

# Preparation and Thermal Behavior of Random Poly(butylene terephthalate/azelate) Copolyesters

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**ABSTRACT:** Poly(butylene terephthalate), poly(butylene azelate), and poly(butylene terephthalate/butylene azelate) random copolymers of various compositions were synthesized in bulk using the well-known two-stage polycondensation procedure, and characterized in terms of chemical structure and molecular weight. The thermal behavior was examined by thermogravimetric analysis and differential scanning calorimetry. As far as the thermal stability is concerned, it was found to be rather similar for all copolymers and homopolymers investigated. All the copolymers were found to be partially crystalline, and the main effect of copolymerization was a lowering in the amount of crystallinity and a decrease of melting temperature with respect to pure homopolymers. Flory's equation was found to describe the  $T_m$ -composition data and permitted to calculate the melting temperatures ( $T_m^c$ ) and the heats of fusion ( $\Delta H_u$ ) of both the completely crystalline homopolymers. Owing to the high crystallization rate, the glass transition was observable only for the copolymers containing from 30 to 70 mol % of the terephthalate units; even though the samples cannot be frozen in a completely amorphous state, the data obtained confirmed that the introduction of the aromatic units gave rise to an increase of  $T_g$ , due to a chain stiffening. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2694–2702, 1999

**Key words:** poly(butylene azelate); poly(butylene terephthalate); random copolymers; copolyesters; thermal properties

## INTRODUCTION

It is well known that in the last decades copolyesters have become more and more important in the industrial field. In fact, these polymers can be obtained with characteristics tailored to fit a wide range of specific applications simply acting on the synthesis process, i.e., introducing appropriate comonomeric units in the polymeric chain, varying their relative amounts, arrangement, etc. Furthermore, as waste disposal is becoming a

serious environmental problem, an ever-growing attention has been paid on aliphatic polyesters, which show high levels of biodegradability. On the other hand, in many cases aliphatic polyesters are characterized by low melting points and poor properties to be used in many common applications. These problems could be overcome using aromatic polyesters modified with the introduction in the chain of proper comonomeric aliphatic units, so preserving their good mechanical, thermal, etc., properties, and in the meanwhile, favoring the degradation in environmental conditions. Recently some patents<sup>1–5</sup> claimed the biodegradability of copolyesters based on poly(butylene terephthalate) (PBT) or poly(ethylene terephthalate) (PET) containing comonomeric units

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derived from different kinds of aliphatic acids. However, a few are reported on the influence of aliphatic units on the most common properties of these polymers, especially in the case of PBT.

The present article reports the results of a detailed thermal characterization of statistical copolyesters based on terephthalic acid and 1,4-butanediol, and containing various amounts of azelate units; our attention has been focused on azelaic acid, because it can be derived from natural substances, and in addition, it has been used for the preparation of biodegradable polymers.<sup>6</sup>

## EXPERIMENTAL

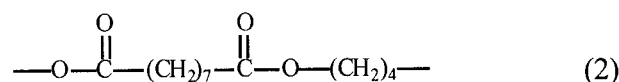
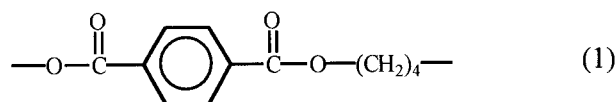
### Products

Dimethylterephthalate (DMT), terephthalic acid (TA), azelaic acid (AA), and 1,4-butanediol (BD) (Aldrich) were reagent-grade products and used as supplied.

