

RING OPENING COPOLYMERIZATION OF SUCCINIC ANHYDRIDE-ETHYLENE OXIDE BY Al (III) ORGANOMETALLIC CATALYSTS

CHEN Xianhai (陈仙海)

(*NSF Biodegradable Polymer Research Center, University of Massachusetts Lowell,
One University Ave., Lowell, MA 01854, U.S.A.*)

ZHANG Yifeng (张一烽) and SHEN Zhiqun (沈之荃)*

(*Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027*)

ABSTRACT

Ring opening copolymerization of succinic anhydride (SA) with ethylene oxide (EO) was successfully carried out by using a series of aluminum-based catalyst in 1,4-dioxane at $62 \pm 2^\circ\text{C}$. The results showed that in-situ $\text{AlR}_3\text{-H}_2\text{O}$ ($\text{R}=\text{ethyl, iso-butyl}$) catalysts gave higher molecular weight ($\overline{M}_w \sim 10^4$), while Al(OR)_3 catalysts gave the higher alternating copolymer structure with slightly lower molecular weight. The in-situ $\text{AlR}_3\text{-H}_2\text{O}$ systems have been evaluated in more detail for the reaction which showed the optimum $\text{H}_2\text{O/Al}$ molar ratio to be 0.5. The copolymers with different composition ($F_{\text{SA}}/F_{\text{EO}} = 36/64$ to $45/55$ mol/mol) were synthesized by using different monomer feed ratio. The melting point (T_m), glass transition temperature (T_g) and enthalpy of fusion (ΔH_f) of these copolymers are depended on the copolymer composition and in the range of $87 \sim 102^\circ\text{C}$, $-12 \sim -18^\circ\text{C}$, and $37 \sim 66 \text{ J/g}$, respectively. The second heating scan of DSC also indicated that the higher alternating copolymer was more easily recrystallized. The onset decomposition temperature was more than 300°C under nitrogen and influenced by the copolymer composition.

INTRODUCTION

Poly(ester-ether)s, which are usually prepared by a two stage melt transesterification process^[1-3], can be synthesized by ring opening copolymerization of cyclic anhydrides or lactones with epoxides^[4-10]. The ring opening copolymerization overcame the disadvantages of condensation reaction, such as high temperature, high vacuum, etc..

* To whom correspondence should be addressed

Maleic anhydride-propylene oxide copolymerization, a model reaction of epoxy resin curing, had been investigated extensively^[11-17]. The obtained poly(ester-ether)s have potential applications as unsaturated resin. However, the molecular weight of maleic anhydride-propylene oxide copolymers were relatively low ($\overline{M}_n = 1000 \sim 3000$). Recently, the succinic anhydride(SA)-ethylene oxide (EO) copolymer had been paid attention due to its interesting structure and thermal properties^[18]. The ether unit in the copolymer is nontoxic, biocompatible polyethylene oxide (PEO or PEG). In addition, the copolymer of SA-EO had been reported to be enzymatic degradable^[19], and the biodegradation rate was significantly affected by the copolymer composition. However, the copolymerization is still rather undeveloped in terms of reaction catalysts, and especially of the solution copolymerization. For aluminum-based catalyst, only $\text{Al}(\text{O}^i\text{Pr})_3$ had been used for the SA-epoxides bulk copolymerization^[18].

A series of active catalysts have been found for the ring opening polymerizations of heterocyclic monomers during the last decade^[20], including ionic^[21], coordinate catalysts^[22-26]. It is of importance to evaluate these catalysts for the novel ring opening copolymerizations and to synthesize a new family of biodegradable copoly(ester-ether)s. In this paper, a series of aluminum catalysts have been selected for the SA-EO copolymerization. The structure and thermal properties of the copolymers synthesized will also be investigated.

EXPERIMENTAL

Materials

Succinic anhydride(SA) from Aldrich was recrystallized from anhydrous benzene before use. Ethylene oxide (Aldrich, purity $\geq 99.7\%$) was used as received without further purification. All of the organic aluminum compounds were purchased from Aldrich in toluene and used as received. 1, 4-Dioxane (Aldrich) was refluxed over CaH_2 and distilled under dry argon or nitrogen. All air sensitive liquid reagents and dry solvents were transferred under an argon or nitrogen atmosphere.

