

# Properties of Aliphatic Polyesters with *n*-Paraffinic Side Branches

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**ABSTRACT:** Effect of ethyl and *n*-octyl branches on the properties of poly(ethylene adipate) (PEA) and poly(butylene succinate) (PBS) were investigated. Glass transition and melting temperature, crystallinity, melt viscosity, and spherulite growth rate were decreased with an increase in the degree of the chain branches. Introduction of ethyl branches as well as *n*-octyl branches into PEA did not improve the tensile strength and modulus, while it reduced elongation and tear strength significantly. The presence of glycerol units less than 0.05 mol/mol of diacid units in PEA as well as in PSB also brought about damaging effects on the properties. Additional amount of glycerol units in the polyesters resulted in the formation of gel. However, addition of *n*-octyl branches improved elongation and tear strength of PBS considerably without a notable decrease of tensile strength and modulus. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 547–555, 2000

**Key words:** poly(ethylene adipate); poly(butylene succinate); *n*-paraffinic side branches; mechanical properties; thermal properties

## INTRODUCTION

Composting of food rubbish is considered as one of the most efficient methods for disposal of biodegradable solid wastes. Success of food rubbish composting depends on the quality of the produced compost, and it is essential to develop biodegradable collection bags that can be composted along with the organic refuses at a reasonably fast rate. Films for the collection bags should possess tear strength high enough to be resistant against propagation of fissures created by sharp bodies such as fish bones.

Adding aromatic groups in polyester chains decreases their biodegradability.<sup>1–4</sup> Mechanical

properties of polymeric films can be improved by increasing the degree of crystallinity. However, aliphatic polyesters made from diacids and diols lack structural regularity and have poor intermolecular interactions resulting in polymers of low crystallinity. Moreover, the aliphatic polyesters usually have molecular weights too low to possess a high degree of entanglement. These effects make enhancement of tear strength quite limited.

Properties of polymers depend strongly on the degree of chain branching. Short-chain branches reduce the degree of crystallinity of polymers, while long chain branches lower melt viscosity and endow elongational viscosity with tension-stiffening behavior.<sup>5</sup> Poly(ethylene-co-1-octene) produced by a metallocene catalyst [constrained geometry catalyst (CGCT)] exhibits a high shear thinning behavior of melt viscosity in spite of its narrow molecular-weight distribution.<sup>6</sup> Polymers of narrower molecular-weight distribution are

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generally known to have less shear thinning behavior than polymers of broader molecular-weight distribution.

In this study, we investigated effects of chain branches of different lengths on the thermal and tensile properties and on tear strength of poly(ethylene adipate) (PEA) and poly(butylene succinate) (PBS). Variation of melt viscosity and crystallization rate also were examined.

## EXPERIMENTAL

Adipic acid (AA), succinic acid (SA), ethylene glycol (EG), 1,4-butanediol (1,4-BD), 1,2-butanediol (1,2-BD), 1,2-decanediol (1,2-DD), glycerol, and titanium(IV) butoxide were reagent grade from Aldrich and were used without further purification.

EG/AA or 1,4-BD/SA were bulk-polymerized in the presence of 1,2-BD, 1,2-DD, or glycerol using 0.05 mol % of titanium(IV) butoxide as a catalyst.<sup>7</sup> Esterification was carried out at 180°C for 3 h under atmospheric pressure, and then the reaction temperature was increased gradually to 210°C with simultaneous reduction of pressure to 0.02 torr. Final polycondensation was carried out for additional 4 h at 210°C under 0.2–0.02 torr. Polymerizations were realized in a glass reactor equipped with a stirrer rotating at 800 rpm. Some of the reactants were distilled off from the reactor during the polymerization, and more volatile reactants were added in excess to meet the final stoichiometric balance. Polymers obtained were dissolved repeatedly 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. Copolymer composition was calculated from <sup>1</sup>H-NMR spectra (250 MHz Bruker AC 250 spectrometer, Billerica, MA; solvent : CDCl<sub>3</sub>).

Copolymer was sandwiched between two aluminum plates and pressed under 200 atm at a temperature 30°C higher than the respective melting point, followed by quenching into liquid nitrogen. The sample was then taken out into an ambient atmosphere and warmed to room temperature. The polymer films thus obtained were secured against distortion and used for measurement of thermal and mechanical properties.