### Synthesis of Polymer Samples

Poly(butylene terephthalate) (PBT), poly(butylene azelate) (PBaz), and poly(butylene terephthalate-co-butylene azelate) copolymers (PBTBaz) were synthesized in bulk, starting from different amounts of AA, DMT, and from BD, using  $\text{Ti}(\text{OBu})_4$  as a catalyst [about 0.2 g of  $\text{Ti}(\text{OBu})_4/\text{kg}$  of polymer]. The syntheses were carried out in a 200-mL glass reactor, with a thermostatted silicon oil bath, equipped with a magnetic stirrer, according to the usual two-stage polycondensation procedure. In the first stage, performed under nitrogen flow, the temperature was raised up to 200°C and maintained there for about 3 h. In the second stage, the pressure was reduced to facilitate the removal of excess BD, and the temperature was kept in the range of 200–240°C (according to the initial composition of the reaction system) for about 2 h. The copolymers obtained, because of the use of  $\text{Ti}(\text{OBu})_4$  as a catalyst and the high temperature that favor redistribution reactions,<sup>7</sup> are statistical both in composition and molecular weight distribution. In all cases a molar ratio of 1 : 1.4 between the diacid mixture and BD was used. Syntheses carried out starting from TA (instead of DMT) showed no significant differences in the characteristics of the copolymers obtained.

The monomeric units are the following:



### Infrared and <sup>1</sup>H-NMR Spectroscopy

Infrared spectra were recorded on a IF48 Bruker FTIR spectrophotometer, using film samples casted on a sodium chloride plate from chloroform solutions. The infrared spectra of copolymers containing high amounts of aromatic units and, therefore, not soluble in chloroform, were obtained by using a solid suspension in nujol.

The molar composition and the chain structure of PBTBaz copolyesters were determined by means of <sup>1</sup>H-NMR spectroscopy. Polymer samples were dissolved (15 mg/mL) in an appropriate solvent with 0.03% (v/v) tetramethylsilane added as an internal standard. The measurements were mainly carried out using chloroform-d solutions at room temperature; in the case of copolymers rich in terephthalate units, a mixture of trifluoroacetic acid/chloroform-d (20/80 v/v) was employed as the solvent. Measurements were recorded on a Varian XL-300 instrument.

### Gel-Permeation Chromatography

Molecular weight data were obtained by gel-permeation chromatography at 30°C using a 1100 Hewlett Packard system with an UV spectrophotometer (at 254 nm wavelength) as a detector, equipped with PL gel 5  $\mu$  Mixed C column (300/7.5 length/i.d., in mm). A mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (75/20/5 v/v) was used as the eluent with a 0.75 mL/min flow, and sample concentrations of about 10 mg/mL were applied; higher concentrations were employed in the case of copolyesters not containing aromatic units. A molecular-weight calibration curve was obtained with several monodisperse polystyrene standards in the range of molecular weights of 3,000–100,000.

### Mass Spectroscopy

The mass spectra were obtained by a VG 7070E spectrometer equipped with a DIGITAL  $\alpha$  data system at an energy of 18 eV, using the standard direct insertion probe for solid material.

**Table I** Molecular Characterization Data for PBTBAz Random Copolymers

Polymer	Mole Fraction of Terephthalate Unit (Feed)	Mol Fraction of Terephthalate Unit (NMR)	$M_n \cdot 10^{-3}$
PBT	1	1	11.4
90PBTBAz	0.90	0.88	13.4
80PBTBAz	0.80	0.80	12.9
70PBTBAz	0.70	0.69	9.1
60PBTBAz	0.60	0.60	8.9
50PBTBAz	0.50	0.48	9.2
40PBTBAz	0.40	0.39	8.9
30PBTBAz	0.30	0.30	6.9
20PBTBAz	0.20	0.20	9.2
15PBTBAz	0.15	0.16	7.2
10PBTBAz	0.10	0.08	8.0
5PBTBAz	0.05	0.05	7.6
PBAz	0	0	7.2

### Thermal Analysis

Calorimetric measurements were carried out by means of a Perkin-Elmer DSC7 instrument equipped with a liquid subambient accessory and calibrated with high purity standards (indium and cyclohexane). Unless otherwise indicated, weighed samples (c.a. 10 mg) were encapsulated in aluminum pans and heated to about 40°C above the fusion temperature at a rate of 20°C/min (first scan) and then rapidly quenched to -80°C. Finally, they were reheated from -80 to a temperature well above the fusion temperature of the sample at a heating rate of 20°C/min (second scan). The glass-transition temperature  $T_g$  was taken as the midpoint of the heat capacity increment  $\Delta c_p$  associated with the glass-to-rubber transition. The melting temperature ( $T_m$ ) was determined as the peak value of the endothermal phenomenon in the DSC curve; when multiple endotherms were observed, the highest peak temperature was taken as  $T_m$ . The enthalpy of fusion ( $\Delta H_m$ ) was determined from the total area of DSC endotherms. Repeated measurements on each sample showed excellent reproducibility.

