

# Structural Characterization and Thermal Properties of Poly(ethylene terephthalate) Copolymers Containing 2-Butyl-2-ethyl-1,3-propanediol

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**ABSTRACT:** Poly(ethylene terephthalate) copolymers (abbreviated PEBEPT) containing 2-butyl-2-ethyl-1,3-propanediol (BEPD) for the whole range of compositions were prepared by bulk polycondensation of either terephthalic acid or dimethyl terephthalate as the diacid monomer with mixtures of ethylene glycol and BEPD. Polymer intrinsic viscosities varied from 0.4 to 0.8 dL/g with weight-average molecular weights oscillating between 25,000 and 90,000. All the copolymers were found to have an almost ideal random microstructure. Melting and glass-transition temperatures of the PEBEPTs decreased with the content in BEPD, whereas

their thermal stability was barely affected by composition. The crystallinity and isothermal crystallization rate of the PEBEPTs rapidly decreased with the incorporation of BEPD. X-ray diffraction revealed that the triclinic crystal structure of PET was retained in the copolymers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1077–1086, 2002

**Key words:** poly(ethylene terephthalate) (PET) copolymers; polyesters; 2-butyl-2-ethyl-1,3-propanediol copolyesters; crystallization; structure

## INTRODUCTION

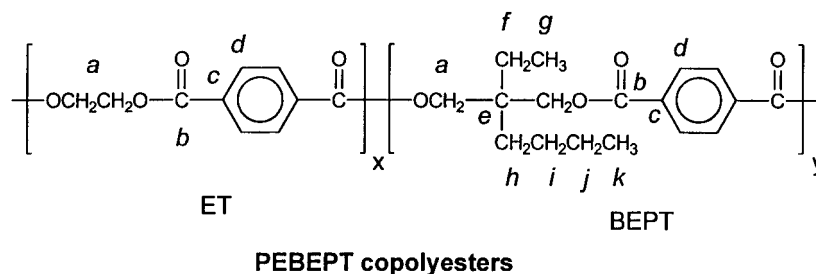
The marked tendency toward crystallization showed by poly(ethylene terephthalate) (PET) constitutes a serious shortcoming for the expansion of this polymer to new application fields in which material transparency is a factor of primary importance. Copolymerization with minor amounts of a second glycol or diacid comonomer is an approach commonly used to make PET less crystallizable. Usually a minor amount of the comonomer is incorporated in PET to reduce the mobility of the chains and to disturb crystal packing without significantly changing the overall pattern of properties of the polymer. Both diacid and diol comonomers have been used for this objective with more or less successful results. Copolymers based on isophthalic acid and 2,6-naphthalene dicarboxylic acid are among the higher qualified examples of the former group.<sup>1,2</sup>

A wide collection of diols has been explored to generate new PET copolyesters with modified prop-

erties.<sup>3–6</sup> Most of them are alkyl-substituted derivatives varying either in the length of the alkyl side groups or in the position of the substituents in the diol.<sup>4,5</sup> Earlier investigations explored the use of 2,3-dialkyl-1,4-butanediols with alkyl side groups longer than butyl.<sup>4</sup> Later, 1,3-propanediol and 2,2-dialkyl-1,3-propanediols with alkyl groups shorter than butyl were examined by Kiyotsukuri et al.<sup>5</sup> In that study, a comparative evaluation of a number of properties was carried out for a variety of substituents. The resulting copolymers were found to present less crystallinity than that of PET and enhanced alkali resistance and dyeability. Among them, 2-butyl-2-ethyl-1,3-propanediol (BEPD) appeared to be the most efficient comonomer to modify the genuine thermal properties of the PET homopolymer. These results, together with the commercial accessibility of BEPD, have made BEPD-based PET copolymers highly attractive for their potential use in the industrial production of highly transparent sheets and plates with greater thickness. In this study we report on these copolymers (abbreviated PEBEPT, Scheme 1), which should be considered a prolongation of the pioneer work reported by Kiyotsukuri et al.<sup>5</sup> A series of nine PEBEPT copolymers, covering a wide range of compositions in addition to the homopolymer entirely made of BEPD, were prepared using two dif-

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Scheme 1 PEPEPT copolyesters.

ferent polycondensation procedures and their thermal properties were systematically studied. Special emphasis has been given to determine the microstructure of the copolymers and to quantify their crystallizability for the relevance that these features have to their new potential applications. Also, the crystalline structure of the copolymers has been examined with regard to PET.

## EXPERIMENTAL

### Materials and measurements

1,4-Dimethyl terephthalate (DMT) (99+%) and 2-butyl-2-ethyl-1,3-propanediol (BEPD, 99+%) were purchased from Sigma-Aldrich Co. Both comonomers were used without further purification. Ethylene glycol (EG, 99+%, Sigma-Aldrich Co.) was reagent grade and used as received. Tetrabutyl titanate (TBT) catalyst (Merck-Schuchardt, Darmstadt, Germany) was used without further purification. Solvents used for purification and characterization were all of either technical or high purity grade, and were used as received. For the polymerization process based on the esterification of terephthalic acid, industrial raw materials (PTA, EG, BEPD, and  $\text{Sb}_2\text{O}_3$ ) were used.