Thermal properties were analyzed using DSC (DSC7; Perkin Elmer, Norwalk, CT). Specimens were heated to 150°C at 20°C/min (first scan) and kept at 150°C for 30 s. Then they were quenched

to –100°C using liquid nitrogen. The second scan thermodiagrams were obtained by reheating them at 20°C/min from –100°C to 150°C.

The morphology of the polyesters was observed using a polarizing microscope (OPTIPHOT2-POL; Nikon, Garden City, NY). Films were heated to 150°C at 20°C/min, held at 150°C for 30 s, and quenched to the predetermined  $T_c$ . Spherulite growth rate was measured by monitoring the spherulite size using a CCD camera.

Molecular weight was measured by using gel permeation chromatography [GPC; Model 201, Waters, Milford, MA; chloroform eluent (1 mL/min) column (styragel 7.8 × 300 mm × 4 each)] calibrated with a polystyrene standard (Shodex) and by using light scattering (BI-200SM goniometer 632.8 nm, He-Ne 35 mW; Brookhaven, Holtsville, NY).

Melt viscosity was measured using a rheometer (model MC-120; Physica) with a cone-plate geometry.

Tensile properties of specimens (70 × 10 × 0.2 mm) were measured according to ASTM D882-88 using a tensile tester (model 4462; Instron, Canton, MA) with cross-head speed of 20 mm/min. Tear strength was determined at 20 mm/min (ASTM D1938-85).

## RESULTS AND DISCUSSION

EG/AA and 1,4-BD/SA were bulk-polymerized in the presence of 1,2-BD and 1,2-DD. Table I shows composition of the copolymers determined from <sup>1</sup>H-NMR spectra as a function of composition of reaction medium. Table II demonstrates the number and weight average molecular weight and polydispersity measured by GPC. Because the stoichiometry of the reactants could not be determined accurately because the reactant molecules distilled off from the reactor, precise control of molecular weight was quite difficult to achieve. The weight average molecular weight ranged from  $2.9 \times 10^4$  to  $19.0 \times 10^4$ . It may well be that molecular weight determined by GPC could be different from the actual molecular weight because the chain branching would decrease the hydrodynamic volume of polymer molecules.<sup>8,9</sup> Molecular weight measured by light scattering decreased (Table II), whereas that determined by GPC increased slightly as the content of 1,2-DD increased. However, the determination of molecular weight below  $10^5$  by light scattering is quite uncertain.<sup>10</sup> Table I shows that the content of

**Table I** Composition of the Aliphatic Polyesters

Sample	Feed Composition (mol/mol of diacid)			Copolymer Composition (mol/mol of diacid)		
	AA	EG	1,2-BD	AA	EG	1,2-BD
PEA	1	1.2	0	1	1	0
PEAB04	1	1.08	0.12	1	0.96	0.04
PEAB09	1	0.99	0.21	1	0.91	0.09
PEAB15	1	0.82	0.38	1	0.85	0.15
	AA	EG	1,2-DD	AA	EG	1,2-DD
PEAD05	1	1.08	0.12	1	0.95	0.05
PEAD08	1	0.99	0.21	1	0.92	0.08
PEAD12	1	0.82	0.38	1	0.88	0.12
	SA	1,4-BD	1,2-BD	SA	1,4-BD	1,2-BD
PBS	1	1.2	0	1	1	0
PBSB04	1	1.08	0.12	1	0.96	0.04
PBSB08	1	0.99	0.21	1	0.92	0.08
PBSB13	1	0.82	0.38	1	0.87	0.13
	SA	1,4-BD	1,2-DD	SA	1,4-BD	1,2-DD
PBSD03	1	1.08	0.12	1	0.97	0.03
PBSD05	1	0.99	0.21	1	0.95	0.05
PBSD12	1	0.82	0.38	1	0.88	0.12
	SA	1,4-BD	GL	SA	1,4-BD	GL
PBSG03	1	1.15	0.05	1	0.97	0.03
PBSG05	1	1.08	0.12	1	0.95	0.05
	AA	EG	GL	AA	EG	GL
PEAG02	1	1.15	0.05	1	0.98	0.02
PEAG04	1	1.08	0.12	1	0.96	0.04

1,2-DD in the polyester was lower than that of 1,2-BD under the identical initial feed composition, even though the reaction medium became richer in 1,2-DD than in 1,2-BD during the polymerization, owing to the lower volatility of the former, indicating that fewer 1,2-diol units with longer side chain were incorporated into the polyester than those with shorter side chain.

