

# Crosslinking and Biodegradation of Poly(butylene succinate) Prepolymers Containing Itaconic or Maleic Acid Units in the Main Chain

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**ABSTRACT:** Poly(butylene succinate)-based prepolymers containing itaconic acid units or maleic acid units in the main chain were synthesized through the condensation reaction of 1,4-butanediol, succinic acid, and itaconic acid or maleic acid. The resulting prepolymers, with weight-average molecular weights in the several thousands, were cured at 115°C with benzoyl peroxide to produce crosslinked polyesters that were insoluble in chloroform. Differential scanning calorimetry analysis revealed that the glass-transition temperature rose with crosslinking and that the melting

temperature and heat of melting decreased with crosslinking. These results implied that crosslinking was successfully carried out and that the crystallinity of the polymer decreased. The crosslinked polymer showed lower biodegradability in the biochemical oxygen demand assay with activated sludge but retained some biodegradability. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 1473–1480, 2005

**Key words:** biodegradable; polyesters; thermal properties

## INTRODUCTION

Unsaturated polyester (UP) is a thermosetting resin used widely in many fields. UP has a relatively high modulus and high strength, and it is often used as a matrix of fiber-reinforced plastics. A typical UP prepolymer is synthesized by the reaction of an aromatic diacid, an unsaturated diacid, and an aliphatic diol, and the crosslinking of the prepolymer is accomplished by copolymerization with alkene monomers such as styrene with radical initiators. The crosslinked polymers are not degraded in soil. On the other hand, many kinds of aliphatic polyester are known as biodegradable polymers, including poly(lactic acid), poly(butylene succinate) (PBS), poly(hydroxybutyrate), and poly( $\epsilon$ -caprolactone).<sup>1,2</sup> In this article, we propose one way of synthesizing biodegradable crosslinked polyester resins.

Some research groups have reported biodegradable crosslinked polyesters, and the biodegradation rate was generally reduced by crosslinking. Tokiwa and Suzuki<sup>1</sup> reported that UPs such as poly(hexamethyl-

ene fumarate) and poly(*cis*-2-butene fumarate) were hardly degraded by lipase because of a few crosslinking points between the polymer chains. Valiente et al.<sup>3,4</sup> showed that an unsaturated prepolymer, poly(1,2-propanediyl fumarate), was degraded by lipase and that the degradation rate of the cured polymer was reduced with an increased degree of crosslinking. Biodegradable crosslinked poly(ester ether) and polyester were also reported by Takasu et al.<sup>5</sup> and Lukaszczuk and Jaszcz.<sup>6</sup> Jin et al.<sup>7</sup> reported the chain extension of PBS containing 2.3 or 5.7 mol % maleic acid (MA) units in the main chain. Its biodegradability was remarkably reduced after chain extension with benzoyl peroxide (BPO).

In this study, UP prepolymers with PBS segments were synthesized by the reaction of 1,4-butanediol (BD), succinic acid (SA), and itaconic acid (IA) or MA and were cured with BPO. IA is industrially produced by fermentation processes with *Aspergillus terreus* or *Aspergillus itaconicus* fungi, and it is a renewable resource. The itaconate-containing prepolymer had C=C bonds as the side chain, whereas the maleate-containing prepolymer had C=C bonds in the main chain. Their reactivity for crosslinking and their thermal properties were studied. Furthermore, the thermal properties and biodegradability of the crosslinked polyesters were compared with those of the corresponding prepolymers.

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TABLE I  
Monomer Compositions of the Prepolymers

	Feed ratio (mol %)			Composition of product (mol %)			
	BD	SA	IA or MA	BD unit	SA unit	IA or MA unit	FA unit
PBSI 5	50	45	5	49.4	47.9	2.7	—
PBSI 10	50	40	10	50.1	44.1	5.8	—
PBSI 15	50	35	15	49.6	39.0	11.4	—
PBSM 5	50	45	5	50.2	46.5	2.2	1.1
PBSM 10	50	40	10	50.4	42.5	4.7	2.4
PBSM 15	50	35	15	50.9	37.8	7.8	3.5

FA = fumaric acid.

