

## Preparation and Characterization of High Molecular Weight Poly(butylene succinate)<sup>†</sup>

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Received Jan. 17, 2002 ; Revised Feb. 21, 2002

**Abstract:** Poly(butylene succinate) (PBS) prepolymers were prepared by the condensation polymerization of 1,4-butanediol (1,4-BD) and succinic acid (SCA) in the presence of titanium (VI) isopropoxide (TIP) catalyst. The PBS prepolymers reacted with 1,4-BD or SCA to obtain hydroxyl or carboxylic acid group terminated PBS. High molecular weight linear or branched PBS was synthesized by a coupling reaction between hydroxyl and carboxylic acid group terminated PBS, or by a branching reaction between carboxylic acid group terminated PBS and glycerol as a branching agent. The weight average molecular weight of the prepared linear or branched PBS was in the range of 100,000-220,000. Both melting point and thermal stability of the high molecular weight linear and branched PBSs were somewhat higher than those of general PBS. From a tensile behavior by Instron test, modulus, tensile strength and elongation at break improved with increase in the molecular weight of the prepared PBS through the coupling or the branching reaction. In particular, the high molecular weight linear PBS had about 2.5 times higher value in modulus than the branched one.

**Keywords :** high molecular weight, aliphatic polyester, branched polymer, poly(butylene succinate), branching reaction.

### Introduction

Every year, several hundred thousand tons of nondegradable plastic products are discarded and filled into marine and earth environments. This affects very serious ecological and environmental problems.<sup>1,2</sup> Therefore, recently biodegradable polymers have received much attention because they can replace nondegradable polymers. A number of biodegradable polymers such as poly(hydroxy alcanoates), poly( $\epsilon$ -caprolactone), aliphatic polyesters, and so forth have been reported.<sup>3-6</sup> Among them, especially, biodegradable aliphatic polyesters derived from aliphatic diols and dicarboxylic acids have been extensively studied since they are relatively easy to be prepared and also much cheaper than the other degradable polymers such as poly(hydroxy alcanoates) and poly( $\epsilon$ -caprolactone).<sup>7-9</sup>

On the other hand, the aliphatic polyesters have not been applied to blow-molded or extruded products, but just to limited articles such as disposable plastic bags and films and

matrix resins for biomedical materials or drug carriers. These limitations in application are due to their low melt strength and viscosity.<sup>4</sup> These rheological properties associated with melt processing are influenced not only by molecular weight and molecular weight distribution but also by branched structures of the polymers. In particular, rheology related to elongation is greatly affected by long-chain branching.<sup>10</sup>

Thus, many researchers have focused on the development of high molecular weight aliphatic polyesters with linear or branched structures to improve their low rheological properties from an industrial point of view. As a result, high molecular weight aliphatic polyesters such as polyethylene succinate, PBS and polybutylene adipate, which are known as BIONOLLE, have been developed first by Showha High-polymer Co., Japan.<sup>11</sup> The weight-average molecular weights of the polymers were in the range of 50,000 to the maximum 1,000,000 and they showed excellent properties in mechanical strength and melt processing. Consequently, they could be utilized in various applications such as film, foamed sheet, blown bottles, or highly expanded foam. However, the method for synthesizing these high molecular weight polymers has been reported only in the patents, and detailed experimental conditions have not been disclosed.<sup>12</sup> This led us to attempt

<sup>†</sup>Dedicated to Dr. Un Young Kim on the occasion of his retirement.

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our work.

In this article we report the synthetic conditions for the preparation of high molecular weight linear and branched PBSs through coupling and chain-branching reactions and also describe their thermal and mechanical properties.

