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Synthesis and thermal characterization of poly(butylene terephthalate-*co*-thiodiethylene terephthalate) copolyesters

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Abstract

Poly(butylene terephthalate-*co*-thiodiethylene terephthalate) copolymers of various compositions were synthesized and characterized in terms of chemical structure and molecular weight. The thermal behavior was examined by thermogravimetric analysis and differential scanning calorimetry. All the polymers under investigation show a good thermal stability. At room temperature they appear as semicrystalline materials: the main effect of copolymerization was a lowering in the amount of crystallinity and a decrease of melting temperature with respect to homopolymers. A pure crystalline phase has been evidenced at high content of butylene terephthalate or thiodiethylene terephthalate units and Baur's equation was found to describe well the T_m-composition data. Amorphous samples (containing 50–100 mol% of thiodiethylene terephthalate units) showed a monotonic decrease of T_g as the content of sulfur-containing units is increased, due to the presence of flexible C–S–C bonds in the polymeric chain. Finally, the Fox equation described well the T_g-composition data. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(butylene terephthalate); Poly(thiodiethylene terephthalate); Random copolymers

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1. Introduction

In recent years the study of the synthesis and of the properties of sulfur-containing polyesters has received a renewed impulse, due to some specific applications proposed for these materials [1,2]. In fact, several articles evidence that the presence of sulfur atoms in a polymeric chain can increase some important properties, such as refractive index, biodegradability, etc. Moreover, it is well known that copolymerization represents an easy way to modify the characteristics of a polymer in order to fit specific applications; for example, crystallinity degree and melting point can be reduced by random copolymerization and adjusted by changing copolymer composition. As a consequence, several copolyesters containing sulfur atoms in the main chain or in side chains were recently prepared and studied [3–9].

In this view, and due to the wide spread use of poly(butylene terephthalate) (PBT), a well-known thermoplastic material with good properties for an ever growing number of applications, we carried out an investigation on the effect of sulfur-containing units on some important characteristics of PBT. Therefore, we synthesized a series of random copolyesters of PBT by direct melt polymerization, starting from dimethylterephthalate, 1,4-butanediol and thiodiethylene glycol. The present paper reports the results of a detailed molecular and thermal characterization of these copolymers, carried out in order to study the structure–properties relationships.

2. Experimental

2.1. Reagents

Dimethylterephthalate (DMT), 1,4-butanediol (BD) and thiodiethylene glycol (TDEG) (Aldrich) were reagent grade products and used as supplied; titanium tetrabutoxide ($Ti(OBu)_4$) (Aldrich) was distilled before use.

2.2. Synthesis of polymer samples

Poly(butylene terephthalate-*co*-thiodiethylene terephthalate) (PBT/TDET) copolymers were synthesized in

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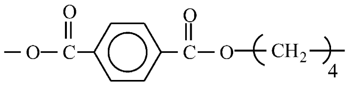
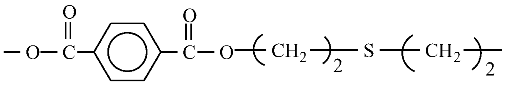
bulk starting from different amounts of BD and TDEG and from DMT, employing $Ti(OBu)_4$ as catalyst (about 0.2 g of $Ti(OBu)_4$/kilogram of polymer). The syntheses were carried out in a 200 ml glass reactor, with a thermostatted silicon oil bath; temperature and torque were continuously recorded during the polymerization. The polymers were obtained according to the usual two-stage polymerization procedure [10]. In the first stage, under pure nitrogen flow, the temperature was raised to 180–190 °C (according to the initial composition of the reaction system) and maintained there for until more than 90% of the theoretical amount of methanol was distilled off (about 3 h). In the second stage the pressure was reduced, in order to facilitate the removal of glycols in excess and the temperature was kept in the range 200–240 °C until a torque constant value was measured. The copolymers obtained, because of the use of $Ti(OBu)_4$ as catalyst and the high temperature, which favor redistribution reactions [11], are statistical both in composition and molecular weight distribution. The comonomeric units are the following:



BT



TDET

2.3. Infrared and ^{1}H NMR spectroscopy

Infrared spectra were recorded on a IF48 Bruker FT-IR spectrophotometer, using film samples cast on a sodium chloride plate from chloroform solutions. The infrared spectra of copolymers containing high amounts of butylene terephthalate units, not soluble in chloroform, were obtained by using a solid suspension in nujol.

The molar composition and the chain structure of PBT/TDET copolyesters were determined by means of ^{1}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 butylene terephthalate units a mixture of trifluoroacetic acid/chloroform-d (20/80 v/v) was employed as solvent. Measurements were recorded on a Varian XL-300 instrument.