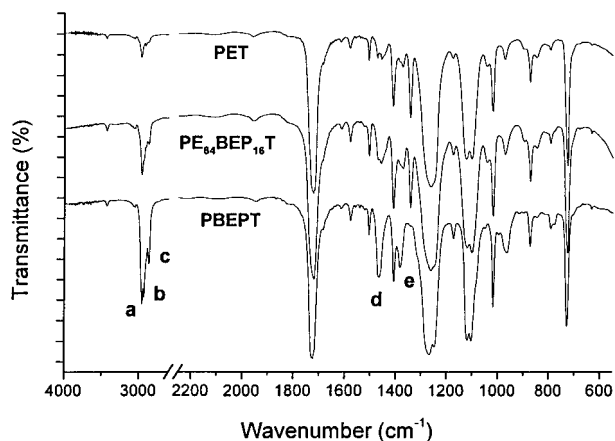
Infrared spectra were obtained on a Perkin-Elmer 2000 FTIR spectrophotometer at room temperature from films cast from 1,1,1,3,3,3-hexafluoro-2-propanol solutions. For each sample, 64 scans at a resolution of  $2\text{ cm}^{-1}$  were collected and signal-averaged.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were recorded on a Bruker AMX-300 spectrometer at  $25.0^\circ\text{C}$  operating at 300.1 and 75.5 MHz, respectively. Polyesters and copolyesters were dissolved in deuterated trifluoroacetic acid (TFA) (8/1 v/v) and spectra were internally referenced to tetramethylsilane (TMS). About 10 and 50 mg of sample dissolved in 1 mL of deuterated solvent were used for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. Sixty-four scans were acquired for  $^1\text{H}$  and 1000 to 10,000 for  $^{13}\text{C}$  with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. For quantitative  $^{13}\text{C}$ -NMR analysis of the microstructure, signals arising from the nonprotonated carbons of terephthalic units attached to either EG or BEPD units were used.

The intrinsic viscosities of the polymers dissolved in dichloroacetic acid were measured with a Ubbelohde viscometer thermostated at  $25 \pm 0.1^\circ\text{C}$ . A Waters system (Waters Associates) equipped with a refractive index detector and two  $7.8 \times 300\text{ mm}$  Styragel columns packed with polystyrene (pore size:  $10^3$  and  $10^4\text{ \AA}$ ) was used for GPC analysis. An *o*-chlorophenol/chloroform mixture (1/9 v/v) at a flow rate of 0.5 mL/min was used as the eluent at  $35^\circ\text{C}$ . Molecular weights and molecular weight distributions were calculated against monodisperse polystyrene standards using the Maxima 820 software. Densities were measured by the flotation method at  $20^\circ\text{C}$  using *n*-heptane/tetrachloromethane mixtures.

The thermal behavior of the polyesters was examined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC Pyris 1 calibrated with indium. DSC data were obtained from 4- to 6-mg samples at heating/cooling rates of  $10^\circ\text{C}/\text{min}$  under nitrogen circulation. Isothermal crystallizations were carried out on amorphous melt-quenched filmy samples at  $120^\circ\text{C}$  for 2 h. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-6 thermobalance at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. X-ray diffraction analysis was performed in a modified Statton camera using monochromatic  $\text{CuK}_\alpha$  radiation of  $\lambda = 1.5418\text{ \AA}$  and the diffraction patterns were recorded on photographic flat films.

### General procedure for the preparation of PEPEPT copolyesters

PEPEPTs containing up to 13 mol % of 2-butyl-2-ethyl-1,3-propanediol units were prepared by polycondensation of terephthalic acid (PTA) with mixtures of EG and BEPD. The molar ratio of EG to PTA was fixed in a range from 1.15 to 1.20 and the ratio of BEPD to PTA changed according to the composition selected for the copolymer. Reactions were carried out in two steps. Final temperatures for esterification and polycondensation reactions were adjusted at  $225$  and  $280^\circ\text{C}$ , respectively. The polycondensation step was carried out under increasing vacuum and in the presence of  $\text{Sb}_2\text{O}_3$  as a catalyst. For the preparation of PEPEPT with



**Figure 1** Fourier transform infrared spectra of PET,  $PE_{84}BEP_{16}T$ , and PBEPT with the following indications. The stretching (a–c) and the bending (d, e) absorption bands of  $CH_2$  and  $CH_3$  are indicated.

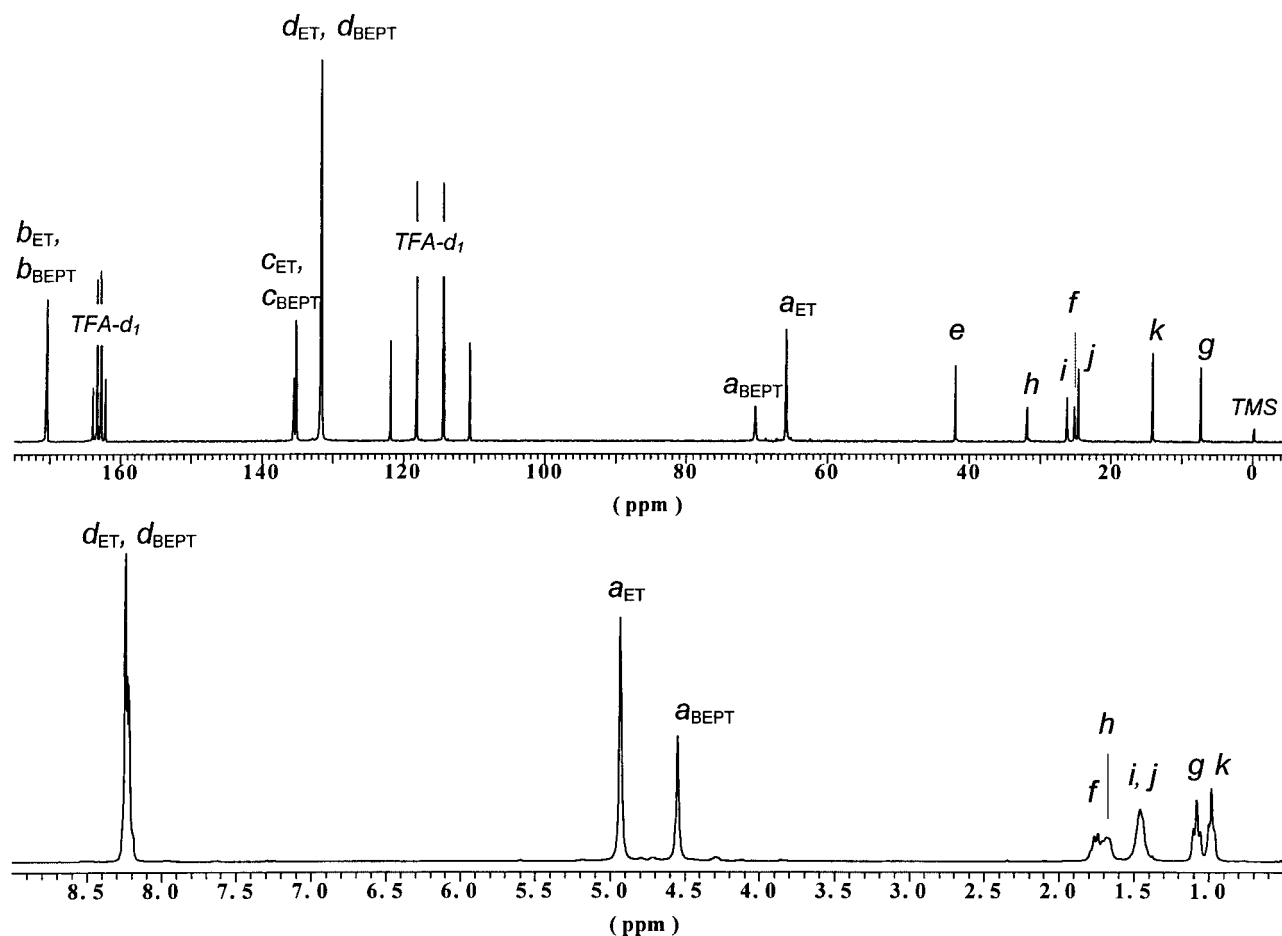
EG-to-BEPD molar ratios of 84 to 16 or less, mixtures of EG, BEPD, and DMT in a 2.2 : 1 molar ratio of the total of two glycols to DMT with approximately 0.6 mmol of tetrabutyl titanate per mole DMT were used. Transesterification and polycondensation reactions