## Experimental

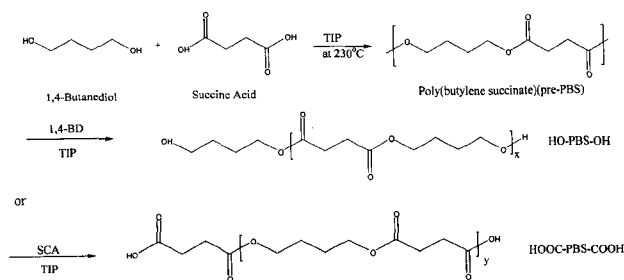
**Materials.** 1,4-Butanediol (99%) and TIP (99.99%) were purchased from Aldrich Chemical Company and used without further purification. Succinic acid (SCA: 99%) was purified by sublimation under a reduced pressure. Glycerol (99%), a branching agent, and triethylamine (TEA: 99.8%) were purchased from TEDIA Chemical Company and used without further purification. In addition, chloroform solvent, an industrial grade, was purified by fractional distillation.

**Measurements.** A fourier transform infrared (FT-IR) spectrum was obtained with a KBr pellet on a Bruker IFS 48 spectrometer. A  $^1\text{H-NMR}$  spectrum was recorded on a Varian Gemini 400 MHz spectrometer for determination of polymer structure.  $\text{CDCl}_3$  was used as a solvent for  $^1\text{H-NMR}$  spectra of PBSs. The inherent viscosity (I.V.) of prepared polymers was measured at concentration of 0.5 g/dL in chloroform at 25 °C using a Cannon-Fenske viscometer. Thermal properties of synthesized polymers were measured by DSC and TGA 1000 plus (Polymer Laboratories Ltd.) at a heating rate of 10 °C/min under nitrogen atmosphere. Molecular weights of the polymers were determined by a Waters gel permeation chromatographer (GPC) using HR4E and HR5E styragel columns with chloroform as solvent and Shodex standard polystyrenes (Showa Denko K. K.) for a calibration curve. Mechanical properties (ASTM D882) of the films 20–30  $\mu\text{m}$  thick were studied on Instron tensile tester (Model TTD) at a strain rate of 20 mm/min. Surfaces of degraded films after hydrolysis in a buffer solution were measured by a scanning electron microscope (SEM: Hitachi S-25000C).

**Synthesis of Hydroxyl or Carboxylic Acid Group Terminated Linear PBS.** SCA (58.0 g, 0.48 mol), 1,4-butanediol (55.20 g, 0.6 mol), TEA (0.224 mL, 1.56 mmol) as a co-catalyst, and TIP (0.30 mL, 1.0 mmol) as a catalyst were added into a 250 mL two-necked round-bottom flask, which was

connected with gas inlet and outlet adapters. The mixture was immersed in a silicon oil bath and then reacted at 200 °C for 100 min under nitrogen atmosphere. The viscous liquid was heated to 220 °C and then polymerized at 2.0 torr for 2 h with the removal of water generated during the first polymerization. At the end of the first-stage polymerization, the pressure in the reaction vessel was reduced to 0.5 torr, whereas the temperature was raised to 230 °C, and then the second polymerization proceeded for 2–6 h to increase the molecular weight of the resulting linear PBS. After the polymerization was completed, the temperature in the reaction vessel was cooled down to room temperature. The PBS prepolymer was dissolved with 80 mL of chloroform, and then 1,4-butanediol (5.52 g, 0.06 mol) and TIP (0.03 mL, 0.1 mmol) were added again into the solution. The homogeneous solution was stirred at 80 °C and atmospheric pressure under nitrogen purging for 1 h to remove the chloroform solvent. The PBS prepolymer was then reacted with the added 1,4-butanediol at 200 °C for 100 min under nitrogen atmosphere. After the end-capping reaction, about 120 mL of chloroform were used to dissolve the product, and then filtered to remove impurities. The filtrate was precipitated into methanol in excess to obtain a white powdery polymer. The filtered polymer was washed with methanol and dried at 25 °C for 24 h in a vacuum oven in order to get a prepolymer with hydroxyl groups at both ends of the PBS chains (Scheme I).

