymer ($M_n = 4500$) was only 2.7 ppm after reprecipitation. Most of the magnesium atom was removed from the copolymers because the amount of magnesium atoms

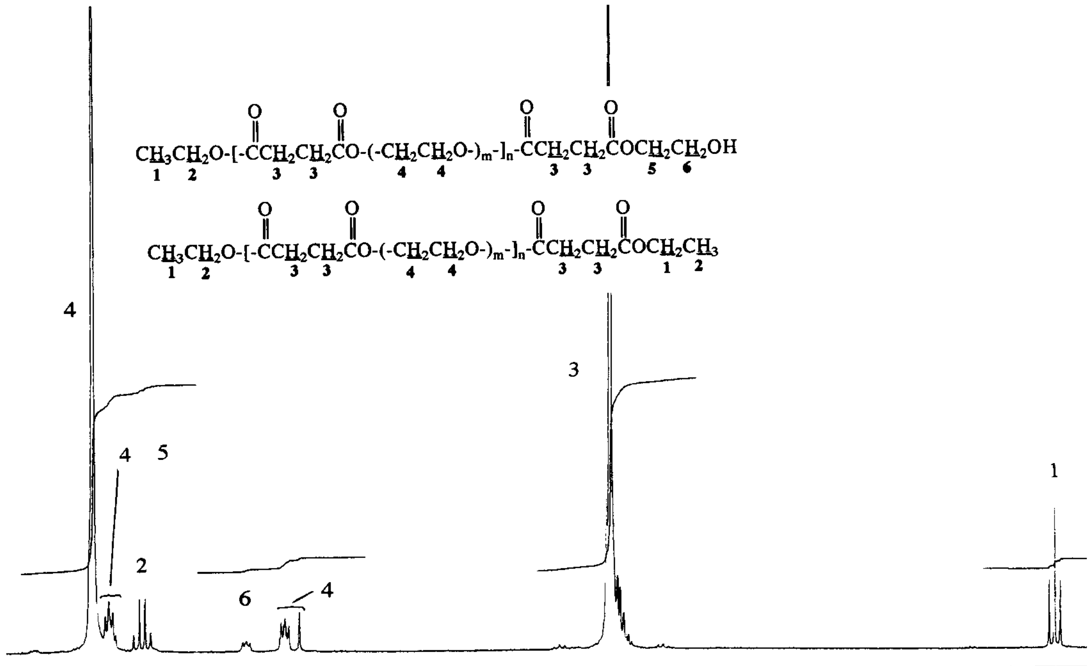


Figure 5 ^{1}H n.m.r. spectrum of the low molecular weight ($M_n = 2600$) copolymer synthesized by the ring-opening copolymerization of SA with EO by ME as an initiator in toluene at 100°C for 24 h. ME was used 2 mol % for the total weight of two monomers (0.4 mol)

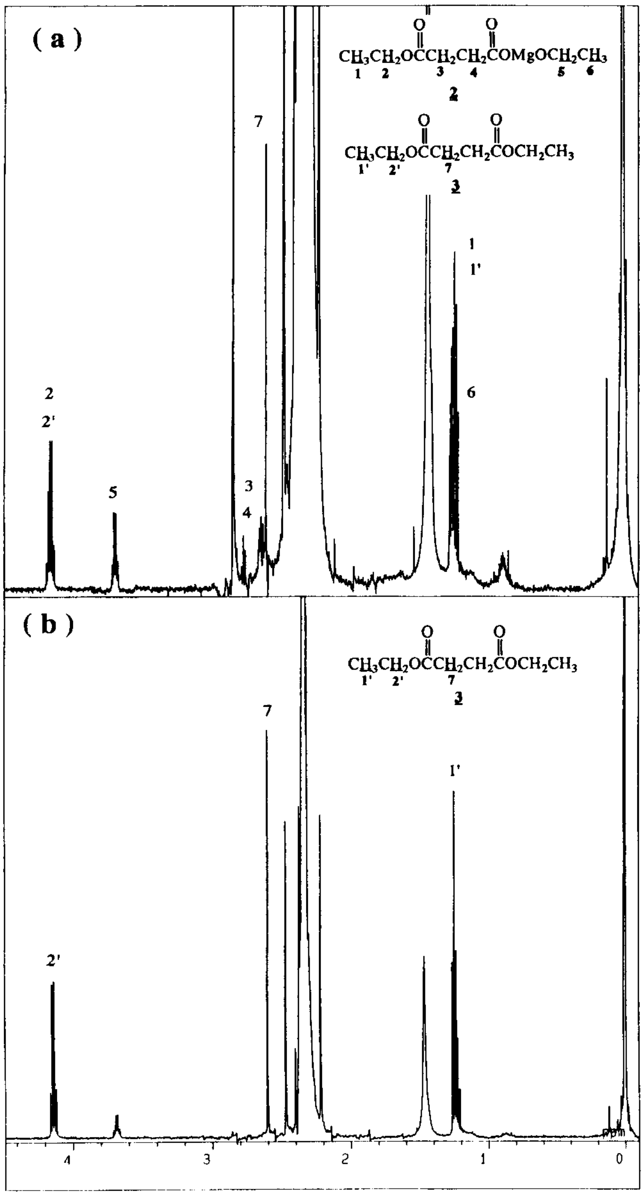
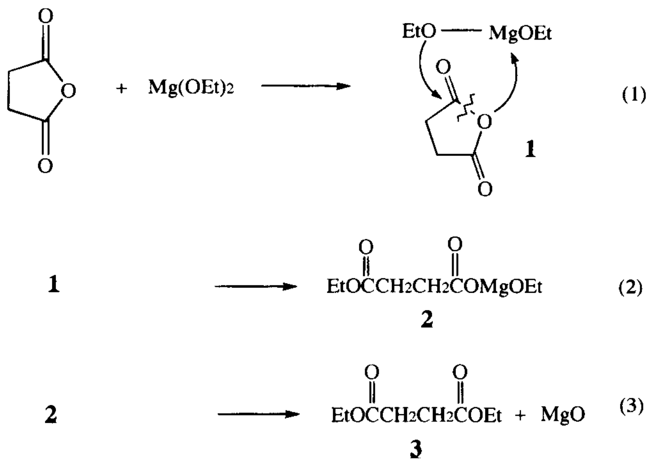