Thermogravimetric curves were obtained both in air and in nitrogen atmosphere using a Perkin-Elmer TGA7 apparatus (gas flow: 50 mL/min) at 10°C/min heating rate up to 900°C.

### RESULTS AND DISCUSSION

At room temperature PBTBAz copolyesters appear as hard or soft semicrystalline solids accord-

ing to the amount of aliphatic units in the chain. The copolymers rich in aliphatic units demonstrated to be highly soluble in the most common organic solvents, i.e., chloroform, tetrachloroethane, tetrahydrofuran, methylene chloride, etc., whereas those rich in terephthalate units show a behavior similar to PBT. The homopolymers and the copolymers synthesized are listed in Table I, which also indicates the number-average molecular weights ( $M_n$ ) obtained by the GPC technique. The chemical structure of all polyesters was determined by FTIR and  $^1\text{H-NMR}$  spectroscopy. The FTIR spectra show a strong absorption at 1734–1731 and 1190–1174  $\text{cm}^{-1}$ , characteristic respectively of C=O and C—O stretching vibration of the ester group; moreover, it is evident that the absence of the band centered at 3400  $\text{cm}^{-1}$  corresponding to the stretching vibration of the hydroxyl group of 1,4-butanediol, which has been removed from the reaction system during the synthesis. The disappearance of most of OH groups can, therefore, be considered as evidence of the fact that the polymerization reaction took place. As far as the chemical structure is concerned, a typical  $^1\text{H-NMR}$  spectrum is shown in Figure 1, together with the chemical shift assignments. In all cases, such spectra were found to be consistent with the expected structure. The copolymer composition was calculated from the relative areas of the  $^1\text{H-NMR}$  resonance peaks of the  $\alpha$ -methylene group in the azelate unit at 2.41 ppm, and the aromatic proton of the terephthalate unit at 8.12 ppm. The results, summarized in Table I, show