In addition, another kind of PBS prepolymer with carboxylic acid groups at both ends was prepared by the same method



**Scheme I.** Synthesis of hydroxyl or carboxylic acid group terminated linear PBS.

**Table I.** Preparation of Hydroxyl or Carboxylic Acid Group Terminated Linear PBS<sup>a</sup>

Prepolymer	Sample No.	Reaction <sup>b</sup> Time (h)	Conversion (%)	$\overline{M}_n$	$\overline{M}_w$	PDI
HO-PBS-OH	P1	-	73	3,300	6,600	2.03
	P2	5	88	58,300	123,400	2.12
HOOC-PBS-COOH	P3	2	82	33,500	68,700	2.05
	P4	6	95	84,600	167,700	1.98

<sup>a</sup>The melt polymerization was carried out at 200 °C for 2 h under an ambient pressure, 220 °C for 2 h under a reduced pressure of 2.0 torr, and finally 230 °C for 2–6 h under reduced pressure of 0.5 torr.

<sup>b</sup>Polymerization time was carried out at 230 °C under reduced pressure of 0.5 torr.

described above except for adding SCA (5.8 g, 0.048 mol) instead of 1,4-butanediol.

**Synthesis of High Molecular Weight linear PBS.** 4.0 g of the hydroxyl group (sample P1 in Table I) and carboxylic acid group (sample P3) terminated PBA prepolymers of was put in a 100 mL one-necked round-bottom flask, respectively, and dissolved with 50 mL of chloroform. 0.10 mL of 10% (v/v) TIP chloroform solution was added into the flask, which was immersed in a silicon oil bath. The mixture was heated to 60°C and stirred for 40 min under nitrogen atmosphere to remove the solvents. The pressure in the reaction vessel was reduced to 0.5 torr, whereas the temperature was heated to 230°C for 3 h for a coupling reaction between the hydroxyl group and carboxylic acid group terminated pre-PBA polymers. After the reaction, 60 mL of chloroform were added into the flask and stirred for 2 h. The solution was filtered to remove impurities. The filtrate was precipitated into methanol in excess to obtain a white powdery polymer. The filtered polymer was washed with methanol and dried at 25°C for 24 h in a vacuum oven in order to get a high molecular weight linear PBS (sample P6 in Table II).

**Synthesis of High Molecular Weight Branched PBS.** 5.0 g of the carboxylic acid group terminated PBS prepoly-

mer (sample P3 in Table I) was put in a 100 mL one-necked round-bottom flask and dissolved in 40 mL of chloroform. 0.125 mL (0.015 g of pure glycerol) of 10% (v/v) glycerol ethanol solution, a branching agent, was added into the flask, which was immersed in a silicon oil bath, with 0.25 mL (0.025 g of pure TIP) of 10% (v/v) TIP chloroform solution. The mixture was heated to 60°C and stirred for 1 h under nitrogen atmosphere to remove the solvents. The pressure in the reaction vessel was reduced to 0.5 torr, whereas the temperature was heated to 210°C for 2 h for a branching reaction between the carboxylic acid group terminated PBS and glycerol. After the reaction, 60 mL of chloroform were added into the flask and stirred for 2 h. The solution was filtered to remove some insoluble gels, cross-linked polymers that were generated during the branching reaction. The filtrate was precipitated into methanol in excess to obtain a white powdery polymer. The filtered polymer was washed with methanol and dried at 25°C for 24 h in a vacuum oven in order to get a high molecular weight of branched PBS (sample P3G6 in Table III) as shown in Scheme II.