2.4. 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 detector, equipped with PL gel 5μ 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 eluent with a 0.75 ml/min flow, and sample concentrations of about 10 mg/ml were applied.

A molecular weight calibration curve was obtained with several monodisperse polystyrene standards in the range of molecular weight 3,000–100,000.

2.5. Wide-angle X-ray measurements

Wide angle X-ray spectra (WAXS) were obtained out at room temperature by means of a Bragg/Brentano diffractometer system (Philips PW1050/61-PW1710), equipped with a graphite monochromator in the diffracted beam. Cu anode was used as X-ray source ($\lambda_1 = 0.15406$ nm, $\lambda_2 = 0.15443$ nm). Data were collected in the range 5–60° (2θ) counting for 5 s at each 0.08° step.

2.6. 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). Weighed samples (ca. 10 mg) were encapsulated in aluminum pans and heated to about 40 °C above fusion temperature at a rate of 20 °C/min (first scan) and then rapidly quenched at −50 °C. Finally, they were reheated from −50 °C 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 Δc_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 (ΔH_m) was determined from the total area of DSC endotherms. Repeated measurements on each sample showed excellent reproducibility. The calorimetric data discussed in the following are not influenced by the molecular weight, since DSC measurements carried out on samples having the same composition but different M_n have given identical results.

Thermogravimetric analysis was carried out both in air and under nitrogen atmosphere using a Perkin Elmer TGA7 apparatus (gas flow: 50 ml/min) at 10 °C/min heating rate up to 900 °C.

3. Results and discussion

At room temperature PBT/TDET copolyesters appear as semicrystalline solids. The solubility of the samples was checked in various solvents. The copolymers rich in

Table 1
Molecular characterization data of PBT/TDET random copolymers

Polymer	TDET (mol%) (feed)	TDET (mol%) (^{1}H NMR)	M_n	M_w/M_n
PBT	0	0	26,000	2.0
PBT/TDET10	10	10	17,700	2.1
PBT/TDET20	20	20	13,300	2.2
PBT/TDET30	30	30	17,200	2.1
PBT/TDET50	50	49	20,300	2.0
PBT/TDET60	60	59	26,000	2.2
PBT/TDET70	70	71	14,200	2.1
PBT/TDET80	80	80	18,000	2.2
PBT/TDET90	90	88	18,600	2.2
PBT/TDET95	95	95	14,200	2.0
PTDET	100	100	21,400	2.2

butylene terephthalate units were found to be fully soluble at room temperature in 1,1,1,3,3,3-hexafluoro-2-propanol and in a mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (75/20/5 w/w), showing a behavior similar to PBT. On the contrary, PTDET and the copolymers containing high amounts of thiodiethylene terephthalate units appeared to be soluble in the most common organic solvents, i.e. chloroform, tetrachloroethane, methylene chloride, etc. The copolymers synthesized are listed in Table 1, which also collects the number-average molecular weights (M_n) data obtained by GPC technique. The chemical structure of all polyesters was determined by FT-IR and ^{1}H NMR spectroscopy. As far as FT-IR analysis is concerned, the characteristic carbonyl stretching frequencies of the ester groups appear at 1733 and 1190–1174 cm^{-1} (C=O and C–O), respectively, whereas the C–H bending vibration of the CH_2–S group is located at 1455 cm^{-1}; moreover, it is evident the absence of the band centered at 3400 cm^{-1} corresponding to the stretching vibration of hydroxyl groups of 1,4-butanediol and thiodiethylene glycol, that reacted or have removed from the reaction system during the syntheses. The disappearance of most of the OH groups can be therefore considered as an evidence of the fact that the polymerization reaction took place. In order to have an understanding into the chemical structure and copolymer composition, the ^{1}H NMR investigation on the samples was performed. The ^{1}H NMR spectra of all copolyesters are consistent with the expected structure: as an example, the ^{1}H NMR spectrum of the PBT/TDET50 copoymer is shown in Fig. 1, together with the chemical shift assignments. The peaks chosen for the determination of the composition, which is reported in Table 1, were the one at 2.21 ppm for the butylene terephthalate unit and that at 3.25 ppm for the thiodiethylene terephthalate unit. From the data of Table 1, it can be seen that in all cases the actual molar composition is very close to that of the feed. Further information on the chemical structure was obtained subjecting the samples to elemental

