Melt Polymerization of Copoly(ethylene terephthalate–imide)s and Thermal Properties

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SYNOPSIS

Copoly(ethylene terephthalate–imide)s (PETI) were prepared by melt polycondensation of bis(2-hydroxyethyl)terephthalate (BHET) and imide containing oligomer, i.e., 4,4'-bis[(4-carbo-2-hydroxyethoxy)phthalimido]diphenylmethane (BHEI). The apparent rate of polycondensation reaction was faster than that of homo poly(ethylene terephthalate) (PET) due to the presence of imide units. The PETI copolymers with up to 10 mol % of BHEI unit in the copolymer showed about the same molecular weight and carboxyl end group content as homo PET prepared under similar reaction conditions. The increase in T_g of copolymer was more dependent on molar substitution of BHEI than on substitution of BHEN, reaching 91°C with 8 mol % BHEI units in the copolymer from T_g = 78.9°C of homo PET. In the case of PETN copolymer, 32 mol % of bis(2-hydroxyethyl)naphthalate (BHEN) units gave T_g of 90°C. The maximum decomposition temperature of PETI copolymer was about the same as that of homo PET by TGA analysis. The char yield at 800°C was higher than that of homo PET. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the more commercially important polymers used as fiber, film, and bottles. Aromatic polyimides are well known for their excellent thermal stability.[1-3] Many papers have appeared on poly(ester–imide)s, to address processing and solubility improvements of polyimides through incorporation of ester linkages.[4-7] this paper describes the synthesis of copoly(ethylene terephthalate–imide)s from bis(2-hydroxyethyl)terephthalate (BHET) and imide containing oligomer, 4,4'-bis[(4-carbo-2-hydroxyethoxy)phthalimido]diphenylmethane (BHEI) by direct melt polycondensation, the preparation method of PET homopolymer. The emphasis here was on the incorporation of BHEI units as a minor constituent in order to maintain the same molecular weight, carboxyl end group content, and crystallization behavior of homo PET. The higher T_g poly(ester–imide) should yield superior performance over PET for the hot filling of blow moulded bottles.[8]

EXPERIMENTAL

Materials and Synthesis of Oligomers

Oxydianiline (ODA), trimellitic anhydride (TMA), and methylene dianiline (MDA) were purchased from Tokyo Kasei Organic Chemicals Co. Zinc acetate dihydrate, antimony oxide used as catalysts, and trimethyl phosphate used as heat stabilizer were reagent grades from Aldrich Chemical Co. These chemicals were used as received. Dimethyl terephthalate (DMT), 2,6-dimethyl naphthalate (DMN), and ethylene glycol (EG) were polymerization grades obtained from Kolon Co.