## EXPERIMENTAL

### Materials

BD, IA, MA, and titanium(IV) tetra-*n*-butoxide were purchased from Kanto Chemical (Tokyo, Japan). SA and BPO was purchased from Kishida Chemical (Osaka, Japan). These reagents were used as received.

### Synthesis of PBS-based prepolymers containing IA units (PBSI) or MA units (PBSM)

PBSI and PBSM were synthesized by the bulk polymerization of BD, SA, and IA (or MA) in a 200-mL, round-bottom flask equipped with a branched glass tube that was h-shaped. At the top end of the branched tube was a condenser, under which another round flask was equipped to trap generated water. The feed ratios of the monomers are summarized in Table I. To the mixture was added 0.05 wt % titanium(IV) tetra-*n*-butoxide as a catalyst, and condensation polymerization was carried out at 160°C under mildly reduced pressure (40 Torr) for 4 h, followed by the reaction at 180°C under 40 Torr for 5 h. After cooling to room temperature, the product was dissolved in chloroform and precipitated with excess methanol. The precipitate was washed with methanol and dried at room temperature under a reduced pressure over 2 days to yield PBSI (or PBSM) as a white or slightly yellow powder in an 80–90% yield.

### Crosslinking of PBSI and PBSM

The prepolymer (PBSI or PBSM) was dissolved in chloroform, and then 5 wt % BPO was added. After stirring for 1 h at room temperature, the solution was poured into a Teflon tray and allowed to stand for 1 day at room temperature so that the solvent could evaporate. The BPO-containing sample was further dried at room temperature under reduced pressure for 1 day. The dried solids of PBSI and PBSM were cured at 115°C under a pressure of 2 MPa for 20 and 40 min, respectively, with a hot-press machine (SA-303 type S tabletop test press, Tester Sangyo Co., Ltd., Tokyo, Japan).

### Characterization and measurement of the thermal properties

<sup>1</sup>H-NMR spectra were recorded on a Bruker AMX-400 (Karlsruhe, Germany) (400 MHz) or DRX-500 (500 MHz) with CDCl<sub>3</sub> as a solvent. Before the measurement, the solution was filtered through a 0.2- $\mu$ m filter. The monomer compositions of the obtained polymers were calculated from peak areas of NMR spectra. Infrared (IR) spectra were recorded on a Shimadzu FT-IR 8100 (Kyoto, Japan) by the KBr-pellet method.

The molecular weight was determined by gel permeation chromatography (GPC) at 40°C on a Shimadzu LC-10A series apparatus equipped with two PL gel GPC columns (Polymer Laboratories, Ltd., Shropshire, UK; molecular weight linear range = 200–400,000) and a refractive-index detector. Tetrahydrofuran was used as an eluent at a flow rate of 0.5 mL/min. Polystyrene standards with a narrow molecular weight distribution [weight-average molecular weight ( $M_w$ ) = 580–377,400] were used for molecular weight calibration.

The gel fraction of crosslinked polymers was determined from the remaining fraction after Soxhlet extraction with chloroform for 48 h.

Thermogravimetric analysis (TGA) was conducted with a PerkinElmer TGA 7 (Wellesley, MA) thermogravimetric analyzer at a heating rate of 20°C/min under a nitrogen atmosphere. The thermal degradation temperature ( $T_d$ ) was defined as the onset temperature of the weight decay curve. Differential scanning calorimetry (DSC) was performed on a PerkinElmer Pyris 1 differential scanning calorimeter under a nitrogen atmosphere. The sample for DSC was weighed (~10 mg) on a small aluminum pan, and this was followed by the sealing of the pan. The heat capacity was scanned from –80 to 150°C at a heating rate of 20°C/min, and then the sample was cooled to –80°C at a rate of 20°C/min. Subsequently, a second heating from –80 to 180°C was carried out. The glass-transition temperature ( $T_g$ ) was taken at the midpoint of the heat capacity change during the second heating process, and the melting temperature ( $T_m$ ) was taken

at the endothermic peak in the DSC curve during the second heating process.