were performed along successive stages with the temperature increasing from 160 to 270°C and with the application of vacuum at the latter stages. The solid mass was dissolved in  $CHCl_3/TFA$  (8/1 v/v) or pure  $CHCl_3$  and the polymer was precipitated with cold diethyl ether, recovered by filtration, and extensively washed with cold methanol and diethyl ether. All samples were dried at 60°C under reduced pressure.

## RESULTS AND DISCUSSION

### Polycondensation

Two different methods were applied for the preparation of the PEBEPT copolyesters studied in this work. In the first method, PTA was condensed with a total excess of the EG and the BEPD glycol in a molar ratio between 1.2 and 1.6, depending on the quantity of BEPD added for each copolymer. In the second method, DMT was used instead of PTA with a molar excess of glycols of 2.2. We previously used the latter method in the preparation of other PET copolymers containing different diacid and diol modified units.<sup>7–10</sup>



**Figure 2** 300.1 MHz  $^1H$ -NMR (bottom) and 75.5 MHz  $^{13}C$ -NMR (top) spectra of  $PE_{65}BEP_{35}T$  recorded in deuterated TFA.

TABLE I  
Composition, Molecular Weights, and Densities of PET, PBEPT, and PEPEPT Copolyesters

Polyester	Feed composition <sup>a</sup> EG/BEPD	Polymer composition <sup>b</sup>		DEG <sup>c</sup> (mol %)	[ $\eta$ ] <sup>d</sup> (dL/g)	Molecular weight		Density <sup>f</sup> (g/mL)
		X <sub>EG</sub>	X <sub>BEPD</sub>			M <sub>n</sub> <sup>e</sup>	PD <sup>e</sup>	
PTA esterification								
PET	100/0	100	0	2.2	0.63	18,300	2.8	1.34
PE <sub>96</sub> BEP <sub>4</sub> T	94/6	95.6	4.4	2.4	0.67	18,400	3.5	1.32
PE <sub>92</sub> BEP <sub>8</sub> T	90/10	92.3	7.7	2.2	0.68	15,800	3.6	1.31
PE <sub>89</sub> BEP <sub>11</sub> T	86/14	89.0	11.0	2.3	0.74	21,300	3.1	1.31
PE <sub>87</sub> BEP <sub>13</sub> T	82/18	86.7	13.3	2.3	0.72	16,700	3.5	1.30
DMT transesterification								
PE <sub>84</sub> BEP <sub>16</sub> T	90/10	84.0	16.0	1.8	0.55	18,400	3.2	1.29
PE <sub>65</sub> BEP <sub>35</sub> T	80/20	65.0	35.0	1.0	0.41	12,600	2.1	1.25
PE <sub>35</sub> BEP <sub>65</sub> T	70/30	35.1	64.9	0.9	0.50	37,100	1.7	1.20
PE <sub>19</sub> BEP <sub>81</sub> T	50/50	18.7	81.3	0.8	0.55	37,500	2.0	1.19
PE <sub>9</sub> BEP <sub>91</sub> T	30/70	8.7	91.3	0.7	0.58	47,400	1.5	1.19
PBEPT	0/100	0	100	0.0	0.65	52,200	1.7	1.18

<sup>a</sup> Molar ratio in the feed.

<sup>b</sup> Determined from the glycolic CH<sub>2</sub> proton resonances observed in <sup>1</sup>H-NMR spectra.

<sup>c</sup> Diethylene glycol content calculated from <sup>1</sup>H-NMR spectra. All copolyesters and PBEPT were found to contain less than 0.4 mol % of di-BEP-glycol.

<sup>d</sup> Intrinsic viscosity measured in dichloroacetic acid at 25°C.

<sup>e</sup> Number-average molecular weights and polydispersities determined by GPC.

<sup>f</sup> Determined for amorphous polymer samples by the flotation method.