Synthetic routes to intermediates and oligomers are shown in Scheme 1. N,N'-(4,4'-Diphenylmethane)bistrimellitimide (DID) was prepared by a one-step precess[9,10] from MDA and TMA using m-cresol as solvent. Trimellitic anhydride (TMA, 0.26 mol) and methylene dianiline (MDA, 0.13 mol) were reacted at 160°C in a 1-L resin kettle equipped with mechanical stirrer and condenser using 500 mL of m-cresol as solvent (Scheme 1). After 6 h reaction, a yellow solid was formed. The precipitate (DID) was filtered and washed with methanol and recrystallized in dimethylformamide. The replacement of
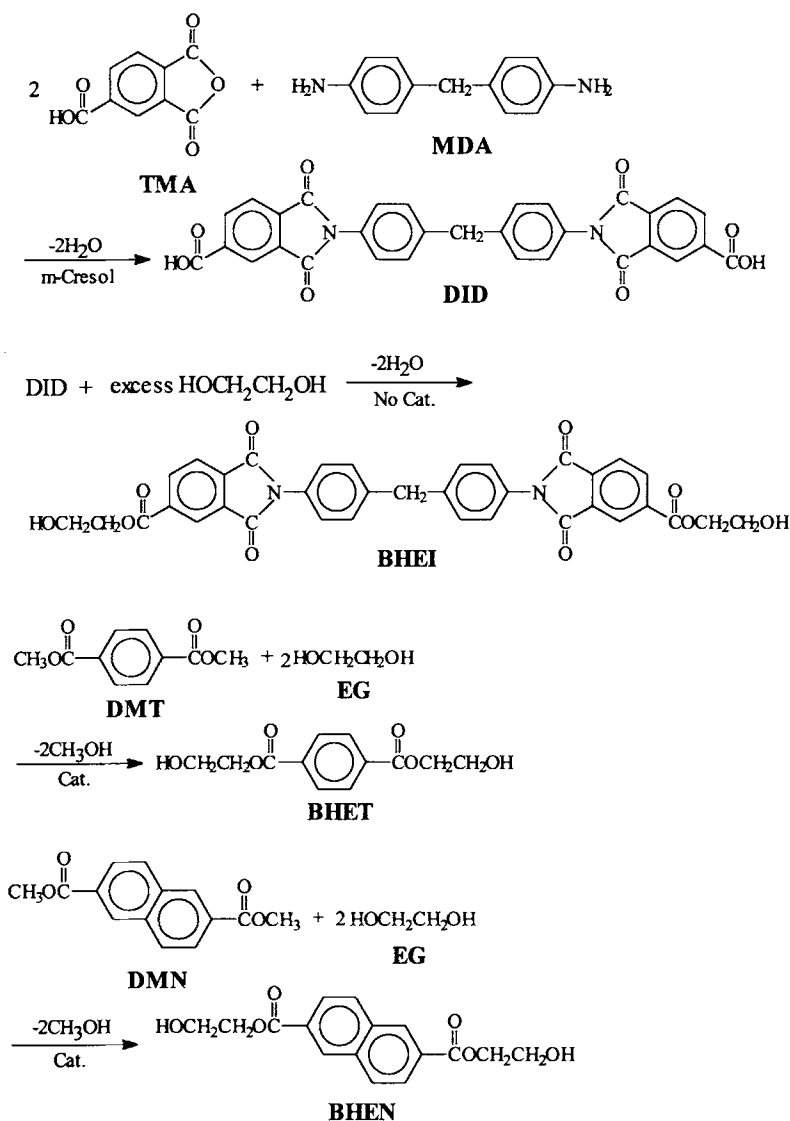
Scheme 1   Synthetic routes to DID, BHEI, BHET, and BHEN.

MDA with ODA in this reaction gave N,N'-(4,4'-diphenylether)bistrimellitimide (DID-2). For the synthesis of BHEI, 0.08 mol of DID was reacted with 3.2 mol of EG in a 1-L resin kettle at 198°C. After the reaction mixture became clear (3 h), it was allowed to react further for 1 h. The product was cooled and poured in excess methanol still hot. The white precipitate (BHEI) was filtered and washed again with methanol to remove excess EG and then finally recrystallized in 1,1,2,2-tetrachloroethane. BHET and bis(2-hydroxyethyl)naphthalate (BHEN) oligomers were prepared by ester interchange reaction of DMT or DMN with EG at the mole ratio of 1 : 2.2 with zinc acetate dihydrate

(100 ppm) as catalyst.[11] DMT (or DMN) and EG were charged in the 1-L resin kettle and the mixture was heated to 190°C. After the mixture was melted, it was stirred and gradually heated to 230°C while collecting methanol from the condenser. When the collected methanol exceeded 95% of the theoretical amount, the product (BHET or BHEN) was poured into an aluminum pan for solidification.

Melt Polycondensation

PETI copolymers were synthesized by transesterification of BHET and BHEI oligomers (from 98/2 to 90/10 mol %). Copoly(ethylene terephthalate–