Gel point or variation in gel fraction was difficult to predict because of the unequal reactivity of the functional groups in glycerol as well as to the unaccurate stoichiometric balance of the reactants. However gum-like gel began to form, though the molecular weight of the remaining sol fraction was still low, as soon as the concentration of glycerol in the initial reaction medium became higher than 0.12 mol/mol of diacid. Polydispersity of the polyesters containing glycerol units was

broader than that of the other linear polyesters. The polydispersity was predicted to broaden and become infinity as the conversion approached the gel point.<sup>11</sup>

Glass transition and melting temperatures of the polyesters measured by DSC are summarized in Table III. PBS showed higher glass transition and melting temperatures than PEA did. Both PBS and PEA exhibited decreasing glass transition and melting temperatures as their degree of chain branching increased. Figure 1 shows first and second scan DSC thermograms of PBSD, PEAD, PBSB, PEAB, PBSG, and PEAG, and Figure 2 demonstrates growth rate of spherulites of PBSD, PBSB, and PBSG observed by the polarized microscope. The temperature at which the growth rate of spherulites appeared maximum was lowered somewhat, and the growth rate was

**Table II Molecular Weight of the Aliphatic Polyesters**

Sample	$M_n (\times 10^4)$	$M_w (\times 10^4)$	PDI	$M_w (\times 10^4)^a$
PBSL	3.8	9.1	2.41	—
PBSH	6.7	19.0	2.85	—
PBSB04	2.1	5.0	2.38	—
PBSB08	2.8	6.5	2.32	—
PBSB13	5.7	15.3	2.68	—
PBSD03	4.2	9.0	2.14	9.0
PBSD05	4.3	9.2	2.14	8.5
PBSD12	4.7	10.0	2.13	7.8
PBSG03	2.2	7.1	3.23	—
PBSG05	1.5	6.6	4.40	—
PEA	4.0	8.8	2.20	—
PEAB04	1.1	2.5	2.27	—
PEAB09	1.3	4.4	3.38	—
PEAB15	1.1	3.3	3.00	—
PEAD05	3.5	5.9	1.69	—
PEAD08	5.1	9.8	1.92	—
PEAD12	3.0	4.9	1.63	—
PEAG02	2.0	7.0	3.5	—
PEAG04	1.7	10.0	5.88	—

<sup>a</sup> Measured by light scattering.

reduced as the degree of chain branching increased. The longer the side chain branches, the more significant the reduction in the spherulite growth rate.