**Measurement of Insoluble Gel.** The high molecular weight branched PBS obtained through a branching reaction

**Table II. Preparation of High Molecular Weight Linear PBS by a Coupling Reaction<sup>a</sup>**

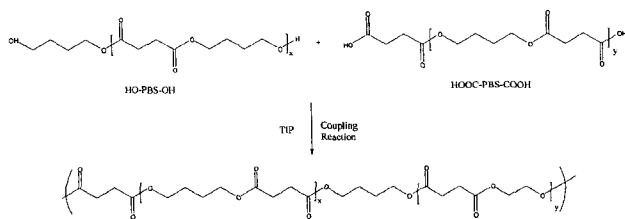
Prepolymer		Sample No.	Reaction Temp. (°C)	Conversion (%)	$\overline{M}_n$	$\overline{M}_w$	PDI
HO-PBS-OH	HOOC-PBS-COOH						
P1	P3	P5	210	86	102,500	205,000	2.00
		P6	230	73	108,800	213,300	1.96
P2	P3	P7	210	92	64,500	142,100	2.20
		P8	230	43	96,300	192,500	2.00
P2	P4	P9	210	91	63,600	134,400	2.11
		P10	230	85	96,300	192,500	2.00

<sup>a</sup>Coupling reaction was carried out at 0.5 torr for 3 h.

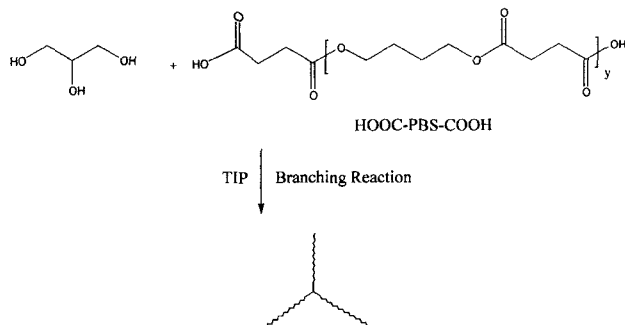
**Table III. Effect of Glycerol Concentration on Molecular Weight of Branched PBS by a Branching Reaction<sup>a</sup>**

Branched PBS	Glycerol (wt% to PBS)	Reaction Temp.(°C)	Conversion (%)	$\eta$	$\overline{M}_n$	$\overline{M}_w$	PDI	Gelation (%)
PG1	0.2	200	88	0.86	35,700	102,100	2.87	-
PG2	0.3		90	0.86	36,200	102,500	2.83	-
PG3	0.4		81	1.27	59,200	146,100	2.47	-
PG4	0.5		70	0.90	37,300	106,800	2.86	-
PG5	0.2	210	89	1.04	36,300	126,100	3.47	2.94
PG6	0.3		83	1.28	60,300	147,600	2.45	8.3
PG7	0.4		48	1.96	113,700	219,600	1.93	35
PG8	0.5		46	1.66	95,500	196,700	2.06	30

<sup>a</sup>Carboxylic acid group terminated prepolymer P3 was used as a substrate polymer for a branching reaction for 2 h. The concentration of TIP as a catalyst was 0.5 wt% in terms of the concentration of the prepolymer P3.



**Scheme II.** Preparation of high molecular linear PBS.



**Scheme III.** Preparation of high molecular weight branched PBS.

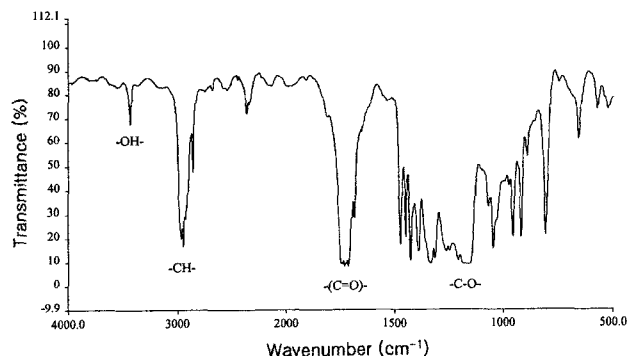
was dissolved in chloroform. The polymer solution was filtered under reduced pressure by using a filter paper. The filtered gel, insoluble polymer, was dried at 25 °C for 24 h in a vacuum oven, and the dried gel was weighed to calculate the ratio of the branched polymer to the gel generated during the branching reaction.

