Synthesis and Properties of Poly(butylene Succinate) with *N*-Hexenyl Side Branches

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ABSTRACT: *N*-hexenyl side branches were introduced into poly(butylene succinate) (PBS) by polymerization of succinic acid (SA) with 1,4-butanediol (BD) in the presence of 7-octene-1,2-diol (OD). Thermal properties and biodegradability of the aliphatic polyesters were investigated before and after epoxidation of the pendant double bonds. The glass-transition temperature (T_g) decreased with the branching density to give a minimum at 0.03 mol of branching units per mole of structural units. Thereafter, T_g increased due to the *in situ* crosslinking of the unsaturated groups during the differential scanning calorimetry (DSC) measurements. *N*-Hexenyl side branches decreased melting temperature (T_m) more significantly than ethyl side branches, but the effect was on par with that by *n*-octyl branches. Epoxidation of the double bonds decreased T_m and melting enthalpy (ΔH_m), but increased T_g of the aliphatic polyester. Biodegradability was enhanced to some extent by the presence of *n*-hexenyl side branches. However, the epoxidation of the unsaturated groups did not notably affect the biodegradability. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2219–2226, 2001

Key words: poly(butylene succinate); epoxidation; crosslinking; biodegradability

INTRODUCTION

A huge amount of synthetic polymers are produced each year in the world for various applications. However, when they are disposed of, they provoke serious environmental problems because of their nonbiodegradable properties. Therefore, research on biodegradable polymers has gained considerable interest in recent years.

Aliphatic polyesters are one of the most economically competitive biodegradable plastics. However, their poor mechanical properties provide obstacles to their commercialization.[1] A number of techniques, such as physical blending or copolymerization, have been tried to improve their properties.[2–5] Chemical modification is a powerful tool for obtaining polymers with new properties and therefore for enlarging the scope of their applications. Unsaturated groups have been introduced to the aliphatic polyesters and functionalized or crosslinked to find applications as biodegradable elastomers, hydrogels, and adhesives.[6–9]

In this study, unsaturated side chains were inserted in poly(butylene succinate) (PBS) by po-
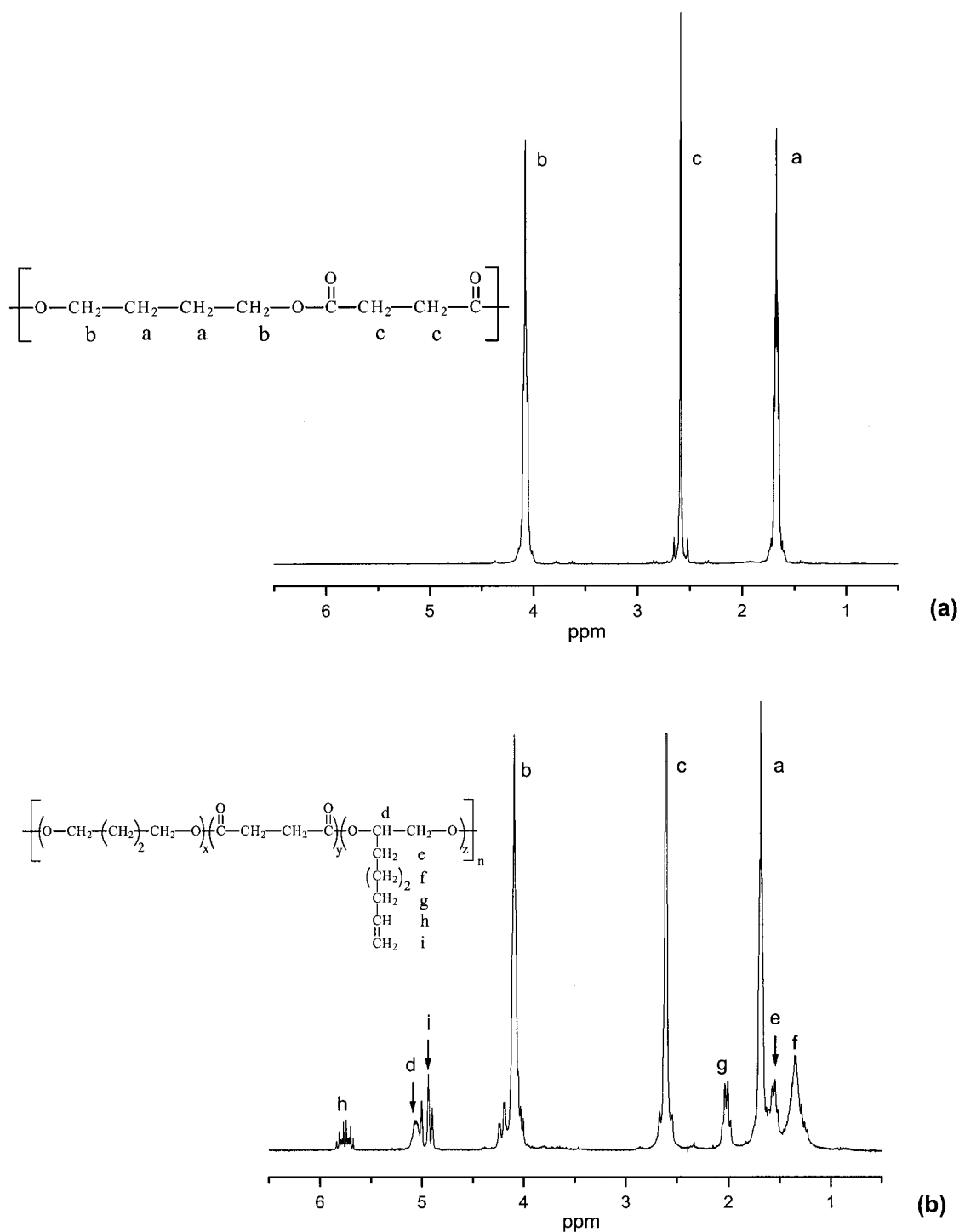
Figure 1   NMR spectra of (a) PBS and (b) PBSO12.