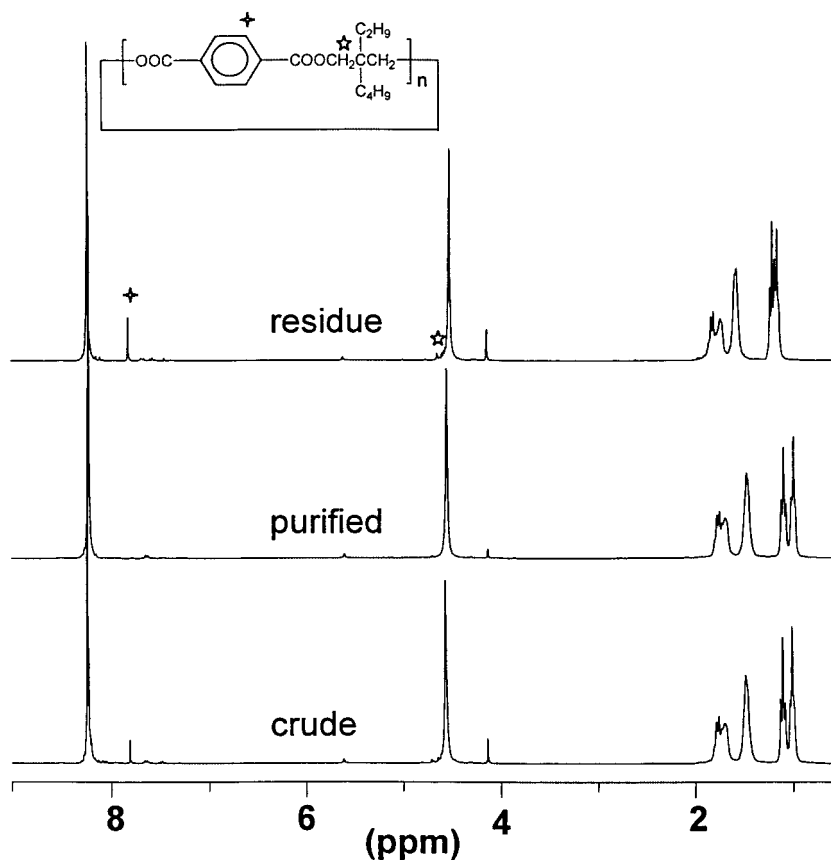
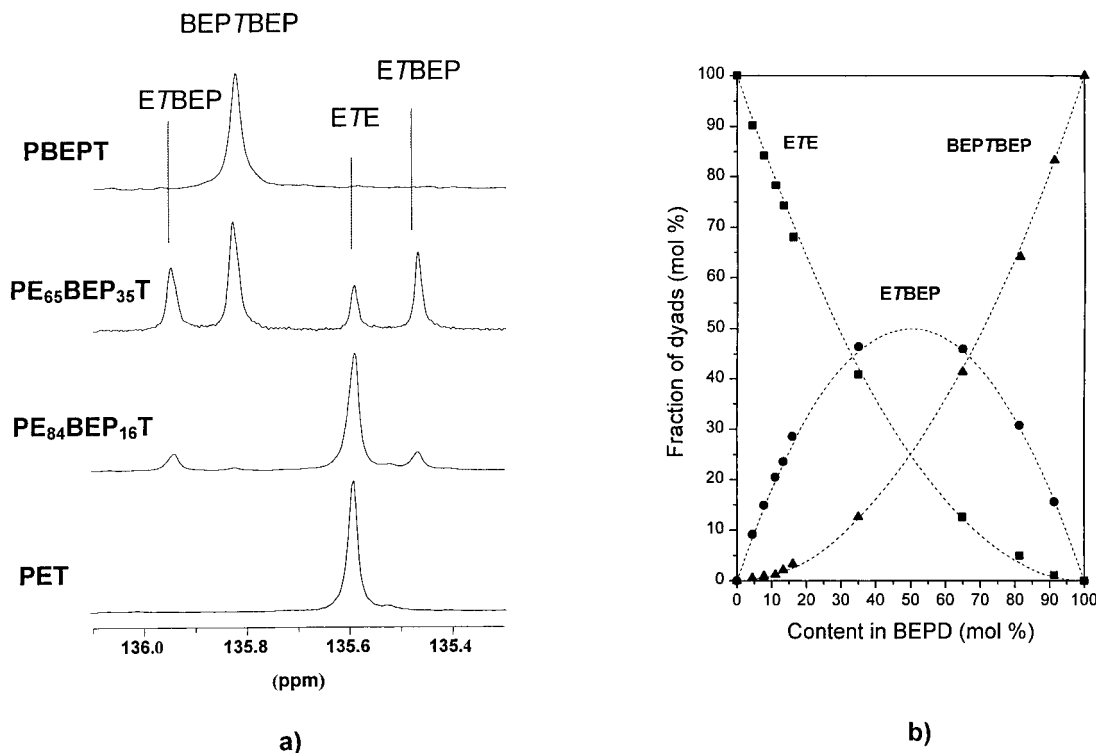


Figure 3 Compared <sup>1</sup>H-NMR spectra of the homopolymer PBEPT before and after reprecipitation and of the remaining soluble fraction.



**Figure 4** (a) Compared  $^{13}\text{C}$ -NMR spectra of the aromatic terephthalic nonprotonated carbons for indicated polyesters and copolyesters. (b) Experimental dyad sequence distributions as a function of the copolyester composition. The lines represent the theoretical distributions calculated by the Bernoullian statistics.