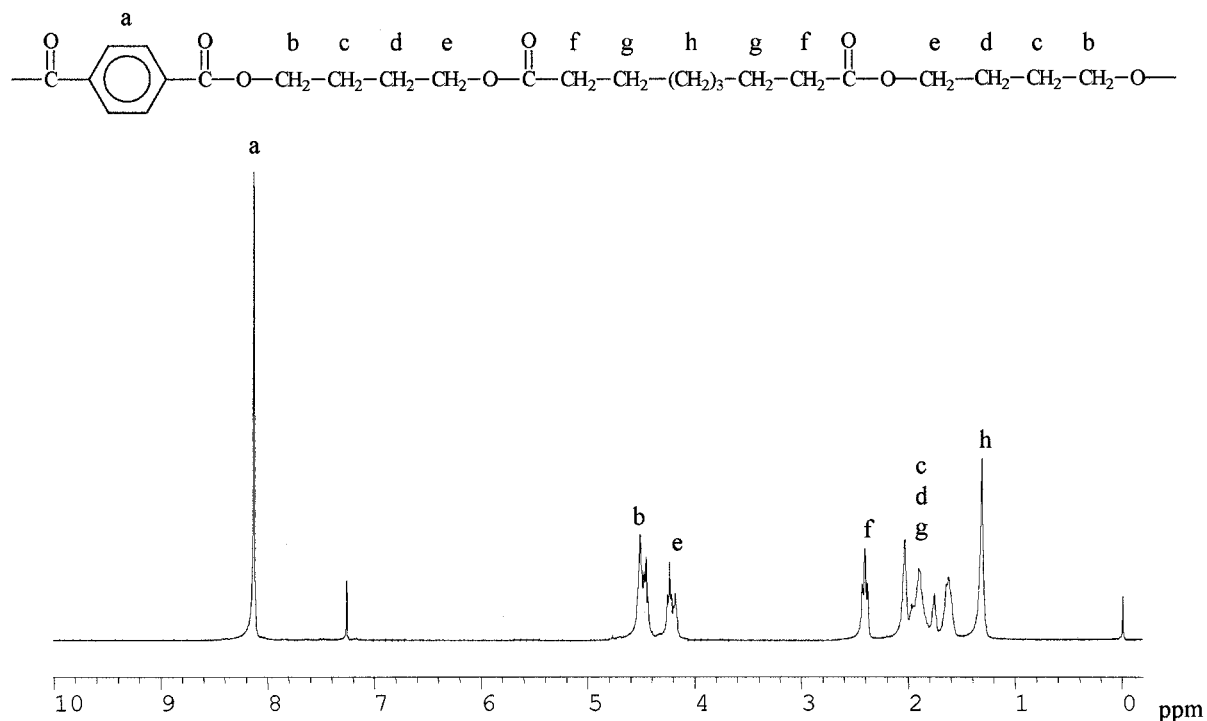


Figure 1  $^1\text{H-NMR}$  spectra of the 60PBTBAz copolymer.

that in almost all cases the feeding composition was confirmed.

The thermal behavior of the polyesters was investigated by means of thermogravimetric analysis (TGA) as well as differential scanning calorimetry (DSC). Figure 2 shows the TGA traces of

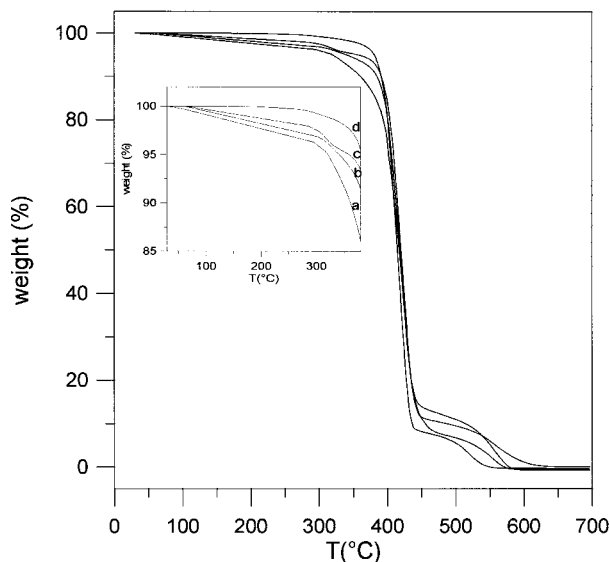
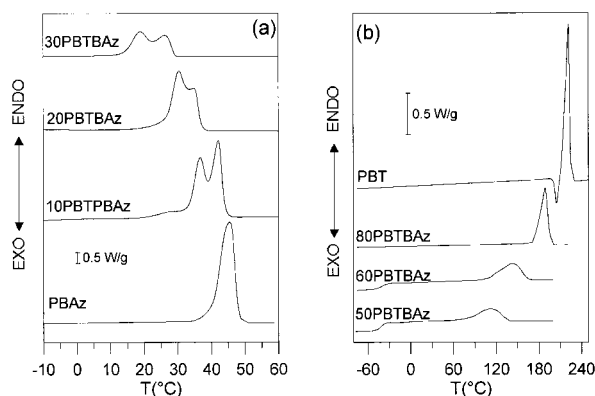


Figure 2 TGA curves in air at  $10^\circ/\text{min}$ : (a) PBAz; (b) 40PBTBAz; (c) 60PBTBAz; (d) PBT.

PBT, PBAz, and some of PBTBAz copolymers in air. In all cases the weight loss takes place practically in one-step, and is of 100%. The thermal stabilities of all the polymers are quite comparable, and they are practically stable up to  $300^\circ\text{C}$ . For all PBTBAz copolymers the temperature at which the weight loss rate is the highest turned out to be in the range of  $423\text{--}428^\circ\text{C}$ , with only a slight difference with respect to PBT. Similar results were obtained when TGA curves were recorded under nitrogen atmosphere. As a matter of fact, a detailed analysis of TGA curves in the  $150\text{--}400^\circ\text{C}$  range (see the window in Fig. 2) permits detection of a slight weight loss at low temperature. The consistence of the phenomenon (approximately of 5% in the case of homopolymer PBAz) is connected with the amount of azelate units, being larger as the content of these is increased.