lymerizing succinic acid (SA) with 1,4-butanediol (BD) and 7-octene-1,2-diol (OD). The double bonds were epoxidized and the attendant variation of properties and biodegradability was explored. The epoxide groups are highly reactive under mild conditions with a variety of reagents and produce derivatives with interesting properties.[10–15]

Table I   Composition of the Unsaturated Aliphatic Polyesters

Polyester	Feed Composition (mol %)			Copolymer Composition (mol %)[a]		
	SA	BD	OD	SA	BD	OD
PBSO01	50	49	1	50	49.1	0.9
PBSO04	50	45	5	50	45.8	4.2
PBSO07	50	40	10	50	42.8	7.2
PBSO09	50	35	15	50	41.0	9.0
PBSO12	50	30	20	50	38.1	11.9

[a] Measured from ^{1}H NMR spectrum.

EXPERIMENTAL

Materials

Succinic acid (SA), 1,4-butanediol (BD), 7-octene-1,2-diol (OD), and titanium(IV)butoxide were reagent grade from Aldrich and used as received. *m*-Chloroperbenzoic acid (MCPBA) was purified by washing the powder in a pH 7.4 phosphate buffer solution, and by drying after filtration under vacuum for 2 days at 20°C. Chloroform for the epoxidation reaction was washed with water to remove the ethanol preservative, dried in magnesium sulfate, and stored in the dark.

Polymerization Procedures[16–19]

Poly(SA/BD/OD) (PBSO) was bulk-polymerized in the presence of SA, BD, and OD using 0.05 wt% titanium(IV)butoxide as a catalyst by a two-step process. In the first step, esterification was carried out at 160 °C for 4 h under atmospheric pressure, and then the reaction temperature was increased gradually to 180 °C with simultaneous reduction of pressure to 0.05 Torr. In the second step, polycondensation was followed for additional 5 h at 180 °C under 0.05 Torr. Polymerizations were realized in a glass reactor equipped with a stirrer rotating at 300 rpm. Polymers obtained were repeatedly dissolved in chloroform and precipitated from methanol to remove unreacted monomers or byproduct oligomers, and then dried at 25 °C in a vacuum oven to attain a constant weight.