**Preparation of Polymeric Thin Films.** The PBA thin films 20–30 μm thick were cast from 10% chloroform solution. Mechanical tests were performed on five specimens (5 × 60 mm) for each sample. Their tensile properties were measured by an Instron tensile tester.

## Results and Discussion

**Synthesis of Hydroxyl Group or Carboxylic Acid Group Terminated Linear PBS.** To prepare high molecular weight linear and branched PBSSs, we first synthesized linear PBS prepolymers with hydroxyl groups or carboxylic acid groups at both ends of the polymer chains through a two-step process shown in Scheme I. In the first stage, low molecular weight linear PBS (P1 in Table I) was prepared from the polyesterification of 1,4-butanediol and succinic acid in the presence of TIP as a catalyst at 220 °C under reduced pressure of 2.0 torr. In the second polymerization stage proceeding at 230 °C under reduced pressure of 0.5 torr, raising the polymerization time from 2 to 6 h increased the weight-average molecular weight of linear PBS prepolymers from 68,700 (P3) to 167,700 (P4) with the time, which are listed in Table I.

After the melt polymerization, the linear prepolymers



**Figure 1.** IR spectrum of the hydroxyl group terminated PBS.

reacted with 1,4-butanediol or succinic acid to produce the corresponding prepolymers with hydroxyl groups or carboxylic acid groups at both ends of the prepolymer chains. Such end-capping reaction showed the best results when the succinic acid (or 1,4-butanediol), an end-group substituting agent, was used to be 10 mol% in terms of the concentration of the monomer used for the synthesis of linear PBS. On the other hand, when used over 10 mol% of succinic acid, we observed that the molecular weights of the prepolymers with carboxylic acid groups decreased because of the transesterification reaction between the linear polymer chains and succinic acid molecules.<sup>4</sup>

In addition, the structures of the hydroxyl and carboxylic acid groups terminated PBS prepolymers were confirmed by FT-IR and <sup>1</sup>H-NMR spectra. Figure 1 is FT-IR spectrum of the hydroxyl group terminated PBS prepolymer having a low molecular weight (P1). The spectrum showed strong and broad stretching bands of methylene, carbonyl, and ether groups around 3000, 1700, and 1200 cm<sup>-1</sup>, respectively, indicating typical characteristic bands of aliphatic polyester. On the other hand, weak and sharp stretching band of the hydroxyl groups at both ends of the low molecular weight prepolymer (P1) chain appeared at 3550 cm<sup>-1</sup>, but the hydroxyl group in the prepolymer P2 with a higher molecular weight was not observed because of its low concentration. <sup>1</sup>H-NMR spectrum of the hydroxyl group terminated PBS prepolymer had three kinds of methylene peaks existing in the polymer backbone at 4.1, 2.6, and 1.7 ppm, respectively: one is due to two methylene groups next to the ether linkage in the polymer and the other to two methylene groups next to the ketone and another to two methylene groups in the middle of the 1,4-butanediol monomer. Their hydrogen integrations matched well with the structure of the PBS.

Glass transition temperature ( $T_g$ ) and melting temperature ( $T_m$ ) of the prepolymers were 40 and 112 °C, respectively. The prepolymers having weight-average molecular weight  $s$  of below 100,000 showed similar transition temperatures.