### Biodegradability

Biodegradability was determined by the measurement of the biochemical oxygen demand (BOD) under an aerobic condition. To a phosphate buffer (pH 7.4, 200 mL) containing 0.25 mM CaCl<sub>2</sub>, 0.09 mM MgSO<sub>4</sub>, 0.09 mM NH<sub>4</sub>Cl, and 0.9 μM FeCl<sub>3</sub>, was added 4.35 mL of activated sludge containing 30 mg of the suspended part, which was obtained from sewage facilities of the Chiba Institute of Technology, and 20 mg of the polymer powder. The suspension was steadily stirred with a magnetic stirring bar. BOD was measured at 25°C with a Taitec 200F (Koshigaya, Japan) BOD tester. CO<sub>2</sub> was absorbed into a 50% sodium hydroxide aqueous concentrate in a cup equipped within the glass bottle. The volume of consumed oxygen was directly measured with a scaled cylinder.

## RESULTS AND DISCUSSION

### Characterization of PBSI and PBSM

The prepolymers PBSI and PBSM, containing different amounts of IA and MA, respectively, were synthesized by the bulk polymerization of the corresponding monomers. Figure 1 shows <sup>1</sup>H-NMR spectra of the prepolymers. Three major peaks appeared: the two peaks at 4.1 and 1.6 ppm are related to methylene protons (—OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O— and —OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O—) of butanediol units, and the rest at 2.6 ppm are related to methylene protons of succinate units. In the spectra of the PBSI series, a weak peak at 4.2 ppm should be related to the methyleneoxy protons [—CH<sub>2</sub>OC(=O)C(=CH<sub>2</sub>)CH<sub>2</sub>C(=O)OCH<sub>2</sub>—] close to one unsaturated carbon atom of an itaconate unit in the main chain. For the PBSM series, a slightly stronger peak was observed at 4.2 ppm, which was reasonably assigned to the methyleneoxy protons [—CH<sub>2</sub>OC(=O)CH=CHC(=O)OCH<sub>2</sub>—] close to two unsaturated carbon atoms of a maleate unit in the main chain. The proton signals of itaconate units were observed at 6.3, 5.7, and 3.3 ppm in <sup>1</sup>H-NMR spectra of PBSI. Only a small number (~9%) of the itaconate units were converted into citraconate or mesaconate units when they were calculated from integral values of the weaker signals at 2.1 and 5.9 ppm (citraconate) and 2.2 and 6.8 ppm (mesaconate). Takasu et al.<sup>5</sup> reported that 20–60% of itaconate isomerized to citraconate or mesaconate in the polymerization of itaconic anhydride and 1,2-epoxybutane. Solanki et al.<sup>8</sup> referred to the mechanism of isomerization of itaconic anhydride and its dependence on basicity and solvent media. Retuert et al.<sup>9</sup> reported that the polycondensation of IA and ethylene glycol induced no isomeriza-

**TABLE II**  
Molecular Weights of the Prepolymers as Determined by GPC

	$M_w$	$M_n$	$M_w/M_n$
PBSI 5	10,000	6000	1.7
PBSI 10	11,000	5000	2.2
PBSI 15	11,000	5000	2.2
PBSM 5	6,600	4100	1.6
PBSM 10	7,300	4800	1.5
PBSM 15	9,000	5200	1.7