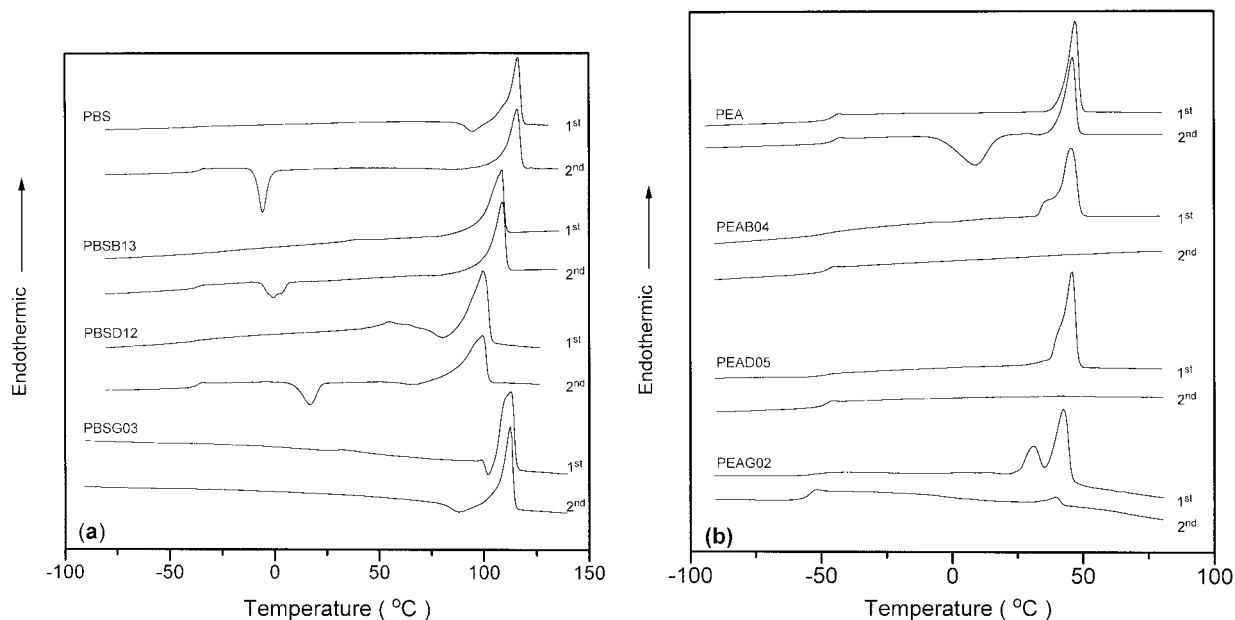
This can be confirmed by the fact that the crystallization peak of PBSD, during the reheating step after quenching with liquid nitrogen, appeared at a higher temperature compared to that of PBSB when molar content of the branching units of the two polyesters was similar (Table III). Crystallization of PBSB was faster than that of PBSD and could be completed earlier during the reheating process. Melting peak of PBS and its copolymers with 1,2-BD, 1,2-DD, or glycerol units were detected during the second scan as well as during the first scan on DSC. In contrast, the second scan melting peak of PEA disappeared as soon as a small amount of the branching units was copolymerized into PEA, except PEAG, whose melting peak was still observed on the second scan DSC thermogram.

During the second scan, the crystallization peaks of PBSB and PBSD appeared sharply and separated completely from the respective melting peaks. In contrast the crystallization peak of PBSG appeared at much higher temperature compared to that of PBSB or PBSD because of the much slower crystallization rate of PBSG and part of the crystallization peak was merged into the melting peak.

Spherulite growth rate of PEA and its branched homologues was difficult to measure using the polarized microscope because of their low

**Table III Glass Transition and Melting Temperatures of the Aliphatic Polyesters Measured by DSC**

	$T_m$ (°C)		$T_c$ (°C)	$T_g$ (°C)	
	1st	2nd		1st	2nd
PBS	115.9	115.8	-5.8	—	-36.6
PBSB04	112.2	111.7	0.5	—	-36.8
PBSB08	110.6	110.0	2.7	—	-37.3
PBSB13	108.8	108.7	-2~-5	—	-38.0
PBSD03	110.3	109.7	4.4	—	-36.8
PBSD05	108.1	107.5	6.2	—	-36.4
PBSD12	99.5	99.5	17	—	-37.0
PBSG03	112.7	112.4	—	—	—
PBSG05	110.3	110.8	—	—	—
PEA	47.2	46.3	9.1	-46.4	-47.2
PEAB04	45.6	—	—	-47.0	-47.4
PEAB09	43.8	—	—	-47.5	-48.0
PEAB15	38.4	—	—	-48.1	-48.2
PEAD05	46.1	—	—	-46.5	-47.1
PEAD08	44.1	—	—	-46.7	-47.5
PEAD12	38.6	—	—	-47.1	-48.0
PEAG02	42.5	39.3	—	-52.8	-54.6
PEAG04	36.5	35.5	—	-53.7	-54.7