Preparation of in situ $\text{AlR}_3\text{-H}_2\text{O}$ catalysts

The in-situ catalysts $\text{AlR}_3\text{-H}_2\text{O}$ (1/0.5, 1/1, 1/1.5) were prepared by modification of a literature procedure^[27]. To a previously silanized, flame dried, and dry argon purged 10 ml schlenk tube, 1 ml AlR_3 (in dry toluene) was injected via syringe under a dry argon (or nitrogen) atmosphere. The solution was cooled in an external dry ice-acetone bath followed by slowly adding a solution of distilled water in 1,4-dioxane (1/9 v/v) with vigorous stirring. After 15 min, the dry ice bath was removed and

the temperature increased to ambient temperature. A clear solution was formed and stored in refrigerator (about 4°C) for up to 1 month prior to use without loss of catalytic activity^[7].

Copolymerization procedure (general)

The following describes the general procedure used for EO/SA copolymerizations. Additional information on polymerization conditions is given in Tables 1–3. All reagents used and polymerization reactions were protected by a dry argon atmosphere. In a previously silanized, flame dried and argon purged ampule, SA was transferred (in a dry nitrogen maintained glovebox), 1, 4-dioxane, ethylene oxide and catalyst solution were then injected by syringe. The ampule was then sealed under dry argon and thermostated in an oil bath for a preset time. Subsequently, the reaction product was dissolved in chloroform (~ 10 ml/g starting monomers) and precipitated into petroleum ether (~ 100 ml). The precipitated material was washed several times with petroleum ether, and then remaining volatiles were removed in vacuo (< 3 mmHg, 40°, 24 h).

Instrumental methods

Nuclear magnetic resonance (NMR): Proton (^1H) NMR spectra were recorded on a Bruker ARX-250 spectrometer at 250 MHz. ^1H NMR chemical shifts in parts per million (ppm) are reported using tetramethylsilane (TMS) as an internal reference. The concentration used was 4% (w/v) in chloroform-d. The instrumental parameters were as follows: temperature 300 K, pulse width 7.80 μs (30°), 32 K data points, 3.18 s acquisition time, 1 s relaxation delay, and 32 transients. Carbon-13 (^{13}C) spectra were recorded at 62.9 MHz on a Bruker ARX-250 spectrometer in chloroform-d solutions, with chemical shifts in ppm referenced relative to CDCl_3 as the internal reference at 77.00 ppm. Polymer spectral acquisitions were conducted as 20% (w/v) chloroform-d solutions using the following parameters: temperature 300° K, 30° pulse width, 64 K data points, acquisition time 1.638 s, delay time 1 s, 15000 to 20000 transients.

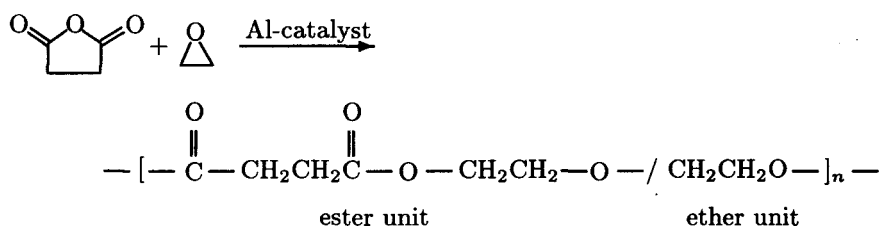
Molecular weight measurements: All molecular weights were determined by gel permeation chromatography (GPC) utilizing a Waters Model 510 pump, Model 410 differential refractometer with 50–, 10²–, 10³–, and 10⁴– nm (1 nm = 10^{–9} m) ultrastyrigel columns placed in series. Chloroform was used as the eluent at a flow rate of 1.0 ml/min. The injection volume was 100 μl and the sample concentrations were $\sim 0.6\%$ (w/v). Polystyrene standards with a low dispersity (Polysciences) were used to generate a calibration curve. Data were recorded and manipulated using the Windows based Millenium 2.0 software package.