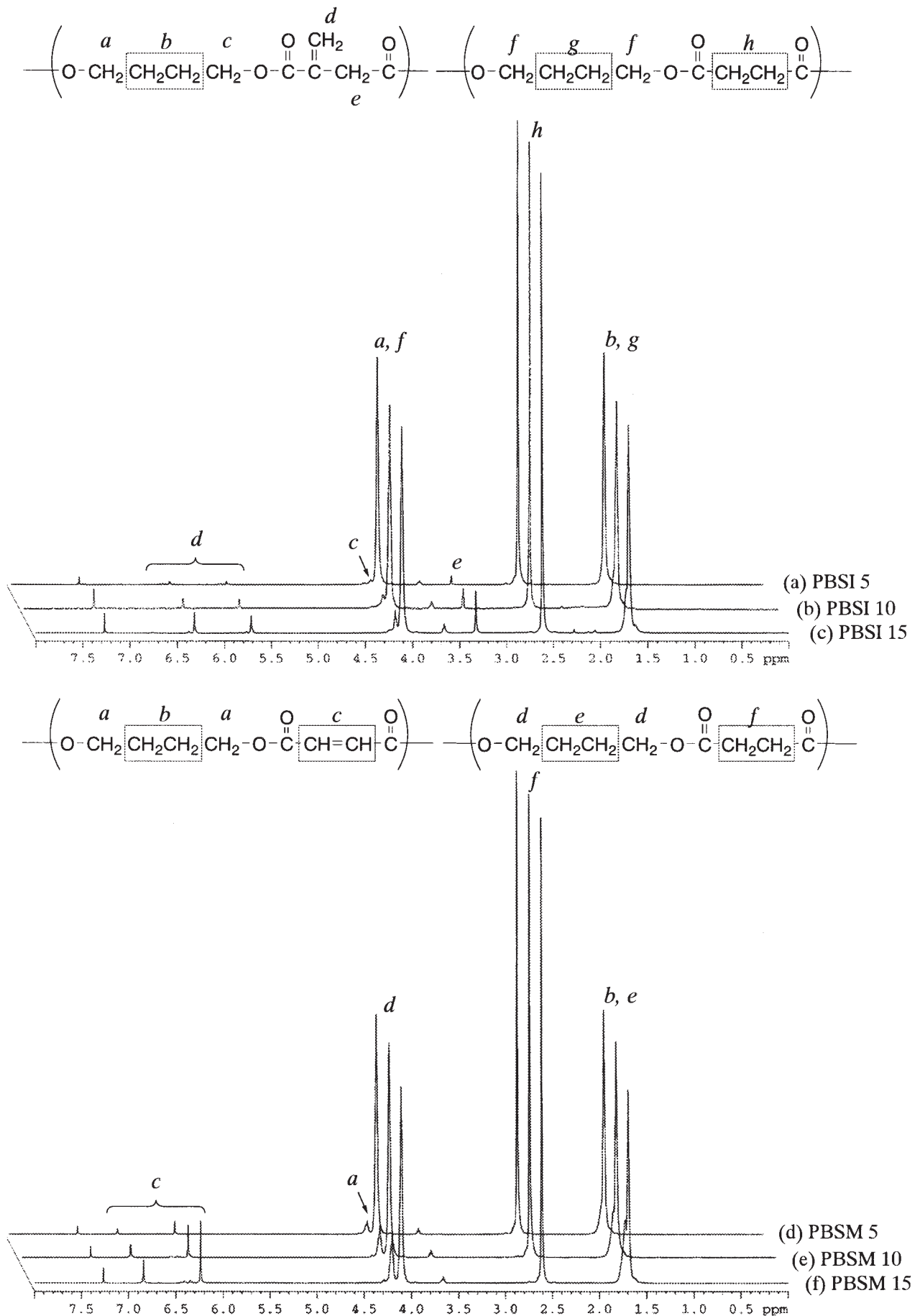
tion under moderate conditions. We considered that the little isomerization in our results may have been due to the use of IA instead of itaconic anhydride, the relatively short reaction time, and the lower amount of the metal alkoxide catalyst.