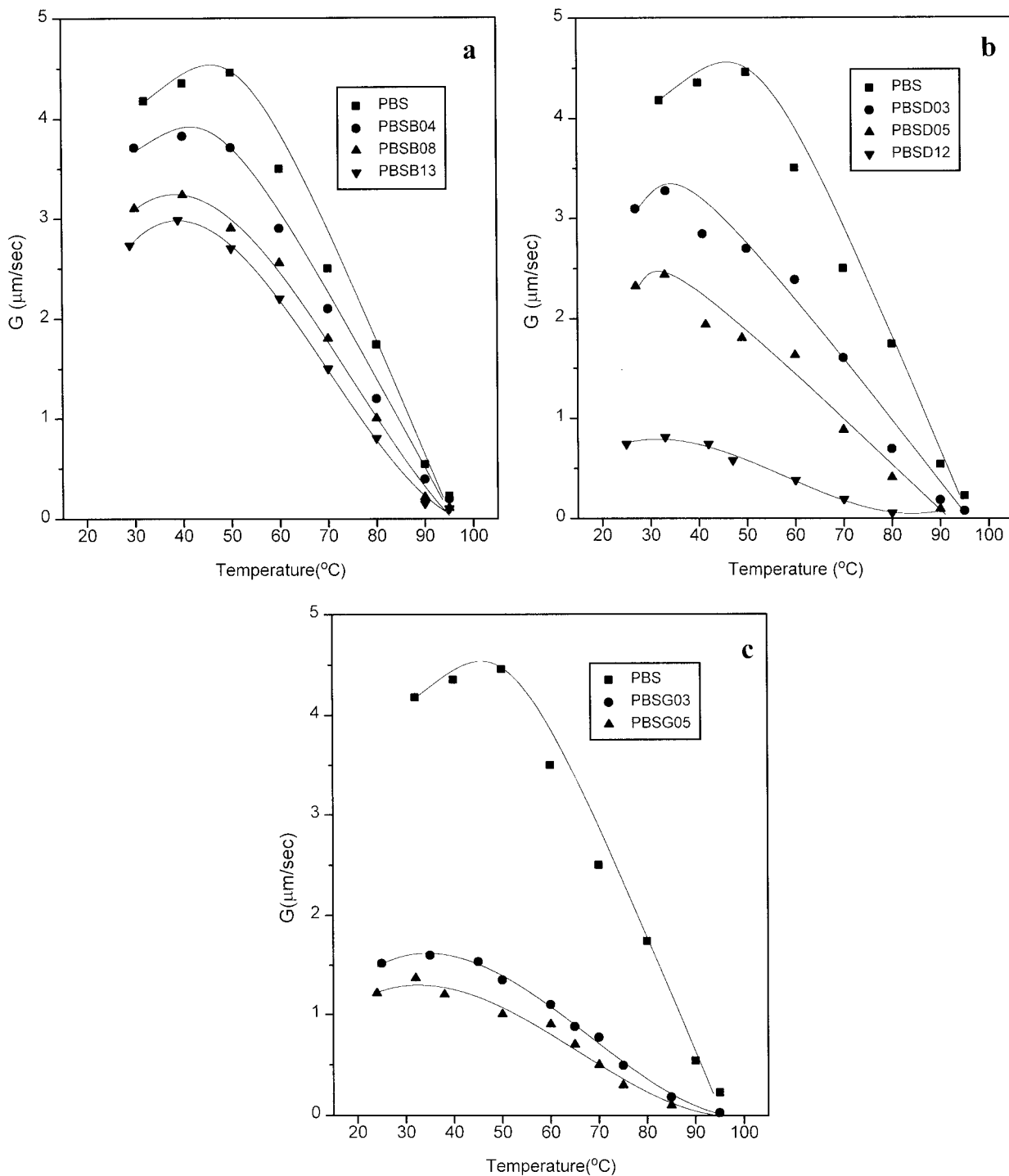


**Figure 1** First and second scan DSC thermograms of the aliphatic polyesters. (a) PBS homologues; (b) PEA homologues.

melting temperatures. However, it is certain that crystallization of PEA took place more slowly than that of PBS because the temperature difference between the crystallization peak and the melting peak of the quenched PEA was smaller than the temperature difference corresponding to PBS.