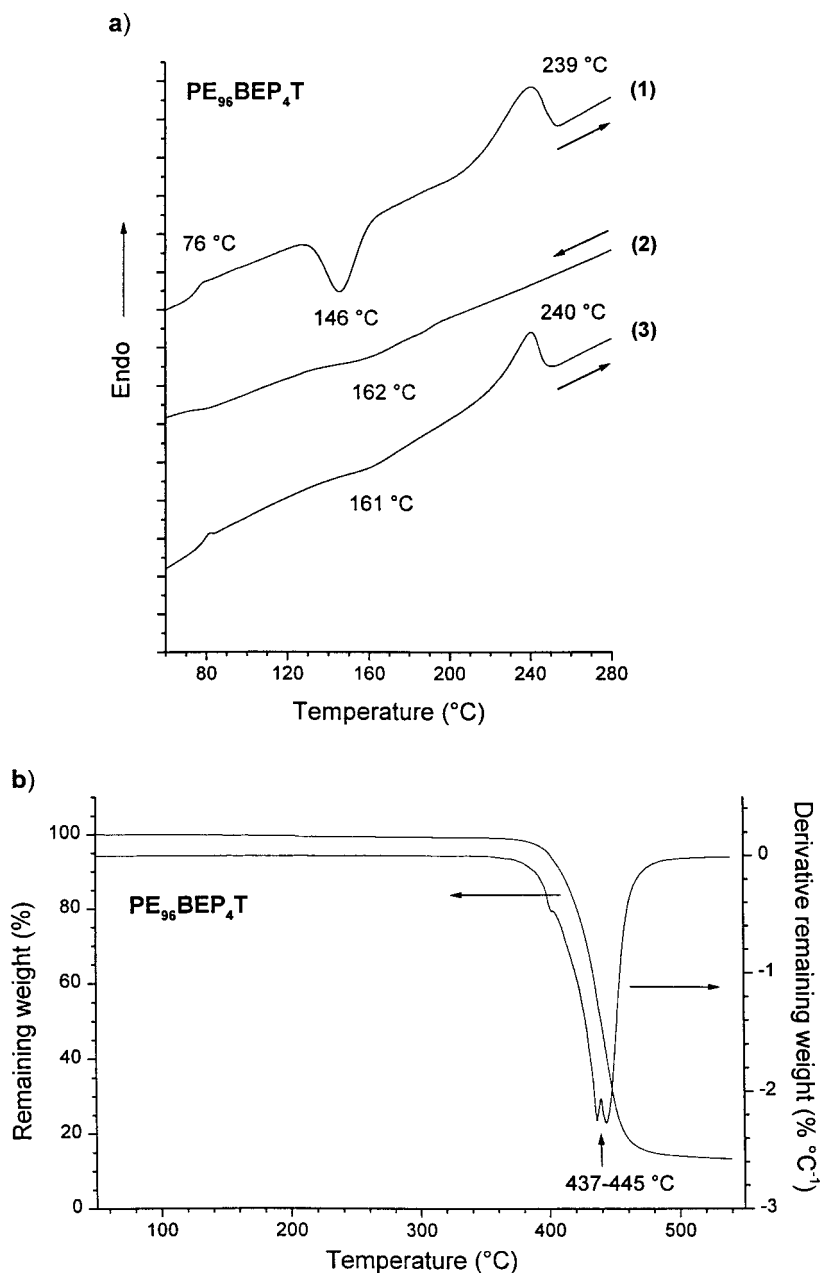
The copolymers resulting from each case were examined by both FTIR and NMR spectroscopies. As expected, FTIR spectra of PET and PEBEPT copolymers appeared to be very similar, the most significant differences among them concerning the alkyl group absorptions. As illustrated in Figure 1, an increase in the intensity of the C—H stretching bands appearing in the  $3000\text{--}2850\text{ cm}^{-1}$  region and of the  $\text{CH}_2$  and  $\text{CH}_3$  deformation bands in the  $1480\text{--}1360\text{ cm}^{-1}$  region were observed with increasing contents of the polymer in 2-butyl-2-ethyl-1,3-propanediol units. The chemical structure of the copolymers could be precisely ascer-

tained by NMR spectroscopy. The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra obtained from  $\text{PE}_{65}\text{BEP}_{35}\text{T}$  with indications of the peak assignments are depicted in Figure 2. Copolymer compositions determined by  $^1\text{H}$ -NMR using the glycolic  $\text{CH}_2$  proton resonances are listed in Table I. A comparison between the feed and copolymer composition data clearly revealed that the incorporation of BEPD in the copolymer largely depended on the procedure used for polycondensation. Although an acceptably good correspondence existed between the comonomer ratio in the feed and in the resulting copolymer for the first method, copolyesters obtained by

**TABLE II**  
Microstructure of PEBEPT Copolyesters<sup>a</sup>

Copolyester	Dyads (mol %)			Average sequence lengths		Randomness, <i>R</i>
	ETE	ETBEP	BEPTBEP	$n_{\text{ET}}$	$n_{\text{BEPT}}$	
$\text{PE}_{96}\text{BEP}_4\text{T}$	90.3 (91.4)	9.2 (8.4)	0.5 (0.2)	20.7 (22.7)	1.1 (1.1)	0.94 (1.00)
$\text{PE}_{92}\text{BEP}_8\text{T}$	84.2 (85.2)	14.9 (14.2)	0.9 (0.6)	12.3 (13.0)	1.1 (1.1)	0.97 (1.00)
$\text{PE}_{89}\text{BEP}_{11}\text{T}$	78.3 (79.2)	20.5 (19.6)	1.2 (1.2)	8.6 (9.1)	1.1 (1.1)	1.01 (1.00)
$\text{PE}_{87}\text{BEP}_{13}\text{T}$	74.3 (75.2)	23.6 (23.0)	2.1 (1.8)	7.3 (7.5)	1.2 (1.2)	0.98 (1.00)
$\text{PE}_{84}\text{BEP}_{16}\text{T}$	68.1 (70.6)	28.6 (26.9)	3.3 (2.5)	5.8 (6.2)	1.2 (1.2)	0.99 (1.00)
$\text{PE}_{65}\text{BEP}_{35}\text{T}$	40.9 (42.2)	46.5 (45.5)	12.6 (12.3)	2.8 (2.9)	1.5 (1.5)	1.01 (1.00)
$\text{PE}_{35}\text{BEP}_{65}\text{T}$	12.6 (12.3)	46.0 (45.6)	41.4 (42.1)	1.5 (1.5)	2.8 (2.8)	1.00 (1.00)
$\text{PE}_{19}\text{BEP}_{81}\text{T}$	5.0 (3.5)	30.8 (30.4)	64.2 (66.1)	1.3 (1.2)	5.2 (5.3)	0.95 (1.00)
$\text{PE}_9\text{BEP}_{91}\text{T}$	1.1 (0.7)	15.6 (15.9)	83.3 (83.4)	1.1 (1.1)	11.7 (11.5)	0.96 (1.00)

<sup>a</sup> Experimental values for the average sequence lengths and randomness were obtained by means of the equations mentioned in text using  $^{13}\text{C}$ -NMR data. Theoretical values (in parentheses) were calculated on the basis of a Bernoullian dyad distribution using the copolyester composition data given in Table I.