The proton signals of the unsaturated groups for PBSM were observed at  $\delta = 6.2$  ppm and  $\delta = 6.8$  ppm. The former was assigned to the maleate unit, and the latter was ascribed to the isomerized fumarate units. About 30% of the maleate units were converted into fumarate units under our reaction condition (Table I). Such cis–trans isomerization has been reported in the literature.<sup>7,10–12</sup>

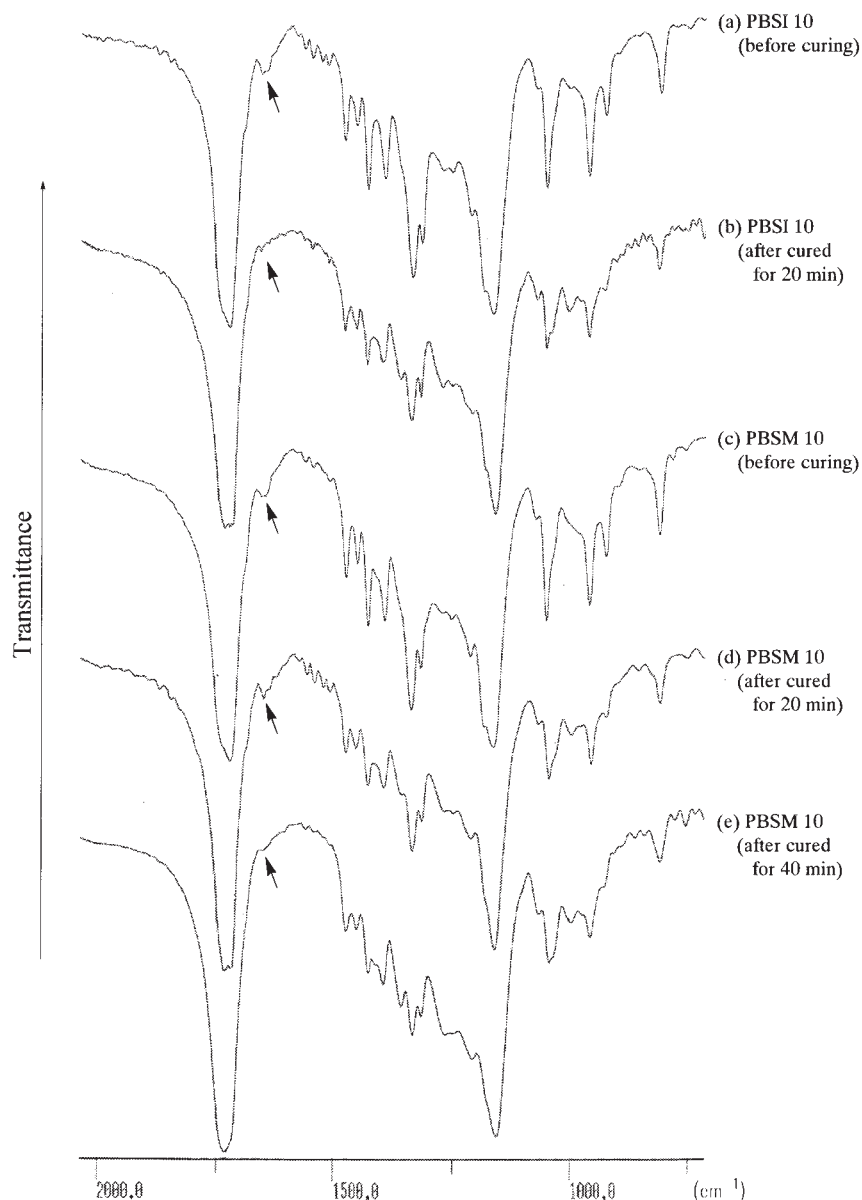
The compositions of the obtained polymers were calculated from peak integral values of <sup>1</sup>H-NMR spectra (Table I). The molar ratio of itaconate units to maleate units in the prepolymers was lower than the feed ratio. This implied that the incorporation efficiency of itaconate and maleate was lower than that of succinate. The molecular weights of the prepolymers are summarized in Table II.  $M_w$  of PBSI was approximately 10,000–11,000, and that of PBSM was 7000–9000. The polydispersity index [weight-average molecular weight/number-average molecular weight ( $M_w/M_n$ )] was 1.5–2.2.