In the same context, the crystallization of the branched PEA should be much more difficult than that of the branched PBS in that melting peak of the branched PEA disappeared on the second scan DSC thermogram as soon as a small amount of branching units were introduced into PEA, whereas that of the branched PBS survived up to a high content of branching units. Melt viscosity of PBSD and PEAD decreased as the content of 1,2-DD units increased (Figs. 3 and 4). Because melt viscosity depends strongly on the polymer molecular weight, the effect of chain branches on the melt viscosity should be investigated on the basis of the same molecular weight. Figure 3 compares the melt viscosity of high molecular weight PBS (PBSH) to that of low molecular weight PBS (PBSL). As the shear rate increased, the effect of molecular weight on melt viscosity became less pronounced. It has been proved experimentally that the zero shear viscosity of polymer melts increases in proportion to 3.5 power of weight average molecular weight.<sup>3,5</sup> However, at high shear rates the dependence of the shear viscosity

is found to be practically linear,<sup>12</sup> indicating that the shear viscosity becomes less dependent on the molecular weight. Weight average molecular weights of PBSL, PBSD03, PBSD05, and PBSD12 were similar to each other, i.e.,  $9.1 \times 10^4$ ,  $9.0 \times 10^4$ ,  $9.2 \times 10^4$ , and  $10.0 \times 10^4$ , respectively. Therefore, it can be said that the decreasing melt viscosity of PBSD should be due to the increasing content of 1,2-DD units. The same conclusion also could be applied to PEA and PEAD, in spite of the uneven molecular weight of PEA and PEADs, because PEAD08 showed much lower melt viscosity than PEA, in spite of the fact that the former had higher weight average molecular weight than the latter. The decrease in the melt viscosity of the branched polyester compared to that of the linear counterpart should be at least partly ascribed to the fact that the polymer molecule having more numerous chain branches has a lower degree of chain entanglement compared to the less-branched counterpart, because the former has smaller hydrodynamic volume than the latter on the basis of the same molecular weight. Melt viscosity in Figures 3 and 4 was measured isothermally at 120°C and 80°C, respectively. Therefore, the degree of superheat increased with increasing 1,2-DD content, because the lower the melting point, the larger the difference between the temperature for the melt viscosity measurement and



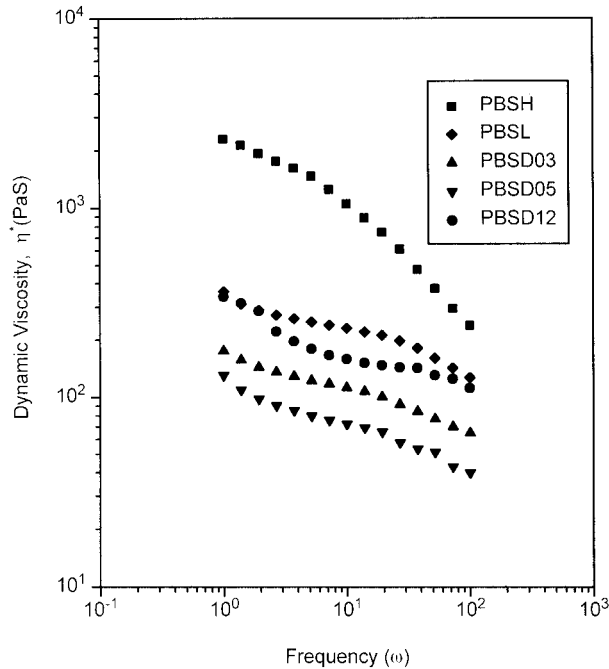
**Figure 2** Radical growth rate of spherulites, of PBS homologues as a function of crystallization temperature. (a) PBSB; (b) PBSD; (c) PBSG.

the melting point. This should be another reason for the decrease of the melt viscosity.

Figure 5 shows that melt viscosity was more sensitive to temperature at a lower measuring temperature.

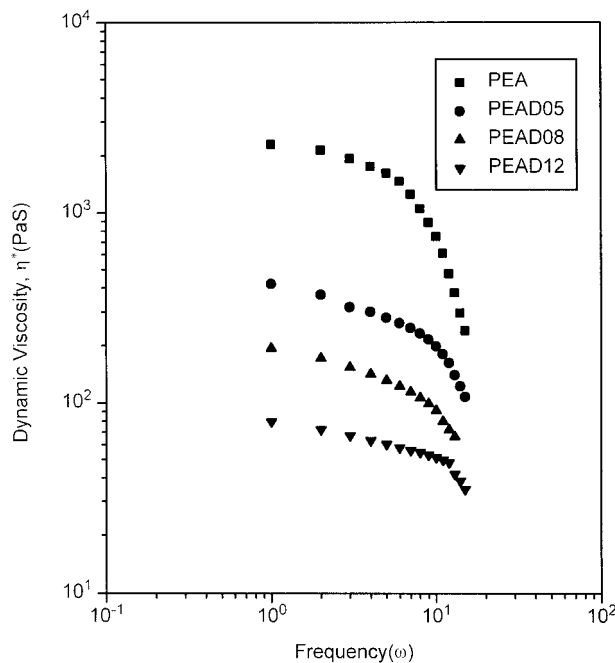
It is to be noted that the introduction of 1,2-DD, a comonomer with relatively long side branches, into PBS or into PEA reduced the shear thinning behavior of the melt viscosity. This is contrasted with the fact that poly(ethylene-co-1-