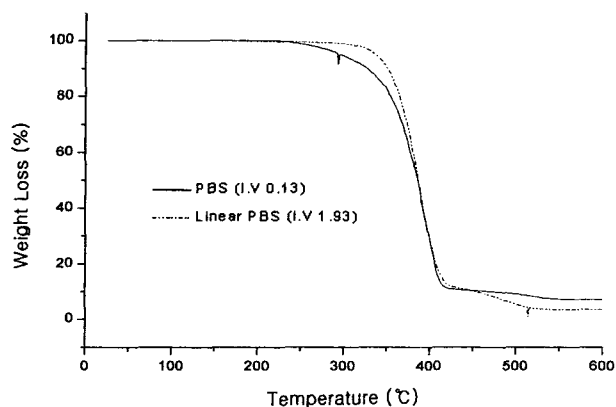
Based on these results, we used the four kinds of hydroxyl and carboxylic acid groups terminated linear PBS prepolymers with different molecular weights as a substrate polymer

for the synthesis of high molecular weight PBSs with a linear or branched structure.

**Preparation of High Molecular Weight Linear PBS.** To prepare PBSs with the weight-average molecular weights of over 100,000, we carried out a coupling reaction between the prepolymers with hydroxyl groups or the carboxylic acid groups at both ends. That is, we examined the influence of the temperature and the molecular weight of the prepolymers on the molecular weight of linear PBS, as shown in Table II. The weight-average molecular weight of the linear PBS increased from 134,400 to 213,300 with the increase in the temperature of the coupling reaction from 210 to 230 °C.

From Table II, we found that the molecular weight of the prepared linear PBS closely related to the molecular weight of the prepolymers selected for the coupling reaction. In other words, when the prepolymers P1 and P3 were used as substrate polymers, synthesized linear PBS had a high molecular weight of over 200,000. However, the molecular weight of the prepared PBS decreased rather than the sum of the molecular weight of each of the prepolymers, when the prepolymers P2 and P4 with a high molecular weight were chosen. It is most likely that such difference is due to mobility of the prepolymers as well as relatively high concentrations of the hydroxyl and carboxylic acid groups in the prepolymers. That is, the prepolymer P1 of a low molecular weight plays a role of a chain extender in the coupling reaction between P1 and P3 prepolymers. On the other hand, the prepolymers P2 and P4 with a relatively high molecular weight have not only lower concentration of the functional groups at both ends of the prepolymers but also slower mobility than P1 and P3. They cause decrease of the molecular weight of the resulting linear PBS. In addition, transesterification reaction between the prepolymers also gets reduced the molecular weight of the linear PBS.

From a DSC measurement, the high molecular weight linear PBS had higher  $T_m$  (115 °C) and  $T_g$  (45 °C) than the prepolymer P1. Figure 2 shows TGA curves of the linear polymer P6 and the P1. As a result, the initial decomposition



**Figure 2.** TGA curves of different molecular weight linear PBSs.

(1.0% weight loss) temperature of the P6 improved from 244 of P1 to 289 °C.

**Preparation of High Molecular Weight Branched PBS.** Recently, branched polymers have been reported to have superior melt strength and melt viscosity compared with linear polymers. In particular, the Introduction of branching to the linear polymers proved effective in enhancing processability based on elongational flows. A few of these processes include fiber spinning, film blowing and casting, and foaming. Branching increases the melt strength and confers tension-hardening properties on the polymer, which help to maintain extension in the polymer processing in which a high degree of orientation is required.<sup>13,14</sup>

On the basis of these merits, it is proposed that branched aliphatic polyesters may be useful in preparing many blow-molded, extruded, or foamed products, by themselves or as an additive to the linear polyesters. For an example, the linear polymers may be modified by blending with the branched polymers to improve their properties. However, few researches have been conducted on the synthesis and characterization of branched polyesters.<sup>15-17</sup>

In the present work we tried to synthesize the branched PBS polymers with weight-average molecular weight of over 100,000 through a branching reaction between the carboxylic acid group terminated PBS prepolymer (P3) and branching agent. As a branching agent, we used glycerol that has three hydroxyl groups. In addition, we examined the influence of the reaction parameters such as concentration of glycerol, reaction temperature, and concentration of catalyst on the molecular weight of branched polymers.