Figure 6 ^{1}H n.m.r. spectra of the products of equimolar amount reaction of SA with ME in toluene at 100°C for 1 h (a) or 2 h (b)



Scheme 2

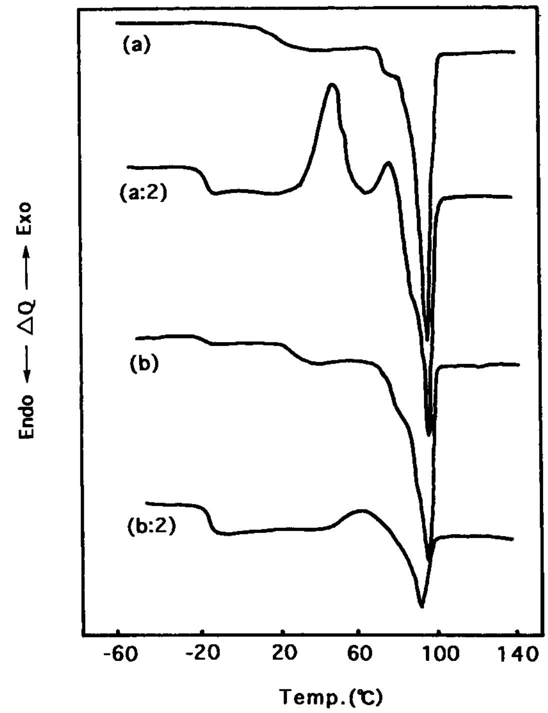


Figure 7 D.s.c. curves of typical copolymers: (a) SA/EO = 49/51, M_n = 13 000; (b) SA/EO = 44/56, M_n = 9000. (2: second run, *ca.* 10°C min^{-1} cooling from the melt)

should be around 5000 ppm if the copolymer (M_n = 4500) had magnesium at either end group. Trace amount of the magnesium residue in the prepolymer had the advantage of doing without considering harmful influences on a catalytic action for the chain-extension reactions of these copolymers.

Thermal properties of copolymers

The thermal properties of various copolymers investigated by d.s.c. are shown in *Table 3*. Melting point (T_m) and fusion heat (ΔH) were measured by the first run. On the other hand, glass transition (T_g) was determined by the second run. T_m varied from 60°C to 100°C and increased with the increase of SA content in these copolymers. ΔH and T_g rose with the increase of SA content. *Figure 7* shows the d.s.c. curves on the first and second runs for typical two copolymers. These curves on the first run measurement had one melting peak. The copolymer (SA/EO = 49/51, M_n = 13 000) of T_m = 96°C (a:2 in *Figure 7*) had two very sharp crystallization peaks at 50°C and 79°C on the second run. This curve indicates a double-peak distribution of crystal sizes or the presence of two different types of morphology in this copolymer. However, both explanations are not supported by the information on the crystal structure from small angle X-ray scattering analyses. On the other hand, in the case of the copolymer (SA/EO = 44/56, M_n = 9000) of T_m = 93°C (b:2 in *Figure 7*), the weaker crystallization peak at 59°C compared to one of the higher SA content copolymer was observed and the endotherm peak on the second run was smaller than one on the first run. This finding indicates that the rate of crystallization of the copolymers increased with increase of SA content in the copolymers. These facts suggest the following: (1) crystalline region spreads over the copolymers with increase in SA content; (2) crystallization of the copolymers is inhibited by the presence

Table 3 Thermal properties of various copoly(SA/EO)s

Run	Polym. comp.[a] SA/EO (mol%)	$M_n{}^b/10^4$	$M_w/M_n{}^b$	$T_m{}^c$ (°C)	ΔH^c (J g^{-1})	$T_g{}^c$ (°C)
1[d]	0/100	5.26	5.5	66	129	ND[e]
2	43/57	0.94	1.6	85	41	−24(−18[f])
3	47/53	1.13	1.6	94	49	−18(−15[f])
4	50/50	0.27	2.2	94	58	−20
5	50/50	0.46	1.5	94	65	ND[e]
6	49/51	0.68	1.5	94	65	ND[e]
7	49/51	1.32	1.7	99	62	ND[e](−13[f])

[a] Determined by ^{1}H n.m.r.

[b] Determined by g.p.c.

[c] Determined by d.s.c.

[d] $(n\text{-}C_4H_9O)_4Al_2O_2Zn$ was used as an initiator

[e] Not detected

[f] From d.s.c. second run

of EO homo sequence; (3) flexibility of polymer chain in amorphous region fell down with increase in SA content.

CONCLUSIONS

Through the ring-opening copolymerization of SA with EO by using mainly ME, the following conclusion can be drawn.

(1) ME was superior to the other initiators with respect to polymerization yield and M_n of the copolymers obtained.

(2) The copolymerization initiated by ME proceeded alternately under any feed monomer molar ratios.

(3) The M_n of copolymers obtained was more than 13000. In that range, the M_n of poly(ethylene succinate) could be controlled on the basis of the monomer/initiator molar ratio (M/I).

(4) The copolymers were a mixture of two copolymers having different end groups. One had both ethyl ester groups connecting with SA, the other had ethyl ester group connecting with SA and hydroxy group connecting with EO.

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