Epoxidation of PBSO[10–15]

For the epoxidation of copolymers, 5 g of PBSO was dissolved in 100 mL of purified chloroform at 17 °C, and then 1.5 equiv. parts of purified MCPBA was added. The reaction was continued with constant gentle stirring at 17 °C for 48–168 h. After completion of the reaction, the solution was slowly poured into 100 mL of cool methanol. The precipitate formed was washed with methanol twice and then dried in vacuum at ambient temperature. Epoxidation yields(%) were determined by proton nuclear magnetic resonance spectroscopy (^{1}H NMR) using the ratio of the resonance peak area of the hydrogen atoms in the epoxy groups at 2.9 ppm to those in the unsaturated groups at 4.9 ppm.

Characterizations

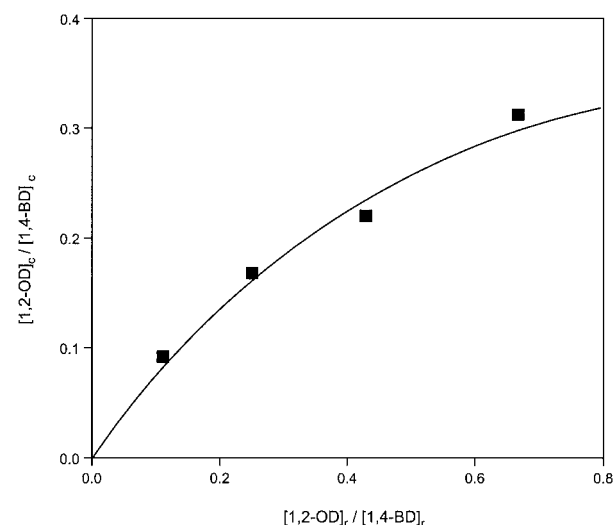Copolymer compositions were determined from ^{1}H NMR spectra (250 MHz Bruker AC 250 Spec-

Figure 2   Plot of $[OD]_c/[BD]_c$ in the copolymers as a function of $[OD]_r/[BD]_r$ in the reaction medium.
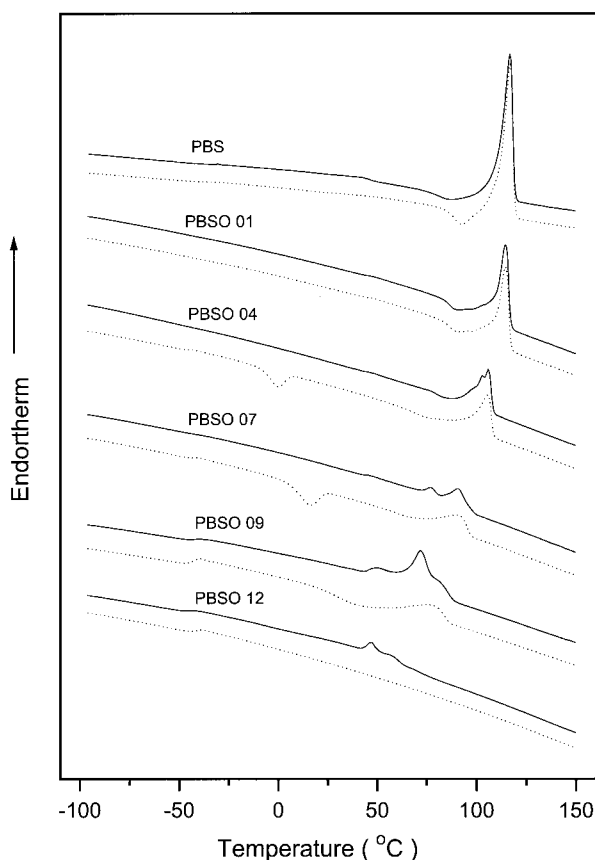
Figure 3   First (solid line) and second (dotted line) DSC thermograms of the unsaturated aliphatic polyesters.

trometer). Sample concentration was 3 wt% in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference.

Molecular weight was measured by gel permeation chromatography (GPC; Waters model 201), with chloroform as eluent (1 mL/min). Calibration was accomplished with a polystyrene standard (Shodex®).