**Effect of Concentration of Glycerol.** To establish the influence of the branching agent on the synthesis of high molecular weight branched PBS, we measured the change of the molecular weight of the branched polymer with the concentration of glycerol as a branching agent. As shown in Table III, the molecular weight of the branched PBA increased from 102,100 (PG1) to 146,100 (PG3) with increase in the glycerol concentration up to 0.4 wt% in terms of the prepolymer P3. When we used more than 0.4 wt% at 200 °C, however, the molecular weight remarkably decreased to 106,800 (PG4).

Such phenomenon appeared even at the condition of the branching temperature of 210 °C: On the other hand, raising the reaction temperature to 210 °C increased not only the insoluble gel content generating during the branching reaction but also the molecular weight from 106,900 to 219,600 with increase in the glycerol content up to 0.4 wt%. However, increasing the glycerol concentration to 0.5 wt% decreased the molecular weight as well as the gel creation. The reason is not clear yet, but their drastic decrease seems to be attributable to the increase of the number of glycerol molecules added as a branching agent. In other words, the number of glycerol molecules compared with the carboxylic acid group terminated PBS chains was too many, and the intermolecular

**Table IV. Effect of Catalyst Concentration on Molecular Weight of Branched PBS by a Branching Reaction<sup>a</sup>**

Branched PBS	TIP (wt% to PBS)	Conversion (%)	$\eta$	$\overline{M}_n$	$\overline{M}_w$	PDI	Gelation (%)
PG 9	0.3	84	0.83	30,500	93,000	3.05	-
PG10	0.4	80	1.24	53,500	126,800	2.37	-
PG 6	0.5	83	1.28	60,300	147,600	2.45	8.3
PG11	0.6	70	1.74	102,100	206,000	2.01	22
PG12	0.7	84	1.54	84,500	181,400	2.15	32
PG13	0.8	34	1.28	60,300	147,600	2.45	45

<sup>a</sup>Carboxylic acid group terminated prepolymer P3 was used as a substrate polymer for a branching reaction. The branching reaction was carried out at 210°C for 2 h in the presence of glycerol of 0.3 wt% to the prepolymer P3.

reaction between low molecular weight branched polymer chains necessary for preparing high molecular weight branched PBS hardly occurred. Such intermolecular branching reaction gives rise to the gel creation. These phenomena are ascertained by the fact that the polydispersity of the prepared branched PBS decreases from 3.47 to 2.06 as the glycerol concentration increases from 0.2 to 0.5 wt%.

Thus, we found that the concentration of the glycerol and the branching reaction temperature has a strong effect on the molecular weight of the branched PBS and gelation

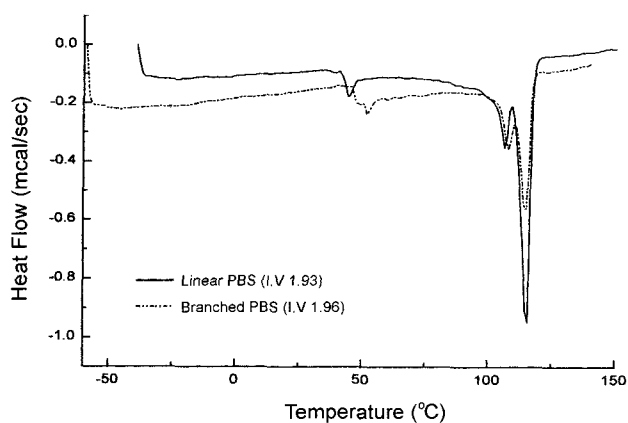
**Effect of Concentration of Catalyst.** We performed the branching reaction by varying the concentration of catalyst TIP to the carboxylic acid group terminated prepolymer P3, keeping the glycerol concentration and reaction temperature constant to investigate the influence of the catalyst concentration on the molecular weight of the resulting branched polymer. As summarized in Table IV, the molecular weight of the branched PBS increased with increase in the concentration of TIP up to 0.6 wt%. However, when more than 0.6 wt% of TIP was used, the molecular weight drastically decreased, meanwhile, the color of the branched polymer became more and more yellowish. At 0.8 wt%, the insoluble gel, crosslinked PBS, was obtained up to 45% during the branching reaction. This phenomenon is due to the increased reactivity between the carboxylic acid group linked to the end groups of the PBS prepolymer and the hydroxyl group of the branching agent. Therefore, it is advantageous to fix the concentration of TIP of below 0.6 wt% to avoid the color change of the polymer and repress the gel creation.