**Figure 5** (a) DSC traces of a glassy PE<sub>96</sub>BEP<sub>4</sub>T sample: (1) first heating, (2) cooling, and (3) second heating. (b) TGA trace of PE<sub>96</sub>BEP<sub>4</sub>T and its derivative curve.

the second method were found to be largely enriched in the 1,3-propanediol units. Apparently, important amounts of the more volatile EG escaped under the process conditions used in this case. Nevertheless, the combination of the two methods afforded a series of PEBEPT copolymers covering the range of EG/BEPD molar ratios from 9/91 to 96/4, as well as the homopolymers PET and PBEPT used in this study for comparison purposes.

It is well known that cyclization and etherification side reactions take place, to a greater or lesser extent, along the transesterification and polycondensation reactions in the preparation of PET and PET-derived

polyesters.<sup>4,11</sup> In fact, two small peaks were observed in the 4.1–4.8 ppm region of the <sup>1</sup>H-NMR spectra of PEBEPT, which are indicative of the presence of diethylene glycol units (–O–CH<sub>2</sub>–CH<sub>2</sub>–O–CH<sub>2</sub>–CH<sub>2</sub>–O–) (DEG) in amounts between 0.7 and 2.4 mol. Furthermore, signals attributed to the presence of di(2-butyl-2-ethyl-1,3-propanediol) units in the copolymers were much weaker, indicating that the tendency to etherification of this substituted diol is much lower than that for EG. In addition to these small ether characteristic peaks, other small signals were detected around 4.7 and 7.8 ppm in the <sup>1</sup>H-NMR spectra of PEBEPT. These signals were ascribed to 2-butyl-2-



TABLE III  
Thermal Properties of PET, PBEPT, and PEBEPT Copolyesters

Polyester	DSC <sup>a</sup>				TGA <sup>b</sup>		
	$T_g$ (°C)	$T_{cc}$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_d^c$ (°C)	$T_{as}^d$ (°C)	RW <sup>e</sup> (%)
PET	79	137	253	46.9	413	450	10
PE <sub>96</sub> BEP <sub>4</sub> T	76	146	239	40.3	410	435–445	14
PE <sub>92</sub> BEP <sub>8</sub> T	75	159	231	29.6	411	430–445	11
PE <sub>89</sub> BEP <sub>11</sub> T	75	172	225	16.7	411	425–445	10
PE <sub>87</sub> BEP <sub>13</sub> T	73	172	224	5.4	406	430–445	7
PE <sub>84</sub> BEP <sub>16</sub> T	72	173	209	0.4	407	425–440	15
PE <sub>65</sub> BEP <sub>35</sub> T	65	—	—	—	410	438	11
PE <sub>35</sub> BEP <sub>65</sub> T	59	—	—	—	414	438	8
PE <sub>19</sub> BEP <sub>81</sub> T	59	—	—	—	411	439	6
PE <sub>9</sub> BEP <sub>91</sub> T	58	—	—	—	418	444	6
PBEPT	54	—	—	—	395	441	4

<sup>a</sup> Glass-transition ( $T_g$ , inflection point), cold crystallization ( $T_{cc}$ ), and melting ( $T_m$ ) temperatures and melting enthalpy ( $\Delta H_m$ ) measured from melt-quenched samples by DSC at a heating rate of 10°C/min.

<sup>b</sup> Thermal decomposition parameters determined by TGA at a heating rate of 10°C/min.

<sup>c</sup> Temperature at which a 10% weight loss was observed.

<sup>d</sup> Temperature for maximum degradation rate.

<sup>e</sup> Remaining weight at 550°C.

ethyl propylene terephthalate cyclic oligomers that presumably were formed by cyclization at the earlier stages of polycondensation. As illustrated in Figure 3, the presence of these compounds became apparent in the residue left by the mother solution used for purification of the crude copolymers.

Molecular weight data of PEBEPT are given in Table I. Intrinsic viscosities were found to oscillate between 0.40 and 0.75 dL/g, which corresponds to number-averaged molecular weights comprised in the range of 6000 to 22,000, as calculated with the Mark-Houwink parameters reported in the literature for PET.<sup>12</sup> GPC measurements afforded  $M_n$  values in the 12,600 to 52,200 range and  $M_w$  values ranging from 26,400 to 90,800 with polydispersities between 1.5 and 3.6. It should be noticed that lower molecular weights and higher polydispersities were found as larger EG-to-BEPD ratios were used for the polycondensation. This result is thought to be a consequence of the better fractional separation attained in the purification step of BEPD-enriched copolymers due to the higher solubility of BEPD-containing oligomers.

### Microstructure of PEBEPT copolyesters

The microstructure of the copolyesters was analyzed by <sup>13</sup>C-NMR using the nonprotonated aromatic carbon resonances, which appeared to be sensitive to dyad sequence effects. The evolution of the C1 and C4 carbon signal with the copolymer composition is illustrated in Figure 4(a). By integration of the peaks included in this signal, the distribution of dyads (ETE, ETBEP and BEPTE, and BEPTBEP) could be calculated. On the basis of such data, the number average sequence lengths and the degree of randomness were estimated for each copolymer and compared with

those calculated for an ideal random copolymer with Bernoullian distribution.<sup>13–15</sup>