naphthalate)s (PETN) were synthesized from BHET and BHEN oligomers (from 95/5 to 70/30 mol %) as shown in Scheme 2. BHET/BHEI or BHET/BHEN oligomer mixtures were pulverized and placed in a cylindrical glass tube equipped with a mechanical stirrer and a vacuum line. Sb_2O_3 catalyst (200 ppm) and trimethyl phosphate thermal stabilizer (300 ppm) based on 200 g of copolymer product were added. The reaction mixture was melted by raising the temperature of the oil bath to 240°C. After melting, the mechanical stirrer was turned on and the reaction temperature was further increased to 280°C with partial vacuum applied over a period of about 40 min (finally ca. 1 mm Hg). At this moment the rotating speed of the stirrer was set to 150 rpm and the decrease of rotating speed due to the viscosity build-up was measured with a tachometer and recorded until the reaction stopped at the stirrer speed of 40 rpm. The resulting polymer melt was forced out of glass tube into a water pool by applying pressure with N_2.
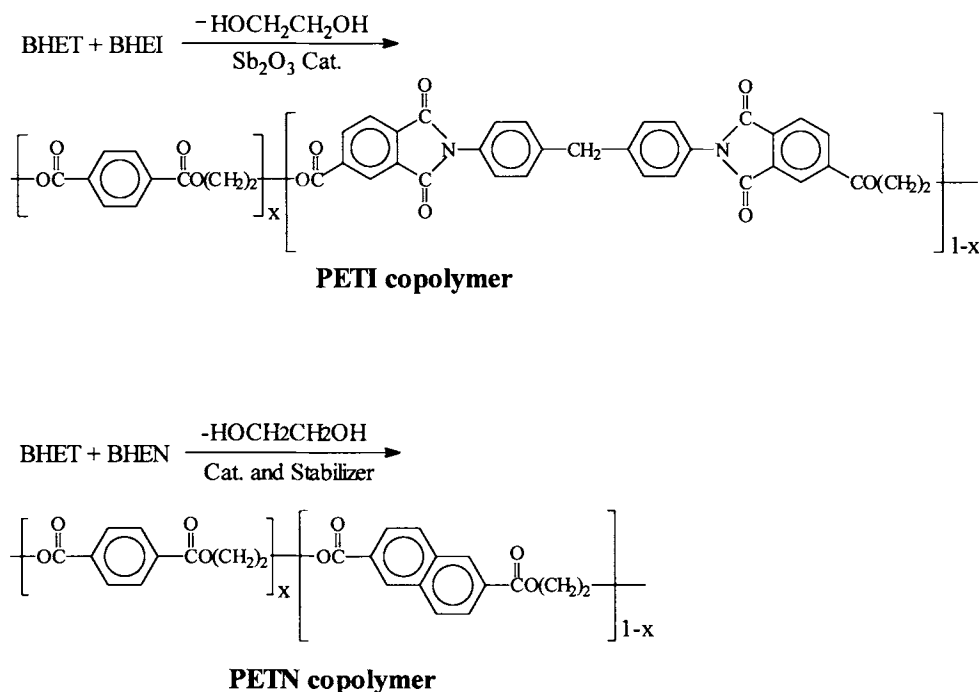
Characterization

The PETI and PETN copolymer samples were purified by Soxhlet extraction with methanol and dried in a vacuum oven for more than 48 h at room tem-

perature prior to characterization. Infrared spectra were recorded with a Midac FTIR spectrophotometer. Mass spectra were obtained with a Shimadzu QP-1000A mass spectrometer. ^{1}H-NMR spectra of copolymer samples were obtained with a Bruker 300-MHz spectrometer (model AM-300) in a mixture solvent $CDCl_3$: CF_3CO_2D (3 : 1 by volume).[12] The molecular weights of copolymers were measured using a Waters Basic GPC against polystyrene standards at 100°C with two E-linear (HT) columns and o-chlorophenol as eluent. A Perkin-Elmer DSC-7 differential scanning calorimeter was employed to determine thermal transition temperatures. Viscosity measurement was made with a Ubbelohde viscometer at 35°C in o-chlorophenol solvent. Carboxyl end group analysis was carried out according to a standard titration method.[13]

RESULTS AND DISCUSSION

Characterization of Intermediates and Oligomers

Elementary analysis data of DID were C 68.23, H 3.32, N 5.13 (calculated), and C 68.58, H 3.43, N 4.94 (found). Mass spectrum of DID showed m/z = 546 corresponding to molecular ion peak. IR spec-