#### Thermal Properties of Linear and Branched PBAs.

**Table V. Tensile Properties of PBS Films<sup>a</sup>**

PBS	I.V	Thickness ( $\mu\text{m}$ )	$\overline{M}_w$	Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
P2	1.01	25	123,400	204	14	55
P6	1.93	25	213,300	508	22	111
PG5	1.04	25	126,100	170	17	55
PG7	1.96	30	219,600	180	24	120

<sup>a</sup>Tensile test were performed on a strain rate of 10 mm/min with a load cell of 10 N at 20°C.

**Figure 3.** DSC thermograms of high molecular weight linear and branched PBAs.

DSC and TGA measurements were employed to observe the thermal behavior and stability of high molecular weight linear and branched PBS polymers. As shown in Figure 3, the branched PBS had higher by about 10°C  $T_g$  than the linear one, whereas its  $T_m$  was almost the same as the linear PBS. The thermal stability of the high molecular weight polymers showed no obvious difference regardless of the linear or branched structure and their molecular weights. The initial decomposition temperature of 1.0% weight loss was in the range of 320–324°C.

**Mechanical Properties of Linear and Branched PBS Polymers.** Tensile properties of the linear and branched PBAs are given in Table V. In stress-strain curves, all the

linear and branched PBSs were observed to decrease in tensile strength at the yield point and thereafter elongate. This demonstrates that the synthesized PBSs have tough-ductile mechanical properties. The tensile strength at break as well as modulus increased as the molecular weight of PBS increased in both linear and branched structures. Comparing the moduli of the PBSs, however, we observed that the modulus of the linear polymers (P2 and P6) before and after the coupling reaction was always higher than that of the branched resulting polymers (PG5 and PG7) although their molecular weights had a very similar value. In particular, the high molecular weight linear PBS (P6) had about 2.5 times higher value in modulus than the branched one (PG7). As can be imagined, the branched PBS has a lower packing density because branched points produce more free volume. Hence, the branched PBS gives rise to lower tensile modulus than the linear one.<sup>18</sup>

The elongation at break of the high molecular weight branched PBS (120%) had a slightly greater value than that of the linear polymer (111%). Thus, the branched polymer had better toughness than the linear one.

## Conclusions

We synthesized high molecular weight linear and branched PBS polymers through a coupling reaction between the PBA prepolymers with hydroxyl groups and carboxylic acid groups at both ends or a branching reaction between the hydroxyl group terminated prepolymer and glycerol, a branching agent. The molecular weight of the linear PBS polymers was dependent not only on the molecular weight of the hydroxyl and carboxylic acid groups terminated prepolymers but also the temperature for the coupling reaction. The molecular weight of the branched PBSs also was governed by the concentration of catalyst and branching agent as well as by the reaction temperature of the branching reaction. Among the conditions, especially, the reaction temperature greatly affected the molecular weight of the branched polymer and the gel content of generation during the branching reaction. The mechanical properties improved with the introduction of the branching into the linear PBS chain. In particular, the branched PBS showed better properties in the tensile strength and the elongation at break than

the linear PBS with similar molecular weight.

**Acknowledgement.** The authors acknowledge financial support from the Center for Advanced Functional Polymers, KAIST. This work also was supported in part by the research program of 2000, Hanyang University.

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