### Crosslinking of PBSI and PBSM

The prepolymers (PBSI and PBSM) were cured at 115°C in the presence of BPO. Figure 2 shows the changes in the IR spectra of PBSI 10 and PBSM 10 during the curing reaction. A strong absorption at 1740 cm<sup>-1</sup> was assigned to the C=O stretching of ester units, and a weak absorption at 1650 cm<sup>-1</sup> was assigned to C=C stretching of itaconate or maleate units. The absorption peak at 1650 cm<sup>-1</sup> became weaker with the curing time, and this indicated the occurrence of a reaction of unsaturated C=C groups. After the prepolymers were cured at 115°C for 20 min, the absorption peak at 1650 cm<sup>-1</sup> almost disappeared for PBSI, whereas the peak was not remarkably reduced for PBSM. This result indicated that the itaconate units were more reactive than the maleate units under the studied reaction conditions. PBSM was cured for 40 min.



**Figure 1**  $^1\text{H}$ -NMR spectra of PBSIs and PBSMs in  $\text{CDCl}_3$ : (a) PBSI 5, (b) PBSI 10, (c) PBSI 15, (d) PBM 5, (e) PBM 10, and (f) PBM 15.



**Figure 2** IR spectra of PBSI 10 and PBSM 10 before and after curing at 115°C: (a) PBSI 10 before curing, (b) PBSI 10 after curing for 20 min, (c) PBSM 10 before curing, (d) PBSM 10 after curing for 20 min, and (e) PBSM 10 after curing for 40 min.

The cured prepolymers were swelled in chloroform, which is a good solvent for PBS, and this indicated the formation of the crosslinked structure. The gel fractions increased with an increase in the unsaturated units (Table III). There was a small soluble fraction (10–20%) in the cured polymers. This result suggested that some products had a very low degree of crosslinking or just a branched structure. In the  $^1\text{H-NMR}$  spectrum of the soluble fraction of cured PBSI 5 in  $\text{CDCl}_3$  (Fig. 3), the peaks around 6 ppm, related to itaconate units, diminished, and peaks at 0.9–1.3 ppm appeared, in comparison with the  $^1\text{H-NMR}$  spectrum of PBSI 5 before curing. This result indicated that the unsaturated group reacted and yielded a saturated group.

**TABLE III**  
Contents of Insoluble Fractions in the Crosslinked Polymers as Determined by Soxhlet Extraction with Chloroform

	Insoluble fraction (%)
Crosslinked PBSI 5	68.4
Crosslinked PBSI 10	76.2
Crosslinked PBSI 15	90.9
Crosslinked PBSM 5	81.1
Crosslinked PBSM 10	86.1
Crosslinked PBSM 15	88.3

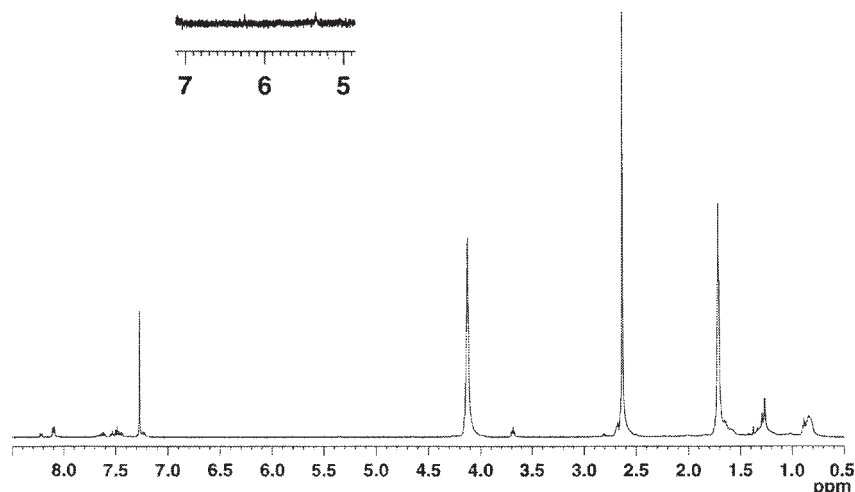


Figure 3  $^1\text{H-NMR}$  spectrum of the soluble fraction of crosslinked PBSI 5 in  $\text{CDCl}_3$ .