PETI copolymer

PETN copolymer

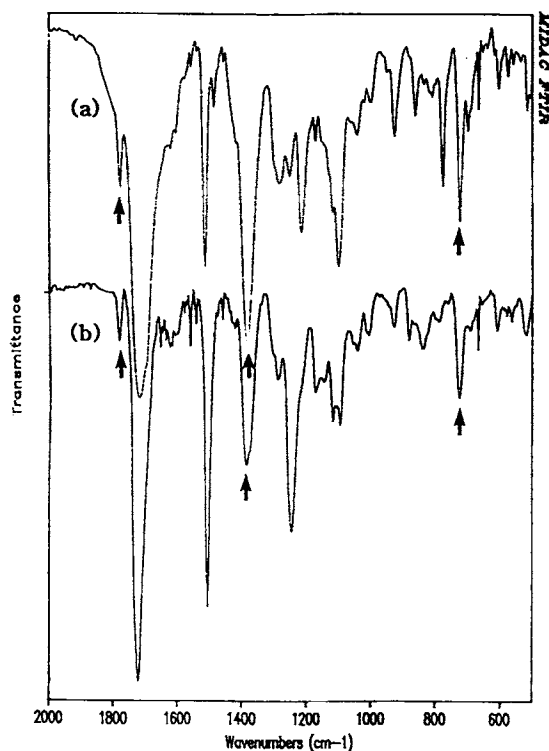**Scheme 2** Polycondensation of BHET/BHEI and BHET/BHEN.

Figure 1   FTIR spectra of DIDs: (a) DID, (b) DID-2.

tra of DIDs showed characteristic imide group absorption peaks at 1780, 1384, and 723 cm^{-1} (Fig. 1). DSC thermogram of DID showed a sharp single melting peak at 367°C. From these data, it was con-

firmed that DID was synthesized by a one-step process. Elementary analysis data of BHEI from DID were C 66.24, H 4.13, N 4.41 (calculated), and C 65.24, H 4.03, N 4.25 (found). Melting temperature of BHEI was 236°C by DSC. ^{1}H-NMR spectrum of BHEI from DID is shown in Figure 2 with the corresponding peak assignments.[7] BHET and BHEN oligomers were prepared according to the previously reported process.[11]

Polycondensation Reaction

The extent of reaction could be conveniently monitored by the change in rotating speed of the stirring shaft. A slowing speed indicated the increase of viscosity of the reaction mixture. The decrease of rotating speed shown in Figure 3 suggested that polycondensation reaction proceeded faster in the case of PETI copolymer compared to the PET homopolymer. This may be due to the presence of electron-withdrawing imide groups in the transesterification step.[14] The reaction, however, did not appreciably proceed without Sb$_2$O$_3$ catalyst as shown in Figure 4.

Characterization of Copolymers

Copolymer composition of PETI samples were obtained from 300 MHz ^{1}H-NMR analysis. The assignment of peaks (Fig. 5) was based on the ^{1}H-