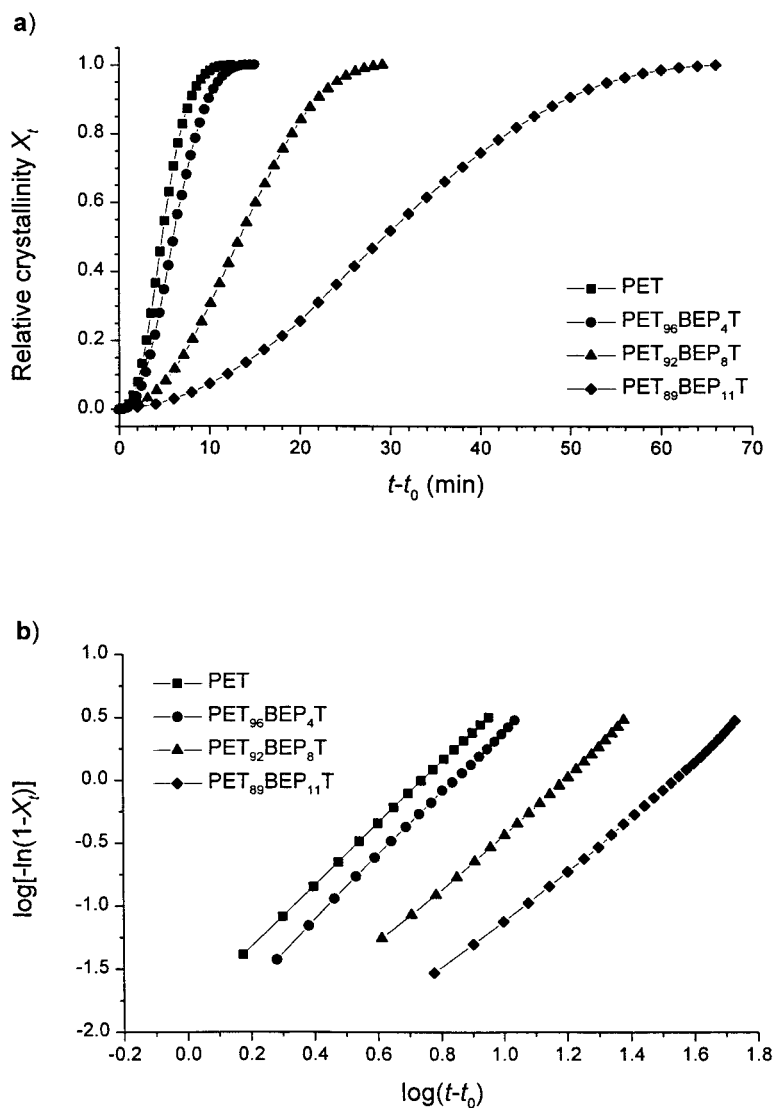
The number-average sequence length of ethylene terephthalic (ET) and 2-butyl-2-ethyl-1,3-propylene terephthalate (BEPT) units,  $n_{ET}$  and  $n_{BEPT}$ , respectively, and the randomness ( $R$ ) of the copolyesters were calculated using the following equations:

$$n_{ET} = \frac{N_{ETE} + \left(\frac{N_{ETBEP}}{2}\right)}{\left(\frac{N_{ETBEP}}{2}\right)}$$

$$n_{BEPT} = \frac{N_{BEPTE} + \left(\frac{N_{ETBEP}}{2}\right)}{\left(\frac{N_{ETBEP}}{2}\right)}$$

$$R = \frac{1}{n_{ET}} + \frac{1}{n_{BEPT}}$$

where  $N_i$  is the molar fraction of every type of sequences. Results from these calculations are given in Table II and illustrated in Figure 4(b), which show that the sequence distribution in PEBEPT copolyesters is statistically at random for the whole range of compositions studied. Furthermore, it was found that the number-average sequence lengths calculated with the <sup>13</sup>C-NMR data were in close correspondence with those calculated for a theoretical random copolymer. It seems therefore that the copolymerization proceeded according to an ideal statistical model, although occurrence of transesterification reactions leading to ran-



**Figure 6** (a) Relative crystallinity  $X_t$  versus crystallization time and (b) Avrami plots for PET and PEBEPT copolyesters isothermally crystallized at 120°C.

domization are also known to occur and their contribution should not be neglected.

#### Thermal behavior and crystal structure of PEBEPT copolyesters

The effects provoked by the incorporation of the branched 2-butyl-2-ethyl-1,3-propylene units in the chain of PET on the thermal behavior of the copolyesters were studied by DSC and TGA. First, amorphous polymer samples obtained by melt-quenching were examined. DSC traces obtained for copolymer  $PE_{96}BEP_4T$  at heating, at cooling, and for the second heating, as well as its TGA trace registered at 10°C/min under an inert nitrogen atmosphere, are shown in Figure 5 for illustration. The characteristic parameters resulting from these measurements are listed in Table

III. The melting ( $T_m$ ) and glass-transition ( $T_g$ ) temperatures were observed to decrease steadily with the content in BEPD. These results are fully consistent with data previously reported by Kityosukuri et al.,<sup>5</sup> although we were unable to observe melting in PEBEPT with BEPD contents greater than 20 mol %. Furthermore, TGA measurements showed that the incorporation of the BEPD units in PET had hardly any influence on the thermal stability of the polymer with the observed differences being within the margin of experimental error.

To evaluate the crystallizability of PEBEPT copolyesters with regard to copolymer composition, amorphous glassy films were isothermally crystallized at 120°C for 2 h. Figure 6(a) shows the evolution of the relative crystallinity versus crystallization time for both PET and crystalline PEBEPT copolymers. No re-



TABLE IV  
Crystallization Parameters of PET and PEBEPT Copolyesters

Polyester	$t_0^a$	Avrami parameters <sup>b</sup>			Thermal properties		
		$n$	$\log k$	$t_{1/2}$	$T_m^c$	$\Delta H_m^c$	$X_c^d$
PET	0.48	2.4	-1.81	4.77	250	41.8	35
PE <sub>96</sub> BEP <sub>4</sub> T	1.09	2.4	-2.06	6.02	241	38.9	32
PE <sub>92</sub> BEP <sub>8</sub> T	8.90	2.3	-2.76	13.22	230	26.9	22
PE <sub>89</sub> BEP <sub>11</sub> T	11.26	2.2	-3.39	29.05	220	23.3	19

<sup>a</sup> Onset crystallization time (min).

<sup>b</sup> Avrami exponent  $n$ , constant of crystallization  $k$  ( $\text{min}^{-1}$ ), and crystallization half-time  $t_{1/2}$  (min).

<sup>c</sup> Melting temperature ( $T_m$ , °C) and enthalpy ( $\Delta H_m$ , J/g) of isothermally crystallized samples registered by DSC at a heating rate of 10°C/min.

<sup>d</sup> Degree of crystallinity estimated from the melting enthalpy against the melting enthalpy of fully crystalline PET ( $\Delta H_m = 119.8$  J/g).

liable data could be obtained for PE<sub>87</sub>BEP<sub>13</sub>T because of the small crystallinity developed by this polymer within the range of times allowed for crystallization.