### Thermal properties of PBSI and PBSM

Figure 4 shows the second-heating DSC thermograms of PBSI 15 and PBSM 15 before and after crosslinking in comparison with PBS. Table IV summarizes the DSC thermal properties of the prepolymers and crosslinked polymers.  $T_m$  and the melting enthalpy ( $\Delta H_m$ ) decreased with increasing itaconate or maleate

units for the prepolymers. In addition, the crosslinked polymers had lower  $T_m$ 's than the corresponding prepolymers. These results indicated that the incorporation of itaconate or maleate units and crosslinking prevented the crystallization of polymer chains. The polymers (e.g., crosslinked PBSI 15) with low  $\Delta H_m$  values, that is, low degrees of crystallization, showed a clear glass transition. On the other hand, the glass

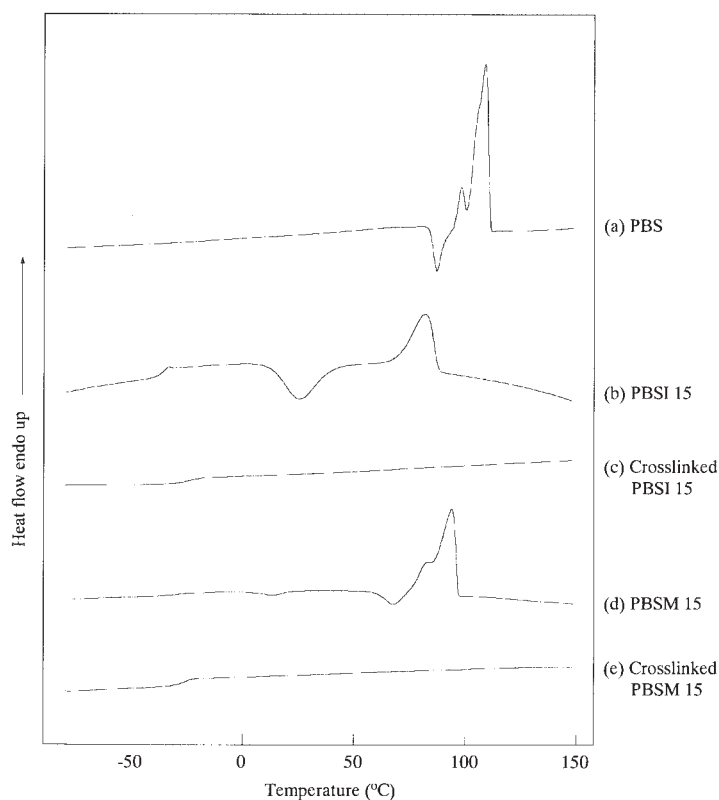


Figure 4 DSC thermograms of (a) PBS, (b) PBSI 15 before crosslinking, (c) PBSI 15 after crosslinking, (d) PBSM 15 before crosslinking, and (e) PBSM 15 after crosslinking. The second heating process is represented. The heating rate was  $20^\circ\text{C}/\text{min}$ .

TABLE IV  
Thermal Properties of the Polymer Products

	$T_g$ (°C) <sup>a</sup>	$T_m$ (°C) <sup>a</sup>	$\Delta H_m$ (J/g) <sup>a</sup>	$T_d$ (°C) <sup>b</sup>
PBS	-24.6	109.3	84.2	389
PBSI 5	-29.0	107.2	73.2	385
Crosslinked PBSI 5	-27.0	91.8	39.3	395
PBSI 10	-29.0	91.5	47.0	380
Crosslinked PBSI 10	-29.3	65.5	9.7	395
PBSI 15	-36.5	82.4	48.0	377
Crosslinked PBSI 15	-25.2	80 <sup>c</sup>	0.4	387
PBSM 5	-29.4	106.6	70.8	378
Crosslinked PBSM 5	-27.1	83.4	50.0	387
PBSM 10	-31.3	100.5	63.0	378
Crosslinked PBSM 10	-29.0	67.8	7.0	388
PBSM 15	-32.9	94.1	57.7	373
Crosslinked PBSM 15	-26.8	72 <sup>c</sup>	1.3	381

<sup>a</sup> Determined in the second heating process of DSC.