Thermal analysis: Differential scanning calorimetry (DSC) studies were conducted on a DuPont DSC 912 equipped with a TA 2000 data station, using between 5 and 8 mg of sample, a heating rate of $10^\circ\text{C}/\text{min}$., a nitrogen purge and heating samples from -50 to 200°C (first scan). The procedure was repeated once again from -60 to 200°C under the same heating rate (second scan). Data reported for the melting temperature (T_m) and enthalpy of fusion (ΔH_f) were taken from the first heating scan. The reported T_m was the peak melting temperature of the largest endotherm transition. ΔH_f values were taken as the cumulative value over the entire melting transition range. The glass transition temperature (T_g) was midpoint of the transition from the second heating scan. TGA analyses were conducted from room temperature to 500°C on Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments) with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

RESULTS AND DISCUSSION

1. Evaluation of Al-based catalysts for SA-EO copolymerization

Because SA is non-homopolymerizable, the structure of the SA-EO copolymer contains ester and ether (if any) units. The reaction equation can be expressed as follows.



Scheme 1. SA-EO copolymerization

A series of aluminum catalysts, including in-situ $\text{AlR}_3\text{-H}_2\text{O}$ (R =ethyl, iso-butyl), Al(OR)_3 (R =ethyl, propyl, butyl) and $\text{AlR}_n\text{X}_{3-n}$ (X =Cl, OCH_2CH_3), have been evaluated for the copolymerization. The results are summarized in Table 1. The composition of the copolymers were calculated according to $^1\text{H-NMR}$ which will be explained later. The data in Table 1 showed that all of the catalysts selected have high activity for the SA-EO copolymerization. The copolymer yield and molecular weight increased with the reaction time for all catalysts. However, the monomer/initiator molar ratio has little effect on the copolymerization results (compare 4 and 5). GPC results showed that all copolymers have uni-modal and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n = 1.1$ to 1.6). As for the copolymer composition, Al(OR)_3 catalysts gave a little higher SA content. For example, copolymers

with $F_{SA} = 0.48$ could be obtained by using $Al(OEt)_3$ or $Al(O^iBu)_3$ systems. The reaction rate was affected by the nature of OR group. $Al(O^iPr)_3$ system had slow polymerization rate in 16 h probably due to its aggregates^[28]. The $Al(O^iPr)_3$ catalyzed solution polymerization resulted in higher yield (48 h, 98%) at lower reaction temperature (60°C) relative to the bulk copolymerization with the same catalyst as reported by Maeda, et al.^[18], 56% yield at 80–140°C for 2–120 h. However, the molecular weight obtained by solution reaction was a little lower. For $AlEt_nCl_{3-n}$ ($n = 1, 2$) systems, $AlEtCl_2$ was more efficient for the copolymerization than Et_2AlCl in terms of both copolymer yield and molecular weight. In-situ AlR_3-H_2O systems, which are well known effective catalysts for synthesizing high molecular weight EO homopolymer, gave higher molecular weight copolymer in 48 h than other catalysts.

Table 1 Succinic anhydride (SA)-ethylene oxide (EO) ring-opening copolymerization¹⁾