The thermal properties were determined by differential scanning calorimetry (DSC; Perkin Elmer DSC7). Specimens were heated to 150 °C at 20 °C/min (1st scan) and kept at 150 °C for 30 s. Then, the specimens were quenched to −100 °C using liquid nitrogen. The 2nd scan thermograms were obtained by reheating them at 20 °C/min from −100 to 150 °C.

Fourier transform infrared (FT-IR) measurements were performed on a JASCO FT/IR-430 Fourier Transform Infrared Spectrometer. Five milligrams of the copolymer were dissolved in 10 mL of chloroform and then the solution was cast onto an AgCl window. The spectra were obtained at the resolution of 4 cm^{-1} and were the average of 32 scans.

The modified Sturm test (ASTM D 5209-91) was carried out using activated sludge harvested from Nanjido waste water plant in Seoul as described in the previous report.[20]

RESULTS AND DISCUSSION

PBS with unsaturated pendant groups was synthesized by bulk polymerization of SA with BD and OD. The ^1H NMR spectrum for PBS is shown in Figure 1a. Methylene protons in BD units exhibit their peaks at 1.65 and 4.1 ppm. Peaks at 2.6 ppm correspond to the methylene protons in SA

Table II   Thermal Properties of the Unsaturated Aliphatic Polyesters Measured by DSC

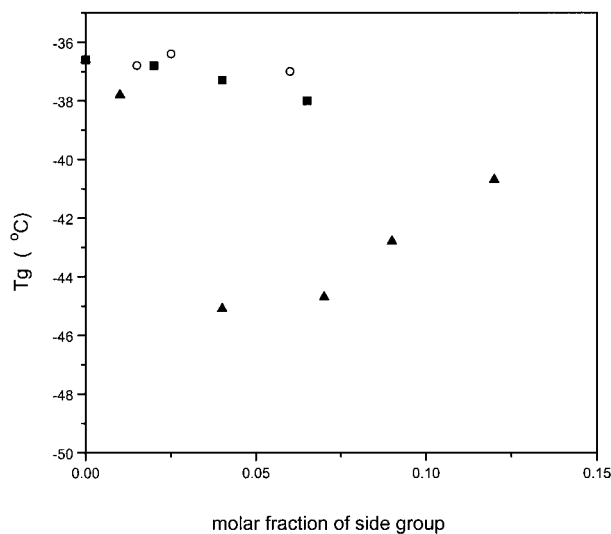| Polyester	T_g (°C) 2nd	T_m (°C) 1st	T_m (°C) 2nd	ΔH_m (J/g) 1st	ΔH_m (J/g) 2nd
PBS	−36.6	115.9	115.8	81.7	80.0
PBSO01	−37.8	114.5	114.1	86.9	85.7
PBSO04	−45.1	105.8	105.6	74.0	71.2
PBSO07	−44.7	90.9	91.2	52.8	52.6
PBSO09	−42.8	71.9	77.8	31.4	21.2
PBSO12	−40.7	47.3	—	29.1	—
PBSOE04	−29.0	111.7	109.5	66.2	68.0
PBSOE07	−35.9	82.0	89.7	70.0	43.2
PBSOE09	−36.4	74.2	80.2	54.4	33.2
PBSOE12	−29.9	47.6	—	20.6	—

Figure 4 The second scan glass transition temperature of polyesters with different side groups. Key: (■) ethyl branch;[7] (○) *n*-octyl branch;[7] (▲ *n*-hexenyl branch.