<sup>b</sup> Determined as the onset of the TGA curve.

<sup>c</sup> The melting peak was so broad that the precise value could not be obtained.

transition of the polymers (e.g., PBS) with high  $\Delta H_m$  values was obscure.  $T_g$  rose with crosslinking as expected, but it was lowered a little by the incorporation of itaconate or maleate units. The hindrance of molecular packing by the incorporation of itaconate and maleate units may have caused the lowering of  $T_g$ .  $T_d$  slightly increased with crosslinking, probably because of an increase in the molecular weight.

### Biodegradability

The biodegradability of PBSIs and crosslinked PBSIs was tested by BOD measurements with activated sludge under aerobic conditions. The degree of degradation was calculated from the BOD values and

plotted as a function of the degradation time. The results of the degradation test are shown in Figure 5. About 7–10% of the prepolymer PBSI was degraded in 50 days, whereas about 2–5% of the crosslinked PBSI was degraded in the same period. It is conceivable that the crosslinked network slowed down biodegradation. This result was very similar to that of Jin et al.<sup>7</sup> However, crosslinking did not completely spoil biodegradability. The biodegradability of a polymer is affected not only by crosslinking but also by the crystallinity of the polymer. It is well known that the biodegradability of a polymer decreases with an increase in the crystallinity.<sup>13–15</sup> The reduction of the crystallinity of PBSI by crosslinking may be related to some retention of biodegradability.

### CONCLUSIONS

Aliphatic unsaturated prepolymers, PBSI and PBSM, were synthesized by a polycondensation reaction. The monomer compositions of the polymers were calculated from <sup>1</sup>H-NMR spectra, and the itaconate or maleate unit contents in the prepolymers varied from 1.8 to 11% with the feed ratios of IA or MA varying from 5 to 15%. The crosslinking of PBSI and PBSM with BPO drastically changed the solubility of these polymers, and FTIR and <sup>1</sup>H-NMR spectra indicated that the crosslinking reaction took place on unsaturated groups. In DSC measurements, a heat capacity change at the glass transition became remarkable, and  $\Delta H_m$  decreased with the crosslinking or incorporation of itaconate or maleate units. About 7–10% of PBSI before crosslinking was degraded in 50 days, and the biodegradation rate was slowed by crosslinking.

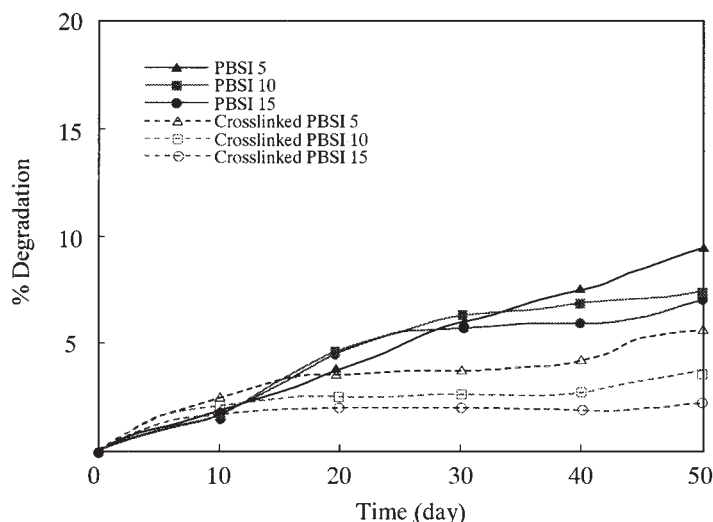


Figure 5 Biodegradability test of PBSIs and crosslinked PBSIs. The biodegradability was measured by BOD tests at 25°C with activated sludge.

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