Run	Catalyst	Time (h)	Yield % ²⁾	$\overline{M}_n$ ³⁾	$\overline{M}_w$ ³⁾	$\overline{M}_w/\overline{M}_n$ ³⁾	F_{SA} ⁴⁾	F_{EO} ⁴⁾
1	$AlEt_3-H_2O$ (1:0.5)	16	39	2,950	4,580	1.56	0.43	0.57
2*	$AlEt_3-H_2O$ (1:0.5)	48	70	8,090	11,700	1.45	0.39	0.61
3	$Al(O^iBu)_3-H_2O$ (1:0.5)	16	77	5,880	8,000	1.36	0.44	0.56
4	$Al(O^iBu)_3-H_2O$ (1:0.5)	48	82	8,650	11,200	1.29	—	—
5*	$Al(O^iBu)_3-H_2O$ (1:0.5)	48	85	7,130	9,160	1.28	0.43	0.57
6	Et_2AlOEt	16	40	2,000	3,240	1.62	0.42	0.58
7	Et_2AlOEt	48	62	4,850	6,880	1.42	0.38	0.62
8	$EtAlCl_2$	16	79	4,140	5,260	1.27	0.46	0.54
9	$EtAlCl_2$	48	100	5,920	7,990	1.35	0.47	0.53
10	Et_2AlCl	16	44	2,480	3,200	1.29	0.43	0.57
11	Et_2AlCl	48	69	4,600	6,560	1.43	0.40	0.60
12	$Al(OEt)_3$	48	86	4,420	5,320	1.20	0.48	0.52
13	$Al(O^tBu)_3$	16	54	2,630	3,480	1.32	0.43	0.57
14	$Al(O^tBu)_3$	48	92	5,480	6,830	1.25	0.45	0.55
15	$Al(O^iPr)_3$	16	20	1,580	2,120	1.34	0.44	0.56
16	$Al(O^iPr)_3$	48	98	4,650	5,980	1.29	0.47	0.53
17	$Al(O^iBu)_3$	16	46	1,800	2,350	1.30	0.42	0.58
18	$Al(O^iBu)_3$	48	94	3,580	3,980	1.11	0.48	0.52

¹⁾ Polymerization conditions: $[M]_{total}/[Al]=100$; $[SA]/[EO]=1 \pm 0.1$; $62 \pm 2^\circ C$; in 1, 4-dioxane (1g SA/7 ml), * $[M]_{total}/[Al]=200$

²⁾ Petroleum ether insoluble product/total monomer $\times 100\%$

³⁾ By GPC, in chloroform, 1 ml/min, polystyrene as standard

⁴⁾ Molar composition of the copolymer measured by ^1H -NMR

2. In-situ AlR_3-H_2O catalysts for the copolymerization

The structure of in-situ AlR_3-H_2O catalysts have three typical stages during the

increasement of $\text{H}_2\text{O}/\text{AlR}_3$ molar ratio. For $\text{H}_2\text{O}/\text{Al}=0.5$, $\text{AlR}_2\text{—O—AlR}_2$ is the major active species; $\text{H}_2\text{O}/\text{Al}=1.0$, oligomeric $[\text{—AlR—O—}]_n$; $\text{H}_2\text{O}/\text{Al}>1.0$, some crosslinking would be formed^[29].

Because the in-situ $\text{AlR}_3\text{—H}_2\text{O}$ catalysts gave higher molecular weight copolymer (48 h reactions, see Table 1), the copolymerization had been investigated in more detail. As shown in Table 2, the effects of $\text{H}_2\text{O}/\text{AlR}_3$ molar ratio and reaction time have been studied. The molecular weight of the copolymer obtained was related to the $\text{H}_2\text{O}/\text{AlR}_3$ molar ratio. The optimum $\text{H}_2\text{O}/\text{AlR}_3$ ratios were 0.5 for both catalysts, which means that $\text{AlR}_2\text{—O—AlR}_2$ is the most active initiator for the copolymerization. When $\text{H}_2\text{O}/\text{AlR}_3$ increased, the structure of the catalysts would be $[\text{—AlR—O—}]_n\text{—}$ or even crosslinking, lower yield and lower molecular weight were obtained by these systems. The copolymer composition seemed to be influenced by the nature of R group attached to aluminum. $\text{Al}(\text{iBu})_3\text{—H}_2\text{O}$ system gave a little higher F_{SA} than $\text{AlEt}_3\text{—H}_2\text{O}$.