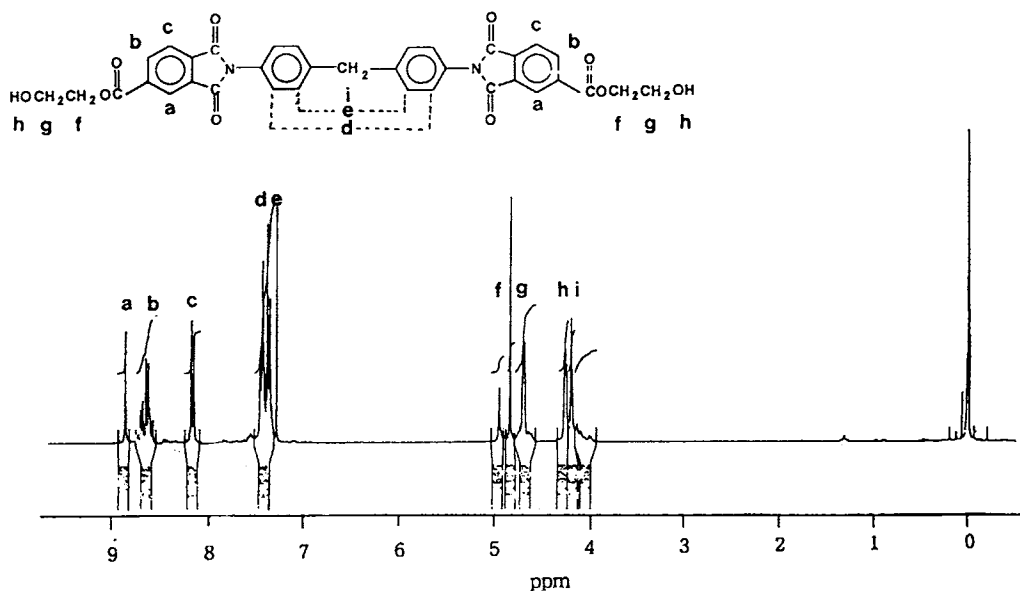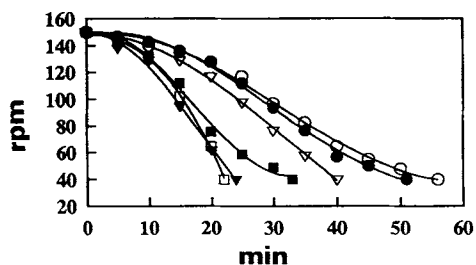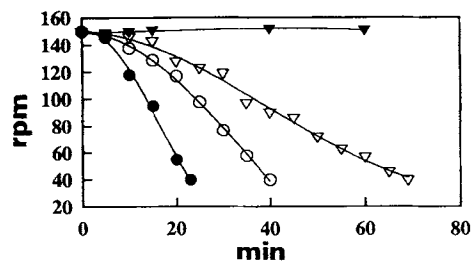**Figure 2** ^{1}H-NMR spectrum of BHEI.

Figure 3 Polycondensation reaction time vs. rpm change [Sb_2O_3 100 ppm: (○) PET, (●) PETI-2, (▽) PETI-4, (■) PETI-6, (▼) PETI-8, (□) PETI-10].

Figure 4 Effect of catalyst content on polycondensation of PETI-4 [Sb_2O_3: (▼) 0 ppm, (▽) 50 ppm, (○) 100 ppm, (●) 200 ppm].

NMR peaks of BHEI oligomer and similar polyesterimides previously reported.[7] The ratio of area (m) due to protons from DMT and TMA acid unit (labeled a, b at 8.17 ppm) to area (n) from MDA diamine unit (labeled c, d at 7.34 ppm) yielded eq. (1).

$$[4 + 2(1 - x)] : [8(1 - x)] = m : n$$

$$x = (4m - n)/(4m + n)$$

BHEI unit in copolymer (mol %)