units. ^{1}H NMR spectra for a copolymer composed of BD, SA, and OD (PBSO) are shown in Figure 1b. Peaks at 4.9 and 5.75 ppm originate, respectively, from CH_2= (i peak) and —CH= (h peak) in the OD units. OD content in the copolymers was determined from the integrated intensity of the h peak (—CH= in OD units) relative to that
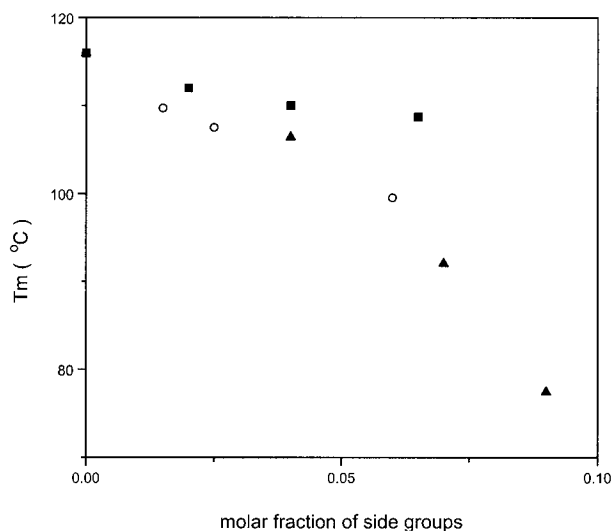

Figure 5 The second scan melting temperature of polyesters with different side groups. Key: (■) ethyl branch;[7] (○) octyl branch;[7] (▲) unsaturated hexenyl branch.
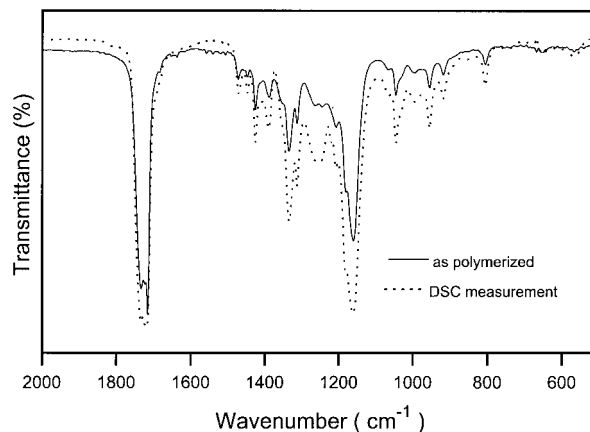

Figure 6 IR spectra of polymerized PBSO07 and that of PBSO07 after the 2nd scan on DSC.

of the c peak (methylene peak in SA units). The relationship between the content of the reaction medium and the copolymer composition is shown in Table I and Figure 2. The actual OD/BD ratio in the reaction medium must be greater than the initial OD/BD ratio because OD was evacuated less than BD from the reactor during the polymerization because of the lower volatility of OD compared with BD. Hence, it can be said that OD is less reactive than BD toward SA, because the OD/BD ratio in the produced copolymer is lower than the initial OD/BD ratio in the reaction medium. The steric hindrance of the *n*-hexenyl side chain, which could decrease the reactivity of the secondary hydroxyl group in OD, should exceed the electron-donating effect of the *n*-hexenyl side chain, which would increase nucleophilicity of the secondary hydroxyl groups.

The 1st and the 2nd scan DSC thermograms are shown in Figure 3. The thermal properties determined from the DSC thermograms are listed in Table II. As the content of OD units increased,