A mass spectrometry analysis was carried out on PBAz to elucidate the origin of the initial weight loss. The mass spectra obtained at a temperature of  $90^\circ\text{C}$  is characterized by the presence of a peak at  $m/z$  242, presumably corresponding to the cyclic molecule formed by one repeating unit, together with peaks deriving from fragment ions. Because usually in polyesters the end-biting



**Figure 3** Calorimetric curves of PBAz, PBT homopolymers, and their random copolymers after the melt quenching.

intramolecular process occurs at high temperatures<sup>8</sup> (>200°C), it is reasonable to suppose that such a cyclic product is present in the bulk polymer at the end of the polycondensation. Therefore, the initial weight loss can probably be ascribed to the volatilization process of this low molecular weight cyclic compound.

Regarding calorimetric results, a preliminary investigation was carried out to evaluate a possible influence of molecular weight on the glass transition and melting of the synthesized polymers. The calorimetric measurements, carried out on samples with the same composition but different  $M_n$ , gave practically identical results. Therefore, the data here reported refer to samples with the highest molecular weight available for each composition.

It is well established that the thermal behavior of a polymer is affected by its previous thermal history. Therefore, to erase it and provide the same heat treatment to all samples, the specimens were subjected to the thermal cycle described in the Experimental section.

Typical calorimetric curves are collected in Figure 3(a) and (b): the DSC traces reported in Figure 3(a), concerning PBAz and the PBTBAz copolymers rich in azelate units, show one melting peak with a slight shoulder in the case of the homopolymer, and multiple endotherms, whose peak location depends on composition, for the copolymers. Owing to the high crystallization rate (higher than the cooling one), the glass transition phenomenon can never be experimentally observed. Regarding the calorimetric curves of PBT and the PBTBAz copolymers rich in terephthalate units [Fig. 3(b)], a melting peak, depending on

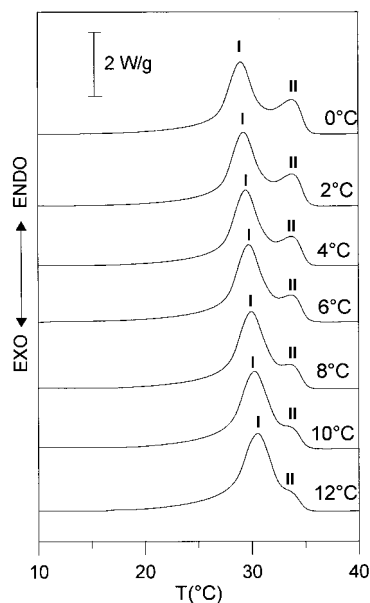
composition, is observed; in addition, for copolymers whose terephthalate unit content ranges from 30 to 70% mol, a glass transition phenomenon is also observed, whose temperature is influenced by the amount of comonomeric units in the chain. For all PBTBAz copolymers, the endotherm region is broader with respect to homopolymers, suggesting the presence of a larger distribution of crystallites with different degrees of perfection. Furthermore, the DSC curves indicate that an increase in the amount of comonomer added to PBAz or PBT leads to a marked reduction of the heat of fusion, and therefore, to a reduced level of crystallinity in the copolymers with respect to the homopolymers, as expected in the case of random copolymers.