$$= (1 - x) \times 100 \quad (1)$$

Copolymer compositions were in good agreement with the corresponding feed ratios as shown in Table I. GPC molecular weights and intrinsic viscosity data of PETI and PETN samples are also shown in Table I. The intrinsic viscosity and carboxyl end group content of copolymers were close to those of PET homopolymer. From Table I it may be concluded that PETI and PETN are prepared from a direct melt copolymerization of BHEI (or BHEN) and BHET oligomer with minimal changes in a typical PET polymerization procedure and equipment. The presence of imide groups in BHEI did not interfere with transesterification reaction (e.g., hydrolysis of
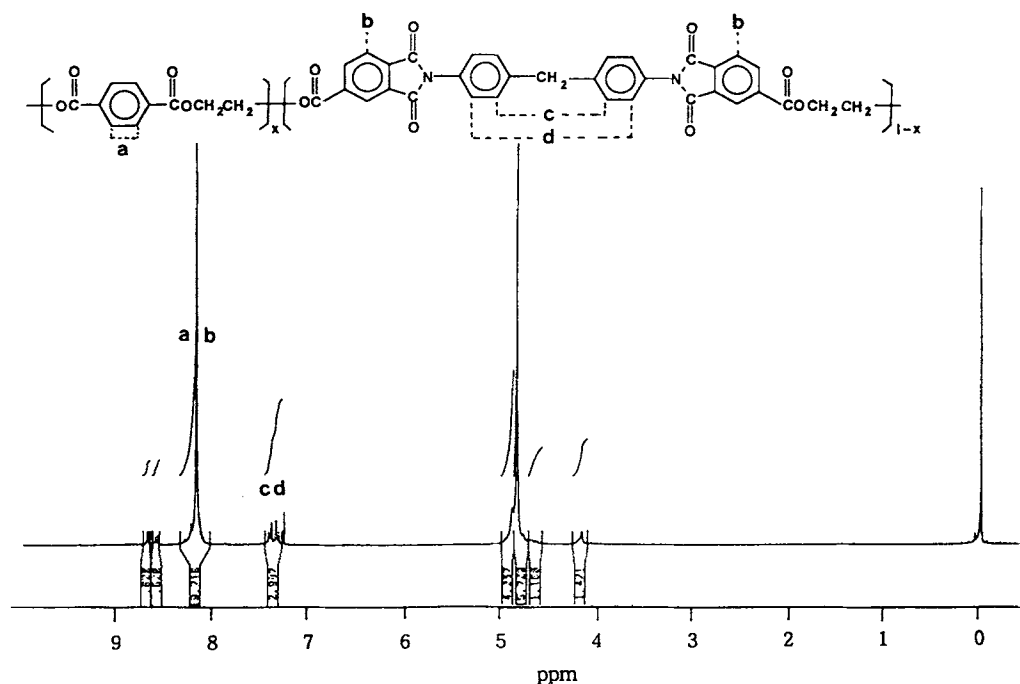
Figure 5 ^{1}H-NMR spectrum of PETI-10.

Table I   Copolymer Composition, M_ws, Intrinsic Viscosity (IV), and Carboxyl End Group Content of PETI and PETN Copolymers

Sample No.	BHET/BHEI Ratio[a]		GPC			IV[b]	Carboxyl End Group (eq/10^6 g)
	Feed	Copolymer	M_n	M_w	PDI		
PET	100/0	100/0	31600	67100	2.12	0.65	18.0
PETI-2	98/2	98.1/1.9	21600	47500	2.20	0.60	20.4
PETI-4	96/4	96.2/3.8	24800	59200	2.39	0.61	16.5
PETI-6	94/6	94.1/5.9	26700	68900	2.58	0.62	20.1
PETI-8	92/8	92.7/7.3	26100	69800	2.68	0.62	22.0
PETI-10	90/10	90.4/9.6	24600	66300	2.69	0.59	19.0
PETI-4-2[c]	96/4	96.1/3.9	28500	68800	2.42	0.63	16.6

Sample No.	BHET/BHEN Ratio		GPC			IV	Carboxyl End Group (eq/10^6 g)
	Feed	Copolymer	M_n	M_W	PDI		
PETN-5	95/5	96/4	29700	62900	2.1	0.60	19.2
PETN-10	90/10	89/11	28000	58500	2.1	0.59	18.7
PETN-20	80/20	81/19	27800	58500	2.1	0.63	20.3
PETN-30	70/30	67/33	25600	53200	2.1	0.58	21.6

[a] BHEI: 4,4-bis[(4-carbo-2-hydroxyethoxy)phthalimido]diphenylmethane.

[b] With o-chlorophenol as solvent at 35°C.

[c] BHEI-2: 4,4-bis[(4-carbo-2-hydroxyethoxy)phthalimido]diphenylether.

imide group or crosslinking). This seemed to be due to the high temperature stability of DID intermediate (T_m = 367°C). The molecular weight of PETI 4-2, made from more flexible BHEI-2 oligomer based on ODA, was found to be slightly higher than that of MDA counterpart (PETI-4).