Table III   C=C (1640 cm^{-1})/C=O (1720 cm^{-1}) Ratio of PBSO

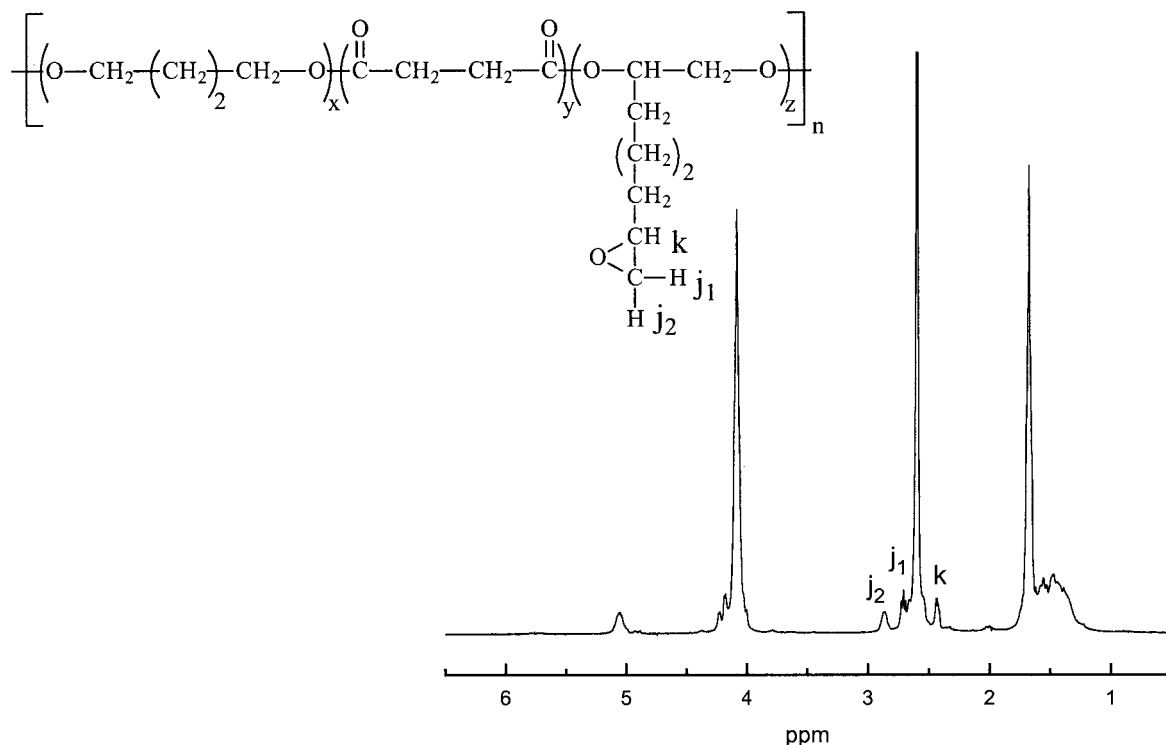| Polyester	As Polymerized	After DSC Measurement	Ratio of the Peak Intensity
PBSO04	0.0019	0.0015	78.9
PBSO07	0.0050	0.0040	80.0
PBSO09	0.0099	0.0057	57.8
PBSO12	0.0223	0.0096	43.1

Figure 7 NMR spectra of a epoxidized aliphatic polyester of PBSOE09.

melting temperature and heat of fusion decreased. PBS usually exhibits its crystallization peak around $-5.8\,°C$ on the 2nd scan DSC thermogram. However, the crystallization peak is not seen in Figure 3 because low molecular weight PBS crystallizes during the quenching process, even with liquid nitrogen.

As the content of OD units went beyond 4.2 mol%, the crystallization peak appeared and shifted to higher temperature, indicating that the crystallization slowed down. The glass-transition temperature (T_g) could not be determined from the 1st scan accurately, and we put more confidence in T_g data from the 2nd scan than in those from the 1st scan.

The T_g of PBS with n-hexenyl side branches (PBSO) in Figure 4 was much lower than those of PBS with ethyl (PBSB) or n-octyl (PBSD) side branches[16] at a similar level of branching density partly because the former polyesters (PBSO) had lower molecular weight ($1.34–3.64 \times 10^4$) than the latter polyesters ($5.0–15.3 \times 10^4$).[16] N-Hexenyl chain branches in PBSO lowered T_m similarly to n-octyl chain branches in PBSD (poly(SA/1,2-BD/1,2-decanediol) as shown in Figure 5). In contrast, the T_m of PBSO was lower than that of PBS with ethyl side branches at a similar level of branching density.

It is curious to note that T_g of PBSO decreased and then increased after a minimum as the con-

Table IV Composition of the Epoxidized Aliphatic Polyesters

	Before Epoxidation			After Epoxidation			
Polyester	SA	BD	OD	SA	BD	OD	Epoxy
PBSOE04	50	45.8	4.2	50	45.8	0	4.2
PBSOE07	50	42.8	7.2	50	42.8	0	7.2
PBSOE09	50	41.0	9.0	50	41.0	0	9.0
PBSOE12	50	38.1	11.9	50	38.1	0	11.9

tent of OD increased. These results are not unexpected in that crosslinking occurred during the DSC measurements. The IR spectra of polymerized PBSO are compared with those of PBSO after the DSC measurements in Figure 6.The ratio of peak intensity due to C=C stretching at 1640 cm^{-1} to peak intensity due to C=O stretching at 1720 cm^{-1} was determined from the IR spectra and the results are summarized in Table III. It can be seen that the C=C (1640 cm^{-1})/C=O (1720 cm^{-1}) ratio decreased after the DSC measurements. Furthermore, the higher the content of OD units in PBSO, the larger the decrease of the ratio, clearly indicating that crosslinking took place.