Table 2 SA-EO ring opening copolymerization with in-situ $\text{AlR}_3\text{—H}_2\text{O}$ catalysts¹⁾

Run	Catalyst	Time (h)	Yield % ²⁾	$\overline{M}_n$ ³⁾	$\overline{M}_w$ ³⁾	$\overline{M}_w/\overline{M}_n$ ³⁾	F_{SA} ⁴⁾	F_{EO} ⁴⁾
2	$\text{AlEt}_3\text{—H}_2\text{O}$ (1:0.5)	48	70	8,090	11,700	1.45	0.39	0.61
19	$\text{AlEt}_3\text{—H}_2\text{O}$ (1:1.0)	48	29	2,360	3,540	1.50	0.37	0.63
20	$\text{AlEt}_3\text{—H}_2\text{O}$ (1:1.5)	48	12	—	—	—	—	—
5	$\text{Al}(\text{iBu})_3\text{—H}_2\text{O}$ (1:0.5)	48	85	7,130	9,160	1.28	0.43	0.57
21	$\text{Al}(\text{iBu})_3\text{—H}_2\text{O}$ (1:1.0)	48	69	3,930	4,960	1.26	0.45	0.55
22	$\text{Al}(\text{iBu})_3\text{—H}_2\text{O}$ (1:1.5)	48	28	—	—	—	0.45	0.55
23	$\text{AlEt}_3\text{—H}_2\text{O}$ (1:0.5)	110	78	7,390	10,300	1.40	0.40	0.60
24	$\text{AlEt}_3\text{—H}_2\text{O}$ (1:1.0)	110	46	—	—	—	0.43	0.57

¹⁾ Copolymerization conditions: $[\text{SA}]/[\text{EO}]=1 \pm 0.1$; 1.0 g SA; $[\text{M}]_{\text{total}}/\text{Al}=200$; $62 \pm 2^\circ\text{C}$; in 7 ml 1,4-dioxane, others are the same as Table 1

Table 3 Synthesis and structure of SA-EO copolymers with different compositions

Run	$f_{\text{EO}}/f_{\text{SA}}$ ²⁾	Yield (%)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	F_{SA}	F_{EO}	L_{ester} ³⁾	L_{ether} ³⁾
25	0.59	53	4,580	7,310	1.60	0.45	0.55	7.18	1.49
26	1.11	83	8,950	14,200	1.59	0.44	0.56	6.68	2.06
27	2.27	79	9,790	18,000	1.84	0.40	0.60	5.53	2.70
28	3.25	65	18,600	30,100	1.62	0.38	0.62	4.74	3.29
29	4.38	53	19,400	32,200	1.66	0.36	0.64	4.30	3.25

¹⁾ Copolymerization conditions: $\text{AlEt}_3\text{—H}_2\text{O}$ (1:0.5); SA, 2g; $[\text{SA}]/[\text{Al}]=200$; 62°C ; in 12 ml 1, 4-dioxane, 48 h. ²⁾ Monomer feed ratio in mole. ³⁾ Average length of ester repeat units (L_{ester}) and ether repeat units (L_{ether}) estimated by $^1\text{H-NMR}$

Different SA/EO initial monomer feed ratios were applied for synthesizing copolymers with different compositions, as shown in Table 3. With the increasing of EO/SA

molar ratio, the copolymer molecular weight and EO content (F_{EO}) were increased. The copolymer yield had a maximum value at EO/SA about 1. The molecular weight increased with higher EO/SA molar ratio.

3. Structure of SA-EO copolymer

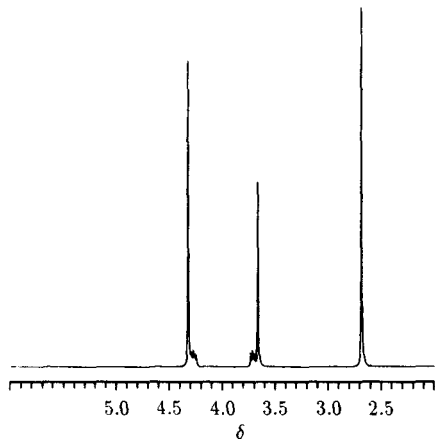


Fig. 1. ^1H -NMR spectrum of SA-EO copolymer with $F_{SA}/F_{EO}=38/62$ (run 28, Table 3)