Thermal Properties of Copolymers

Typical DSC thermograms of PETI samples are shown in Figure 6. The thermal transition temperatures and enthalpy data of copolymers are summarized in Table II. Glass transition temperature of the PETI copolymer increased as BHEI content increased, indicating the effect of stiffer aromatic imide units incorporated in the chain. The cold crystallization temperature (T_{cc}) also increased with increasing BHEI units in the copolymer. The T_m and ΔH_m values of PETI copolymers, however, decreased as the imide units in the copolymers increased. This was considered to be due to the incorporation of noncrystallizable impurity (BHEI units) in the copolymer. At about 10 mol % BHEI unit in the copolymer, crystallization could not be detected by DSC with a scan rate of 20°C/min.
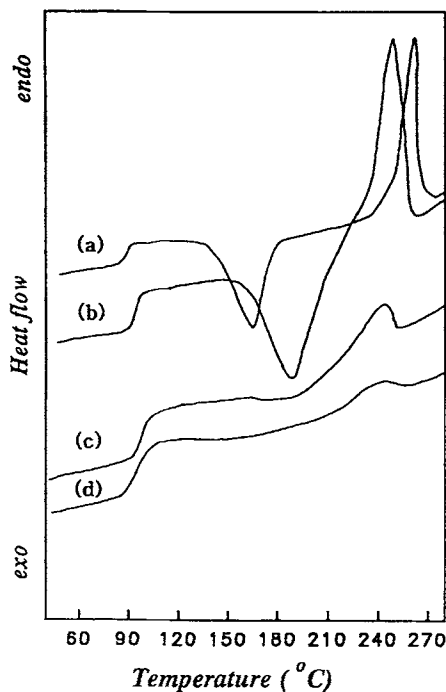
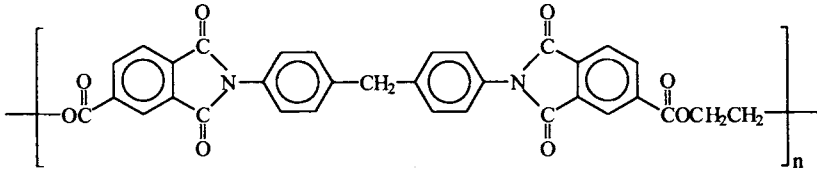**Figure 6**   DSC thermograms: (a) PET, (b) PETI-4, (c) PETI-8, (d) PETI-10.
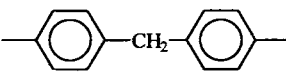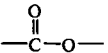
Table II   DSC Thermal Data of PETI Copolymers

Sample No.	Copolymer Comp. BHET/BHEI[a]	T_g (°C)	T_{cc} (°C)	T_m (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)
PET	100/0	78.9	154.1	252.5	−34.64	37.37
PETI-2	98/2	81.7	160.3	248.1	−34.74	34.11
PETI-4	96/4	85.2	179.1	243.4	−29.22	26.97
PETI-6	94/6	88.0	186.2	236.3	−7.67	9.33
PETI-8	92/8	90.3	181.5	231.7	−4.84	5.31
PETI-10	90/10	91.6	—	225.7	—	0.89
PETI-4-2[b]	96/4	85.2	180.8	242.2	−27.21	27.08

[a] BHEI: 4,4-bis[(4-carbo-2-hydroxyethoxy)phthalimido]diphenylmethane.
[b] BHEI-2: 4,4-bis[(4-carbo-2-hydroxyethoxy)phthalimido]diphenylether.

Table III   Calculation of T_g of Polyesterimide Homopolymer by van Krevelen's Equation

Group	Y_{gi}	M_i
	2 × (95	145.1)
	65	166.2
	2 × (13.3	44.0)
	2 × (4.3	14.0)
	$\Sigma Y_{gi}=290.6$	$M=572.4$

$$T_g = \frac{\sum Y_{gi} \times 1000}{M} = \frac{290.6 \times 1000}{572.4} = 507.68K = 234.68°C$$

Table IV Comparison of Experimental and Calculated T_g Values of PETI Copolymers

| Sample No.	W_1	W_2	T_g from Fox Eq. (°C)	T_g from Exp. (°C)
PET	1	0		78.91
PETI-2	0.9415	0.0585	82.10	81.70
PETI-4	0.9085	0.0942	84.14	85.22
PETI-6	0.8625	0.1375	86.84	87.97
PETI-8	0.8216	0.1784	89.51	90.34
PETI-10	0.7828	0.2172	92.20	91.55
PEI	0	1		234.68[a]

[a] Estimated value from van Krevelen's equation.