As can be seen in Figure 3(a), multiple melting peaks are present in the DSC traces of PBTBAz copolymers rich in azelate units. It is well known that a lot of semicrystalline polymers as well as their copolymers and blends show multiple endotherm peaks.<sup>9–23</sup> There has been much discussion in the literature as to the possible origin of the phenomenon. Multiple endotherm peaks could be due to the presence of two or more groups of crystals with different morphologies;<sup>9–14</sup> alternatively, they can be ascribed to a recrystallization process occurring during the DSC scan.<sup>15–23</sup> In particular, the multiple endotherm behavior is typical of many polyesters, for the best-studied of which the phenomenon has always been ascribed to a reorganization processes taking place during the DSC scan.<sup>20–23</sup>

To study the nature of these multiple endotherms different kinds of experiments can be carried out by DSC equipment. In particular, our samples, i.e., PBAz as well as the copolymers rich in azelate units, have been subjected to the two different thermal treatments described in the following: (a) heating scan well above melting temperature, keeping there for 3 min to cancel the previous thermal history and then rapid cooling to a chosen crystallization temperature ( $T_c$ ;  $T_c$  range investigated: 0–12°C) up to a completion of the crystallization process. The isothermally crystallized samples were subsequently analyzed by heating directly from  $T_c$  at a heating rate of 10°C/min; (b) cooling scan from the melt at different rates (1°C/min, 20°C/min, and rapid quenching) and a subsequent heating scan at 20°C/min.

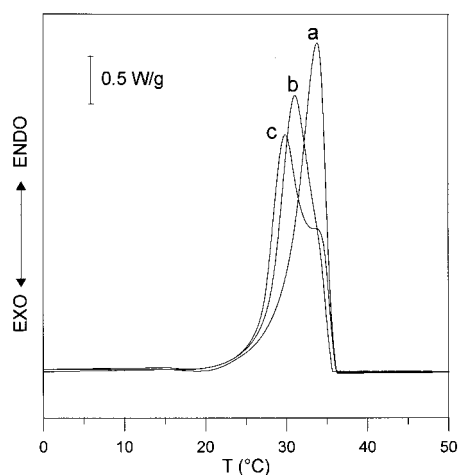
As an example, the DSC heating curves of the copolymer 20PBTPBAz subjected to the two thermal treatments described above are reported in Figures 4 and 5, respectively. In Figure 4 two





**Figure 4** DSC melting endotherms of the 20PBTAz copolymer after isothermal crystallization at the indicated  $T_c$ s (heating rate 10°C/min).

endotherms are observed in all cases: for the sake of clarity, the peak at the lower temperature is called I, whereas that at higher temperature is II. As can be seen, the I peak depends on the crystallization temperature, and moves to higher temperatures as  $T_c$  rises. On the contrary, the location of peak II shows no dependence on  $T_c$ ; this suggests that a reorganization process takes place during the DSC scan, due to a continuous



**Figure 5** Melting endotherms of the 20PBTAz copolymer at a heating rate of 20°/min after cooling from the melt at different rates: (a) 1°/min; (b) 20°/min; (c) rapid quenching.

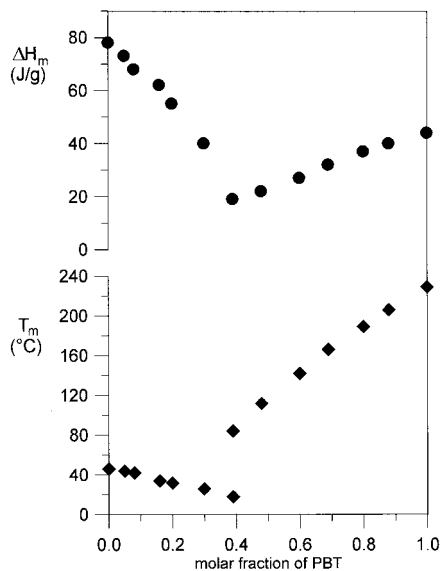
**Table II** Calorimetric Data of PBTBAz Random Copolymers (Second DSC Scan, After Rapid Quenching from the Melt)

Polymer	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_g$ (°C)	$\Delta c_p$ (J/g °C)
PBT	229	44		
90PBTBAz	206	40		
80PBTBAz	189	37		
70PBTBAz	166	32	-31	0.178
60PBTBAz	142	27	-39	0.189
50PBTBAz	112	22	-43	0.250
40PBTBAz	18/84	19	-48	0.138
30PBTBAz	26	40	-52	0.095
20PBTBAz	32	55		
15PBTBAz	34	62		
10PBTBAz	42	68		
5PBTBAz	44	73		
PBAz	46	78		

melting and recrystallization in line with evidences frequently reported in the literature.<sup>20,23</sup>