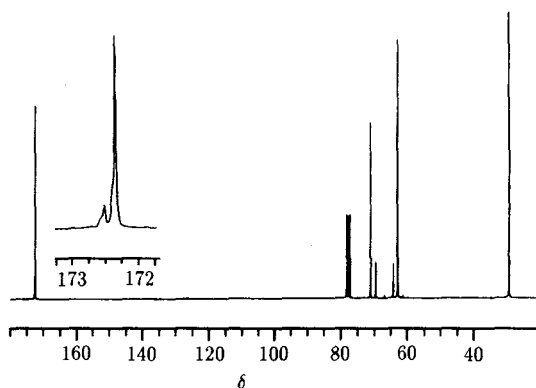
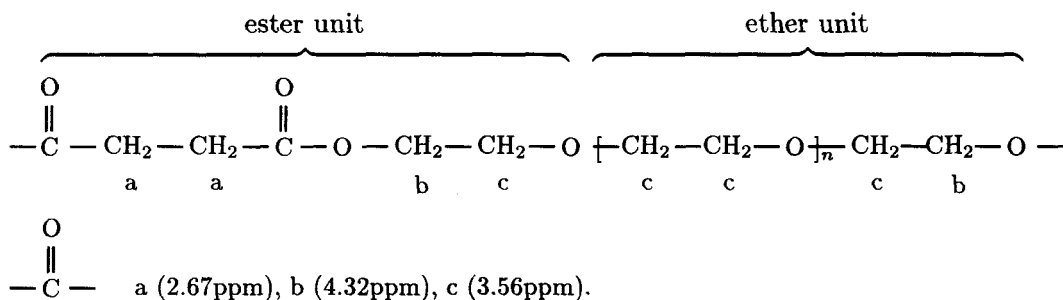


Fig. 2. ^{13}C -NMR spectrum of SA-EO copolymer with $F_{SA}/F_{EO} = 38/62$ (run 28, Table 3)

The structure of the copolymer obtained was analyzed by ^1H -NMR and ^{13}C -NMR. Fig. 1 shows the ^1H -NMR spectrum of SA-EO copolymer with F_{SA}/F_{EO} 38/62 (run 28 in Table 3). The chemical shifts can be assigned by the following way:



Besides the main signals, two weak peaks (triplet) in ^1H -NMR were also observed at 4.27 ppm and 3.72 ppm, respectively. The chemical shift at 4.27 ppm is due to the methylene from EO in ester-ether (i.e. $\text{SA}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$) unit, and 3.72 ppm the methylene from ethylene oxide in $\text{SA}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$ which were assigned by $^1\text{H}-^1\text{H}$ correlation COSY 45 NMR. Therefore, the average lengths of repeat ester (L_{ester}) and ether (L_{ether}) units can be calculated by $I_{4.32\text{ ppm}}/I_{4.27\text{ ppm}}$ and $I_{3.56\text{ ppm}}/I_{3.72\text{ ppm}} + 1$ respectively. The ester unit content of the copolymer

(EU%) can be calculated by the following equation (Eq. 1):

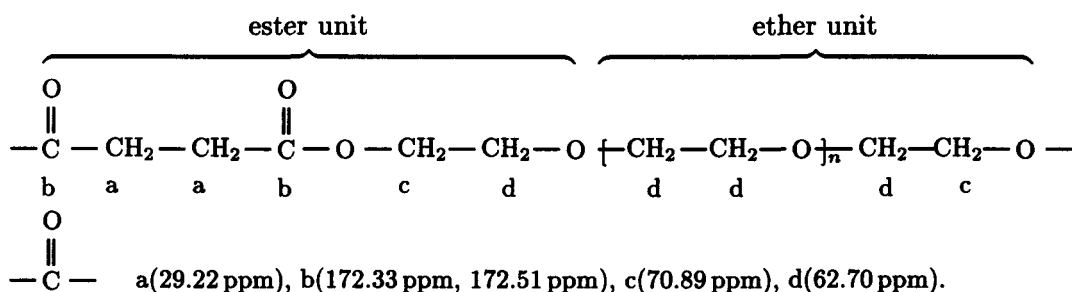
$$EU\% = 100 \times I_{2.67 \text{ ppm}} / (I_{2.67 \text{ ppm}} + I_{3.56 \text{ and } 3.72}) \quad (1)$$