The resulting sigmoid curves were found to shift to longer crystallization times for PEBEPT with higher contents in BEPD. Estimation of the Avrami parameters was accomplished by means of the double-logarithmic representation of the equation

$$\log[-\ln(1 - X_t)] = \log k + n \log(t - t_0)$$

where  $X_t$  is the relative crystallinity developed at time  $t$ ;  $t_0$  is the onset crystallization time; and  $k$  and  $n$  are the crystallization rate and the Avrami exponent, respectively. The resulting plots, shown in Figure 6(b), illustrate the linear tendency characteristic of primary crystallization. The crystallization parameters calculated from such plots, together with the respective thermal parameters obtained by DSC of the isothermally crystallized polymers, are given in Table IV. It can be clearly seen that the crystallization rate and crystallinity rapidly decayed with the content of BEPD units for the polymer. Note that the incorporation of

about 10 mol % of BEPD makes the crystallization half-time sixfold longer and reduces the crystallinity to near the half-value of PET.

Samples of PEBEPT without signs of crystallinity may be readily prepared by quenching from the melt. Density data of amorphous samples of both homopolymers and copolymers, listed in Table I, show that the density of the copolyesters steadily decreased with the increasing content in BEPD. Such a trend is logical, given that an increase in the free volume of the disordered state should be expected from the incorporation of branched units in the polymer chain. Conversely, samples coming directly from polymerization displayed different degrees of crystallinity according to the composition. Results obtained by powder X-ray diffraction of the pristine samples of PET and PEBEPT copolyesters were consistent with DSC results and data previously reported by other authors.<sup>5</sup> Discrete scattering was observed for the copolyesters containing BEPD units up to 13 mol %. The three high-intensity reflections characteristic of the triclinic structure of PET,<sup>16</sup> with Bragg spacings around 5.2, 3.9, and

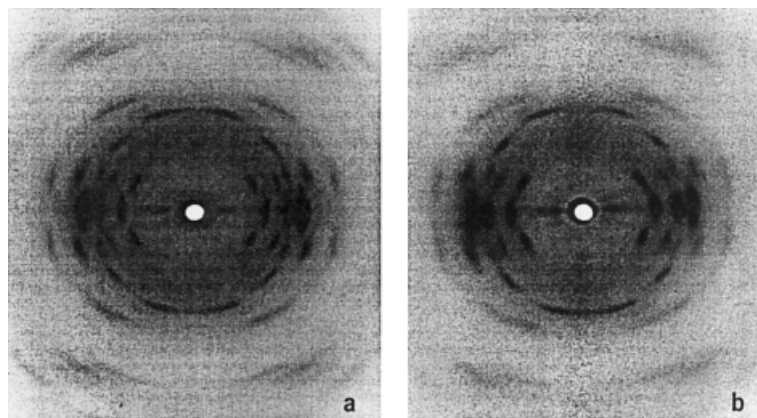


Figure 7 Fiber X-ray diffraction patterns of (a) PET and (b) PE<sub>92</sub>BEP<sub>8</sub>T. The fiber axis is vertical in both cases. Indexing was made on the basis of the triclinic structure reported for PET.<sup>16</sup>

TABLE V  
Observed and Calculated Fiber X-ray Spacings (Å) of  
PET and PEBEPT Copolyesters<sup>a</sup>

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> <sub>cal</sub>	<i>d</i> <sub>obs</sub>		
				PET	PE <sub>92</sub> BEP <sub>8</sub> T	PE <sub>84</sub> BEP <sub>16</sub> T
0	1	0	5.06	5.08	5.10	5.06
1	-1	0	3.94	3.93	3.97	3.95
1	0	0	3.47	3.45	3.41	3.50
0	-1	1	5.40	5.41	5.43	5.44
-1	1	1	4.17	4.11	4.18	4.15
-1	0	1	4.13			
0	1	1	3.78	3.75	3.76	3.73
1	-1	1	3.20	3.20	3.22	3.21
0	-2	1	2.74	2.70	2.73	2.70
1	0	1	2.73			
-1	2	1	2.72			
-1	-1	1	2.70			
-1	1	2	3.60	3.60	3.61	3.57
-1	0	3	3.37	3.38	3.40	3.38
-1	1	3	2.85	2.88	2.87	
0	-2	4	2.12	2.15	2.17	

<sup>a</sup> Indexing and spacings calculated for a triclinic unit cell of parameters  $a_0 = 4.56$  Å,  $b_0 = 5.94$  Å,  $c_0 = 10.75$  Å,  $\alpha = 98.5^\circ$ ,  $\beta = 118^\circ$ , and  $\gamma = 112^\circ$ .<sup>16</sup>

3.4 Å, were found to be present in the crystalline copolymers. It seems reasonable to conclude, therefore, that the crystalline structure of PET is also adopted by the crystalline copolyesters. Fiber X-ray diffraction gave definite support to this interpretation. The diffraction patterns obtained from fibers of PET and PE<sub>92</sub>BEP<sub>8</sub>T, prepared by stretching under heating, are compared in Figure 7. The two patterns are quite similar in both spacings and intensities, and susceptible to be indexed therefore on the basis of the same triclinic crystal lattice of PET with  $a_0 = 4.56$  Å,  $b_0 = 5.94$  Å,  $c_0 = 10.75$  Å,  $\alpha = 98.5^\circ$ ,  $\beta = 118^\circ$ , and  $\gamma = 112^\circ$ .<sup>16</sup>

Experimentally observed and calculated data are compared in Table V. In PET copolymers composed of comonomeric units with markedly different geometry or size, like poly(ethylene terephthalate-*co*-5-*tert*-butylisophthalate)<sup>9</sup> or poly(ethylene terephthalate-*co*-5-nitroisophthalate)<sup>17</sup> copolymers, selective rejection of the minor comonomer from the crystalline phase is

generally assumed to occur. Although it could also be the case for PEBEPT copolymers, incorporation of BEPD units in the crystal lattice of PET cannot be absolutely discarded because structural differences between EG and BEPD are not so apparent as those existing between terephthalic and isophthalic units. The situation is similar to that displayed by other PET copolymers containing branched 1,4-butanediol units and whose crystal structure has been recently examined.<sup>10</sup>

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