As can be seen from Figure 5, the melting peak at lower temperature reveals a decrease in both the heat of fusion and melting temperature as the cooling rate is increased. On the contrary, the location of the higher temperature peak remains fairly constant, regardless of the cooling rate used to crystallize the sample. This suggests that a reorganization process takes place during the cooling step: in fact, if the sample is allowed to crystallize slowly, the original less perfect crystallites can reorganize, forming thicker crystals that melt at higher temperatures. In addition, as a result of a progressive crystallite improvement, the melting range narrows. In conclusion, both DSC experiments give more value to the hypothesis that the multiple endotherms are due to the fusion process of crystallites having different degrees of perfection and/or size. Consequently, as already pointed out in the Experimental section, the highest peak temperature is taken as  $T_m$ .

The  $\Delta H_m$  and  $T_m$  values are collected in Table II and plotted in Figure 6 as a function of the PBT unit content. Both the minimum in the heat of fusion and the melting point composition dependence, represented by two independent curves, are typical of random copolymers, where both comonomers are able to crystallize but at each composition only the unit present in major proportion takes part in the crystallization process.<sup>24,25</sup> A different fusion behavior is shown by the 40PBTBAz copolymer, which is characterized



**Figure 6** Composition dependence of  $T_m$  (◆) and  $\Delta H_m$  (●) for PBTBAz random copolymers.

by two distinct melting phenomena (see Table II), whose peak temperatures each lie on a separate curve in the  $T_m$ -composition plot. The lower melting peak ( $T_m = 18^\circ\text{C}$ ) can, therefore, be attributed to the crystals formed by aliphatic chains, while the higher temperature ( $T_m = 84^\circ\text{C}$ ) may be associated with the crystals formed by aromatic units. It is reasonable to think that for this copolymer there is a coexistence of the crystalline lattices of the two homopolymers. This behavior was already observed for similar copolyesters.<sup>26</sup> As far as the  $\Delta H_m$  value is concerned, the datum reported in Table II is the sum of the heats of fusion associated with the two distinct melting phenomena.

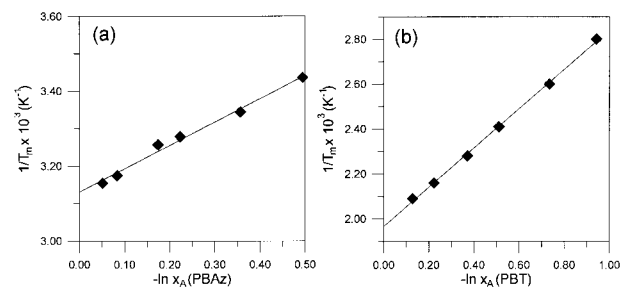
According to Flory's theory,<sup>27</sup> the  $T_m$  at which crystallinity disappears in the copolymers is related to the molar fraction  $x_A$  of the crystallizing A units by the equation:

$$1/T_m - 1/T_m^\circ = -(R/\Delta H_u)\ln x_A$$

where  $T_m^\circ$  and  $\Delta H_u$  are the melting temperature and the heat of fusion of the completely crystalline A homopolymer, respectively. According to this relationship, the plot  $1/T_m$  vs.  $-\ln x_A$  should be a straight line with a slope  $R/\Delta H_u$ . The results obtained are shown in Figure 7: in Figure 7(a) the data, considering PBAz as homopolymer A, are reported. The experimental  $T_m$  of the copolymers under investigation fit very well onto a straight