Epoxidation was carried out on PBSO using MCPBA. The ^{1}H NMR spectra for the unsaturated polyester after epoxidation (PBSOE) are shown in Figure 7. The CH$_2$= peak (i peak) and —CH= peak (h peak) disappeared. Instead, the —CH— peak (k peak) and —CH$_2$— peaks (j$_1$ and j$_2$ peaks) corresponding to the epoxy ring appeared, respectively, at 2.44, 2.70, and 2.85 ppm. Moreover, the ally proton peak (g in Figure 1) vanished, confirming that epoxidation was almost completely achieved. The content of the epoxy groups was determined by comparing the —CH— proton peak (k peak) to the methylene peak (c peak) of SA, and the results are shown in Table IV.

According to the results in Table V, molecular weight decreased during the epoxidation. T_m and ΔH_m decreased, but T_g increased as a result of the epoxidation (Table II), indicating that the epoxidation increased the steric hindrance of the side chain.

Table V Molecular Weight of the Aliphatic Polyesters

Sample ID	M_n ($\times 10^4$)	M_w ($\times 10^4$)	Polydisperity
PBS	1.98	4.59	2.32
PBSO01	1.43	2.81	1.97
PBSO04	1.64	2.06	1.26
PBSO07	1.36	3.64	2.68
PBSO09	0.99	1.34	1.35
PBSO12[a]	0.88	1.92	2.18
PBSOE04	0.84	1.11	1.32
PBSOE07	0.91	2.45	2.67
PBSOE09	0.84	1.57	1.89
PBSOE12[a]	1.03	1.76	1.72

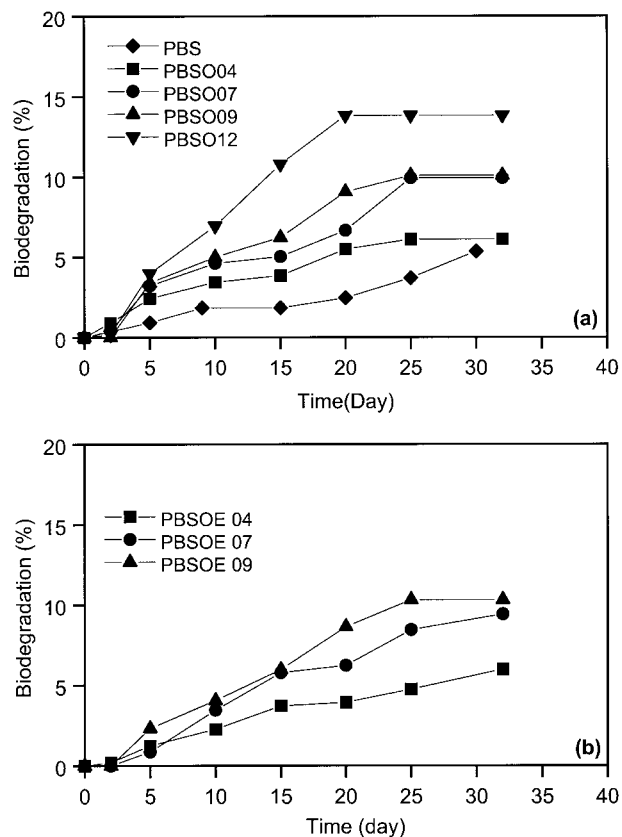[a] Gelation took place and molecular weight data are for the sol fraction.

Figure 8 Biodegradability of (a) PBSO and (b) PBSOE.

Biodegradability of PBSO and PBSOE measured by the modified Sturm test is shown in Figure 8. PBSO became more biodegradable as the content of OD increased because of the decrease in crystallinity. However, the epoxidation did not bring about any significant change in the biodegradability.

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