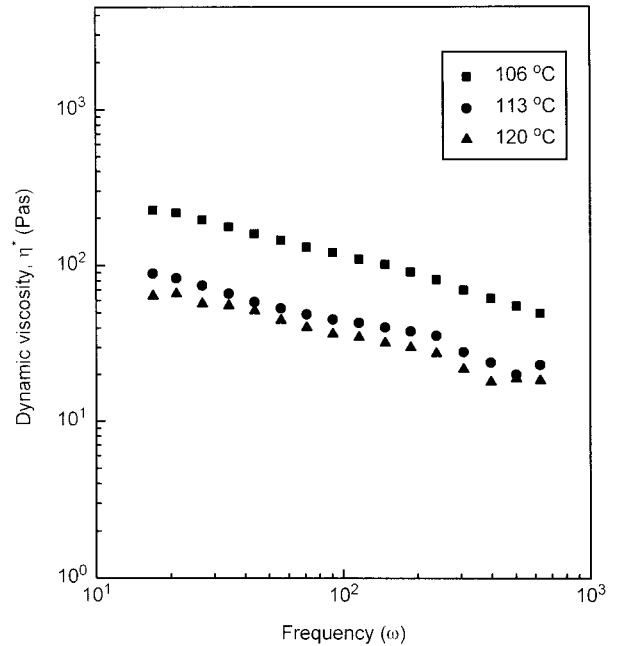


**Figure 3** Dynamic complex viscosity versus frequency for PBS at 120°C.

octene) made by the CGCT catalyst has a shear thinning melt viscosity comparable to low-density polyethylene, whose polydispersity is far broader