line. From its slope a value of  $\Delta H_u = 55 \text{ J/g}$  can be obtained, whereas from the intercept a  $T_m^\circ = 47^\circ\text{C}$  was determined for PBAz. Regarding the PBTBAz copolymers rich in terephthalate units, the data plotted in Figure 7(b) are also well correlated by Flory's equation. The value of  $\Delta H_u$  (43 J/g) for PBT is in rather good accord with that obtained previously by some of us in investigating similar copolyesters,<sup>28</sup> and significantly lower than that determined by other methods.<sup>29</sup> The equilibrium melting temperature ( $T_m^\circ$ ), calculated by Flory's equation, is equal to  $236^\circ\text{C}$ . The fact of obtaining lower  $\Delta H_u$  is, however, a wide-spread observation that has been reported in the literature for several different statistical copolymers, and has been ascribed to the inability of a real random copolymer system to achieve the conditions postulated by the equilibrium theory. Theory requires a melting temperature relative to the disappearance of very long sequences of A units; on the contrary, in real conditions, the amount of such sequences in random copolymers is relatively low, and decreases as the counit content increases. As a consequence, experimental  $T_m$  values are lower than predicted. The  $\Delta H_u$  of PBAz is higher than that of PBT, as already found for other copolymers formed by aromatic and aliphatic units.<sup>26</sup>

To study the influence of chemical structure on the glass transition of random copolymers, the phenomenon should be examined in the absence of the crystallinity, because it acts as a crosslink and raises  $T_g$  through its restrictive effect on segmental motion of amorphous polymer chains. Rapid cooling (quenching) from the melt is the method commonly used to prevent crystallization and to obtain polymers in a completely amorphous condition. The thermograms, shown in Figure 3(a) and (b), indicate that both homopolymers as well as copolymers cannot be frozen in a completely amorphous glassy state due to their high rate of crystallization. Nevertheless, in the DSC



**Figure 7**  $1/T_m$ -composition plot according to Flory's equation for PBAz (a) and PBT (b).

curves of partially crystalline PBTBAz copolymers having intermediate composition (30–70 mol % of terephthalate units) it is evident an endothermal baseline deviation that can be associated with the glass transition. The values of  $T_g$  are collected in Table II, and show a clear dependence on composition, increasing as the content of terephthalate units is increased. The second-order transition temperature is generally considered as a measure of the flexibility of the chain polymers: the more flexible chains are, the lower the  $T_g$ . The aliphatic polyesters, having very flexible chains in the presence of methylene groups, are characterized by very low  $T_g$  values. The increase in the glass transition temperature on introducing *p*-phenylene linkages into the chains can, therefore, be due to a stiffening effect of these groups. Anyway, because the equations proposed in the literature to predict  $T_g$  as a function of comonomer concentration are valid for completely amorphous random copolymers, they cannot be used to correlate our experimental data.

## CONCLUSIONS

The development of polymeric materials able to degrade in environmental conditions is one of the solutions to the problem of waste disposal. An ideal biodegradable polymer should have adequate thermal and mechanical properties that are needed for practical applications, as well as good degradability. Often the best way to achieve all the desirable properties is to copolymerize different monomers. On this ground, our attention was focused on random poly(butylene terephthalate/butylene azelate) copolyesters, owing to the wide diffusion of PBT and the well-known degradability of PBaz.

PBTBAz copolyesters of different composition, in the complete range from PBT to PBaz, were synthesized and studied in terms of molecular structure and thermal properties. All samples had a good thermal stability, similar to that of PBT. They showed to be semicrystalline materials with a glass transition phenomenon experimentally observable only for samples containing from 30 to 70 mol % of terephthalate units. Their fusion behavior can be interpreted, for the copolymers rich in terephthalate units, on the basis of the formation of the crystal structure characteristic of PBT. Alternatively, the PBTBAz copolymers rich in azelate units showed a melting phenomenon attributable to the disappearance of the

crystal lattice of PBaz. An exception is represented by the sample containing 40 mol % of terephthalate units where there is coexistence of both crystalline structures.

The  $T_m$ -composition plots obtained are typical of statistical copolymers, and the application of Flory's equation permitted us to calculate the melting temperatures ( $T_m^c$ ) and the heats of fusion ( $\Delta H_u$ ) of both completely crystalline homopolymers. The results are in agreement with previously reported data.

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