The change of T_gs of copolymers was examined by Fox's eq. (2)

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \qquad (2)$$

where T_g = glass transition temperature of copolymer T_{g1}, T_{g2} = glass transition temperature of each homopolymer W_1, W_2 = weight fraction of each component in copolymer.

T_g values of homo-polyesterimide (234.7°C) was estimated by using van Krevelen's equation[15] and group contribution constants as shown in Table III. It was not possible to synthesize homo-polyesterimide by direct melt polymerization of BHEI oligomer due to the excessive viscosity build-up even at 300°C.

As observed from the data in Table IV and the plot in Figure 7, the experimentally determined T_gs
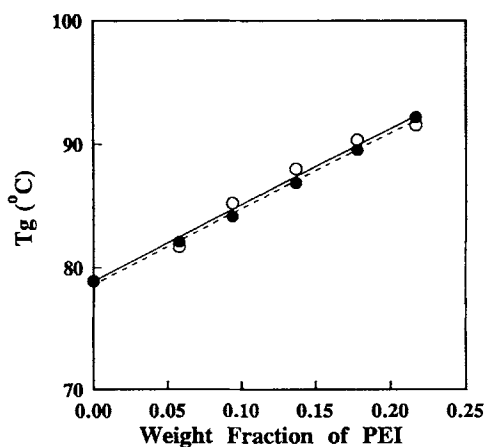
Figure 7 Effect of imide content on T_g of PETI copolymer: (O) experimentally determined T_g, (●) calculated T_g from Fox's equation.
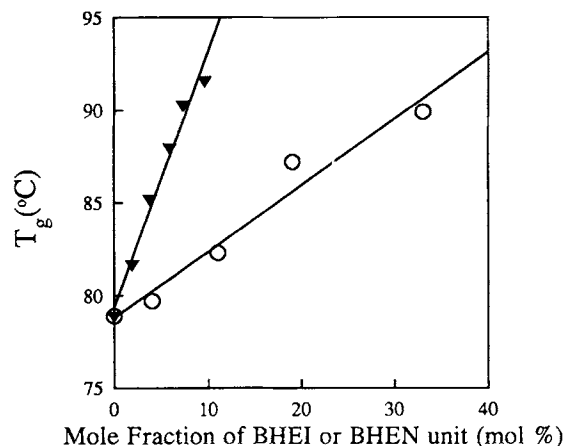
Figure 8 Comparison of T_g of PETI (▼) and PETN (O) copolymers.

of PETI samples were in good agreement with Fox's equation. The change of T_gs of PETI and PETN samples were compared in Figure 8 with mole fraction of BHEI or BHEN unit in the copolymer. It can be seen from Figure 8 that the increase in T_g is more dependent on molar substitution of BHEI than on substitution of BHEN. Since the crystallization property of PETI was not affected so much up to 4 mol % of the BHEI unit in the copolymer, this type of poly(ester–imide) may be a good candidate for PET bottles for use in the hot filling process.

TGA data of PETI-10 sample were compared with that of the PET homopolymer in Table V. Although the incorporation of imide unit in the copolymer was effective in increasing glass transition temperature, its influence on the decomposition temperature of copolymer was not significant. This may be interpreted by the preferential cleavage of weaker ester units in the copolymer chain.[6] The residue at 800°C after thermal decomposition, however, was more in the case of PETI copolymer than that of PET homopolymer.

Table V Comparison of TGA Data of PET and PET-10 Copolymer (N₂ Atmosphere)

Sample No.	IDT^a (°C)	$PDT_{max}{}^b$ (°C)	$Y_{c(000°C)}{}^c$ (%)
PET	455.9	480.9	11.6
PETI-10	457.2	480.2	19.0

[a] Initial decomposition temperature.
[b] Maximum polymer decomposition temperature.
[c] Char yield at 800°C.

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