**Figure 4** Dynamic complex viscosity versus frequency for PEAD at 80°C.

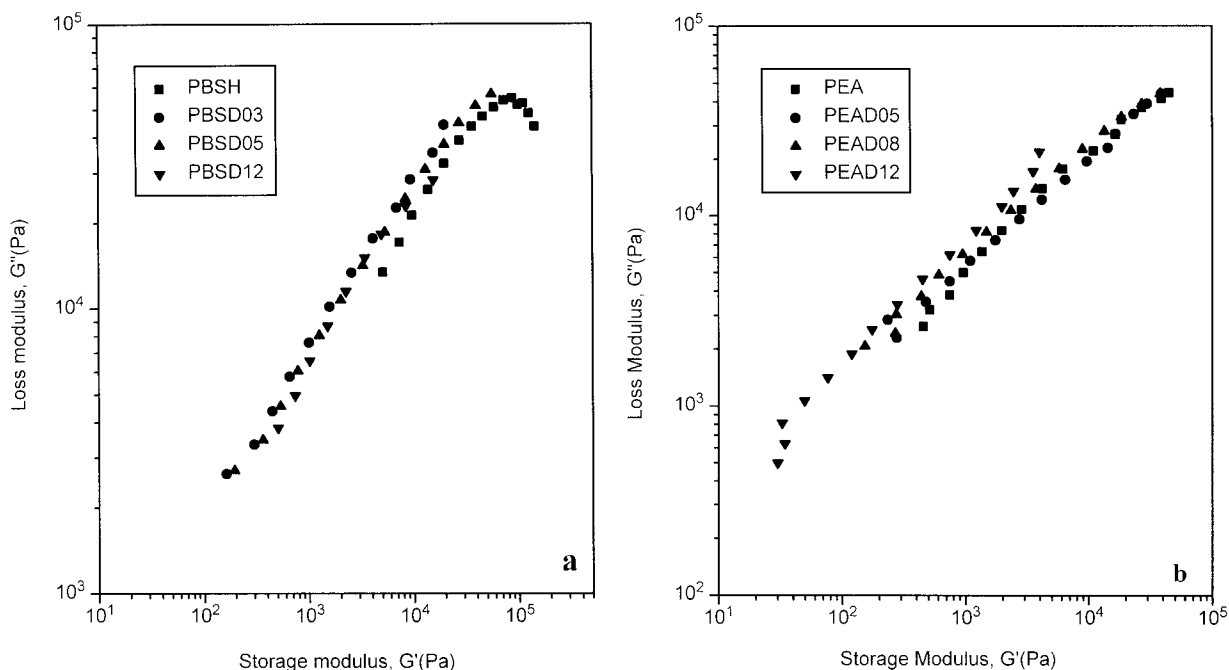


**Figure 5** Dynamic complex viscosity of PBSD12 at different temperatures.

than that of the former ethylene copolymer. The discrepancy between the shear thinning behavior of the aliphatic polyesters and that of the ethylene copolymers comes from the fact that long-chain branches were formed by the CGCT catalyzed copolymerization of ethylene and 1-octene with the *in situ*-produced vinyl terminated polyethylene, due to the chain termination by  $\beta$ -hydride elimination and/or transfer to monomers, because long-chain branched polymers have higher shear sensitivity compared to the linear counterparts. Wang et al.<sup>13</sup> observed long-chain branches up to 0.44/10,000 carbons were formed during ethylene homopolymerization with CGCT in a continuous stirred-tank reactor operating at 35 atm and 140–190°C.

Figure 6 are cole–cole plot results,<sup>14–17</sup> respectively, for PBSD and PEAD. Elasticity of polymers usually increases with increase in the chain branching, but elasticity of PEAD and PBSD was nearly independent of the degree of chain branching.

Table IV summarizes mechanical properties of the polyesters.<sup>18–20</sup> The tensile properties are an average of at least 5 measurements, and the propagation tear resistance results are an average of at least 10 samples. With addition of 1,2-BD or 1,2-DD units to PEA, the tensile strength and the modulus as well as elongation decreased sharply.



**Figure 6** Modified Cole–Cole plot of (a) PBSD and (b) PEAD.

Propagation tear strength of PEAB and PEAD was not enhanced considerably by the introduction of the branches.

As the polymer becomes more and more chain branched, glass transition and melting temperatures go down, and the mechanical strength becomes weaker. However, in contrast to the case of

PEAB or PEAD, it is interesting to observe that elongation and tear strength of PBS were improved significantly without a great loss of tensile strength or modulus by the addition of 1,2-DD units.

Copolymerization of glycerol with 1,4-BD/SA or EG/AA yielded crosslinked polymers when the con-

**Table IV** Mechanical Properties of the Aliphatic Polyesters

Sample	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Propagation Tear Resistance (N/cm)	
				Max	Ave
PEA	312.8	13.2	362.1	12.7	7.0
PEAD05	167.5	5.2	245.3	16.3	13.5
PEAD08	172.3	4.3	114.4	14.9	13.7
PEAD12	174.9	3.5	4.5	6.2	3.3
PBSH	1901.0	37.2	47.0	20.5	15.6
PBSD03	1671.7	40.1	30.6	14.8	13.8
PBSD05	1512.4	30.9	69.0	25.6	19.8
PBSD12	1222.8	27.4	328.0	51.3	40.6
PEAB04	254.4	12.1	248.3	25.1	14.5
PEAB09	227.1	10.7	153.6	14.8	9.7
PEAB15	119.0	5.3	71.0	6.7	4.6
PBSG03	575.6	30.2	13.2	32.4	32.4
PBSG05	310.8	8.3	12.8	—	—
PEAG02	314.4	9.2	48.0	11.3	9.7
PEAG04	290.9	8.0	28.8	7.0	5.9



tent of glycerol in the reaction medium was above 0.12 mol/mol of diacid. The addition of small amount of glycerol units decreased elongation without any amelioration of tensile strength, tensile modulus, and tear strength. In contrast, Hujanen-Vainio et al.<sup>21</sup> found tensile modulus and elongation of  $\epsilon$ -caprolactone/D,L-lactide copolymers were almost independent of the chain branching.

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