Here I represents the intensity of the peak absorption. Therefore, the copolymer composition can be calculated by equation 2 and 3:

$$F_{\text{SA}} = EU / (1 + EU) \quad (2)$$

$$F_{\text{EO}} = 1 - F_{\text{SA}} \quad (3)$$

The results are summarized in Table 3. Higher F_{SA} copolymer (run 25) has higher average length of ester repeat units. Fig. 2 represents the ^{13}C -NMR spectrum of the same copolymer sample. By expanding the spectrum, it can be found that the chemical shift of carbonyl split into two peaks, which indicated two kinds of $\text{C}=\text{O}$ in the copolymer, one is that in ester-ester repeat units, the other is that in ester-ether linkages. The chemical shift can be assigned as described below.



The chemical shift at 69.32 ppm was assigned as $\text{SA}-\underline{\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}}-$ and 64.18 ppm as $\text{SA}-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}-$.

4. Thermal properties

Fig. 3a shows the first heating scan DSC of the copolymers with different compositions prepared by solution polymerization catalyzed by in-situ $\text{AlEt}_3\text{-H}_2\text{O}$ (1:0.5). All of the curves showed only one melting transition, which indicated there was no EO homopolymer or long PEO block in the product. This is in agreement with the results of average ether repeat unit length. The T'_m s were around 100°C and related to the composition and molecular weight of the copolymer. Higher alternating copolymer has higher T_m and higher ΔH_f . Slightly lower T_m of sample 25 (100°C) than that of sample 26 (102°C) might be caused by the lower molecular weight of sample 25. Maeda et al. reported the DSC results of SA-EO copolymers prepared by bulk copolymerization. The T_m and ΔH_f were significantly depended on the

copolymer composition and the catalyst used for the copolymerization. Two melting transitions were occasionally observed^[18]. Compared with the data in reference [18], the melting point of the SA-EO copolymer synthesized by us with solution polymerization was much higher than those from bulk copolymerization for the copolymers with the same composition (see Table 4), especially for the high F_{EO} copolymers. The second heating scan DSC (Fig. 3b) showed that the glass transition (T_g) was influenced by the copolymer composition. High alternating copolymer (sample 25) had a little higher T_g (-12°C). The T_g 's of SA-EO copolymers from solution polymerization are also higher than those from bulk polymerization reported by Maeda et al.. In addition, higher alternating copolymer was more easily recrystallized, as seen in Fig. 3b. After F_{SA}/F_{EO} reached 36/64, the recrystallization peak disappeared. The recrystallization temperatures are about 60°C . The T_m and ΔH_f of the second heating scan were lower than those of first heating scan. The thermal property of SA-EO copolymers are summarized in Table 4.

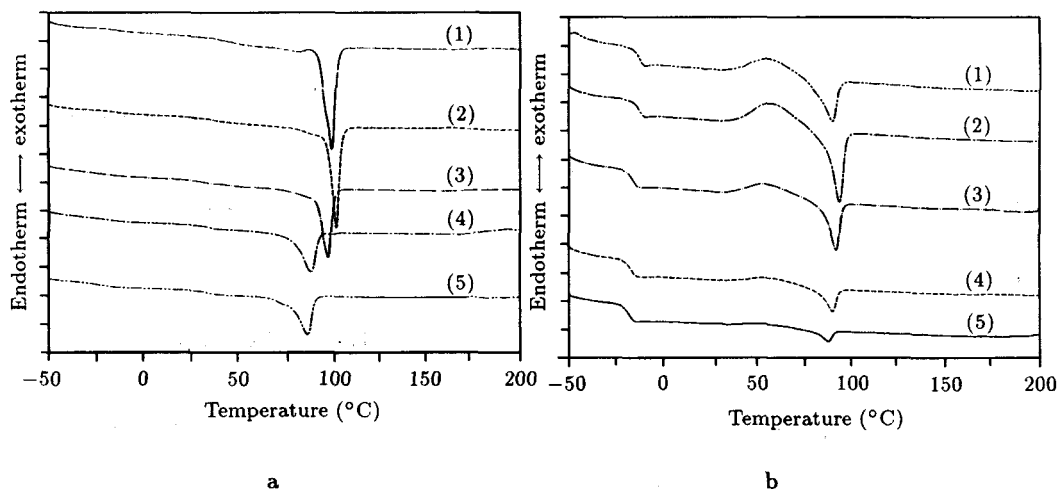


Fig. 3 DSC thermograms of SA-EO copolymer with F_{SA}/F_{EO} (1) 45/55 (run 25 in Table 3), (2) 44/56 (run 26), (3) 40/60 (run 27), (4) 38/62 (run 28), (5) 36/64 (run 29)
a, first scan; b, second scan

TGA results (Fig. 4) show that the SA-EO copolymers have high thermal stability. The onset decomposition temperatures (T_d) which were defined as the intersection of the two tangents generated by program TGA-5.0 are more than 300°C . Furthermore, high SA content copolymer (sample 25) is more stable than that with low SA content (sample 29). The big gap between T_m and T_d is valuable for processing.

In conclusion, a series of aluminum organometallic compounds have been eva-

luated for the novel ring-opening copolymerization (solution) of succinic anhydride with ethylene oxide. The structure of the copolymer had been analyzed by ^1H -NMR and ^{13}C -NMR in detail. The copolymers obtained have interesting T_m (around 100°C) and high thermal stability.

Table 4 Comparison of T_m and ΔH_f of different SA-EO copolymers

Polymn.	Catalyst	$F_{\text{EO}}/F_{\text{SA}}$	$\overline{M}_n$	$T_m(^{\circ}\text{C})$	$\Delta H_f (\text{J/g})$	$T_g(^{\circ}\text{C})$
Bulk ¹⁾	$\text{Al}(\text{O}^i\text{Pr})_3$	52/48	20,000	91	57	-22
	$\text{Al}_2\text{-Zn-}\mu\text{-oxoalkoxide}$	54/56	19,000	40,80 ²	58	-35
	$\text{Al}(\text{O}^i\text{Pr})_3$	56/44	17,000	88	49	N/D
	ZnEt_2	61/39	29,000	53,74 ²	25	-26
	$\text{Al}_2\text{-Zn-}\mu\text{-oxoalkoxide}$	66/34	27,000	46	19	-28
	ZnEt_2	68/32	28,000	39	16	-27
Solution	in-situ $\text{AlEt}_3\text{-H}_2\text{O}$ (1:0.5)	55/45	4,580	100	66	-12
		56/44	8,950	102	58	-12
		60/40	9,790	98	47	-16
		62/38	18,600	89	37	-17
		64/36	19,400	87	38	-18

¹⁾ data from reference [18]. ²⁾ two peaks observed

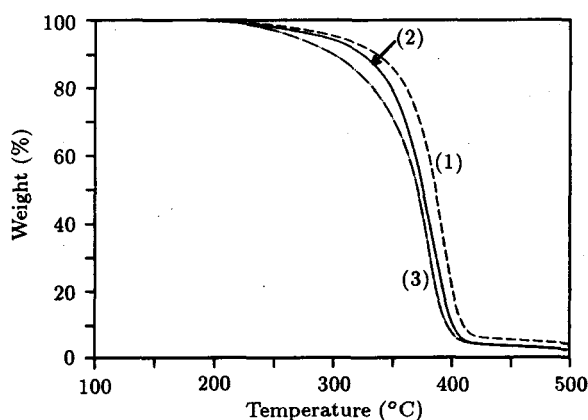


Fig. 4 TGA analysis of SA-EO copolymer with (1) 45/55 (run 25 in Table 3), (2) 40/60 (run 27), (3) 36/64 (run 29)

Keywords:

Succinic anhydride; Ethylene oxide; Ring opening copolymerization; Aluminum organometallic catalyst; Biodegradable polymer

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