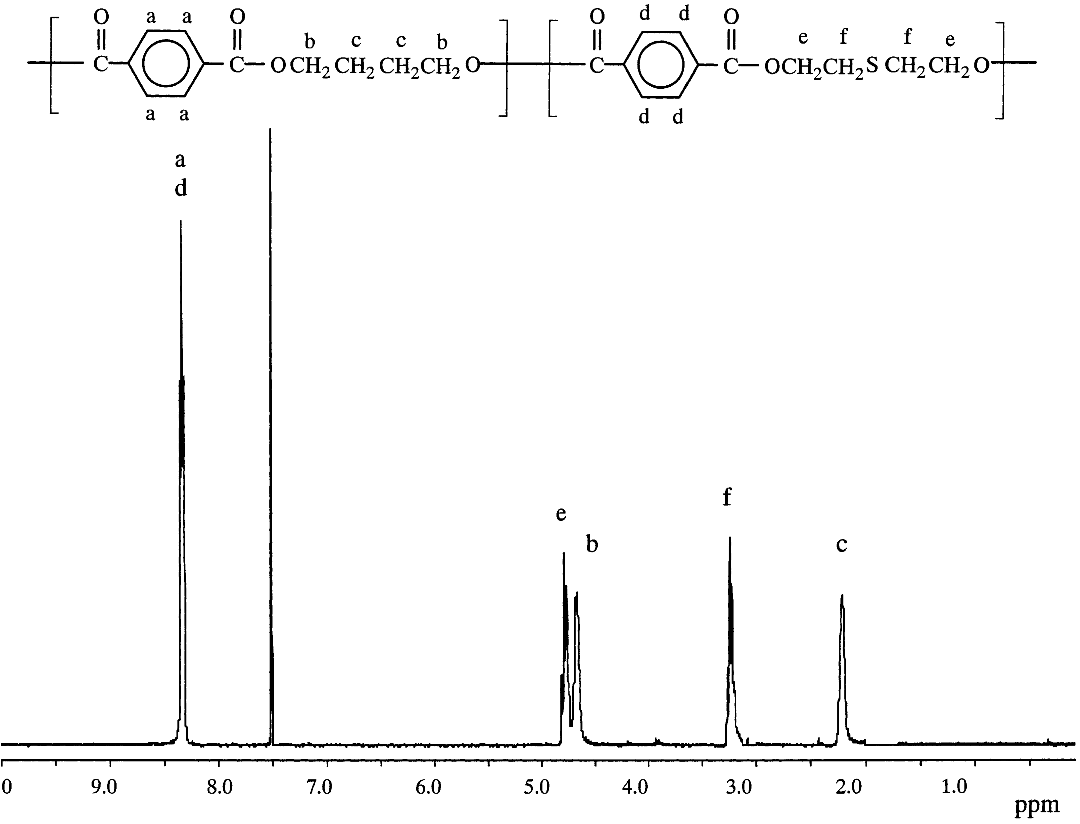


Fig. 1. ^{1}H NMR spectrum of PBT/TDET50 copolymer.

Table 2
Elemental analysis data of PBT/TDET random copolymers

Sample	Theoretical values (mol%)				Experimental values (mol%)			
	C	H	S	O	C	H	S	O
PBT	65.45	5.49	–	29.06	65.38	5.53	–	29.09
PBT/TDET10	64.51	5.41	1.43	28.65	64.21	5.50	1.48	28.81
PBT/TDET20	63.60	5.34	2.82	28.24	63.55	5.40	2.50	28.55
PBT/TDET30	62.71	5.26	4.18	27.85	62.30	5.56	4.32	27.82
PBT/TDET50	61.01	5.12	6.77	27.1	60.78	5.18	6.87	27.17
PBT/TDET70	59.41	4.98	9.23	26.38	59.30	5.12	9.69	28.89
PBT/TDET80	58.63	4.92	10.41	26.04	58.29	5.26	10.69	25.76
PBT/TDET90	57.88	4.86	11.57	25.69	57.55	4.98	11.63	25.84
PBT/TDET95	57.51	4.83	12.13	25.53	57.28	5.08	12.23	25.41
PTDET	57.14	4.80	12.69	25.37	57.32	5.03	13.09	24.56

analysis. The results are reported in Table 2: as can be seen, the experimental values are in good agreement with the calculated ones, confirming the chemical composition of all the samples under investigation.

The copolyesters were afterwards examined by thermogravimetric analysis and differential scanning calorimetry. The investigation on the thermal stability was carried out both in air and under nitrogen atmosphere. Fig. 2 shows the thermogravimetric curves of some samples in air, from which the temperature of initial decomposition (T_{id}) and the temperature corresponding to the maximum weight loss rate ($T_{\max}$) were determined; the values obtained are collected in Table 3. It can be seen that in all cases the weight loss takes place in one-step and is practically 100%. The thermal stability of all samples depends on composition, being lower as TDET content increases; an analogous behavior was found by us and by other Authors for different kinds of sulfur-containing polymers [9,12]. Anyway, it has to be noted that the thermal stability stays good if the amount of TDET units is not too high. Similar results were obtained by means of TGA measurements carried out under nitrogen atmosphere.

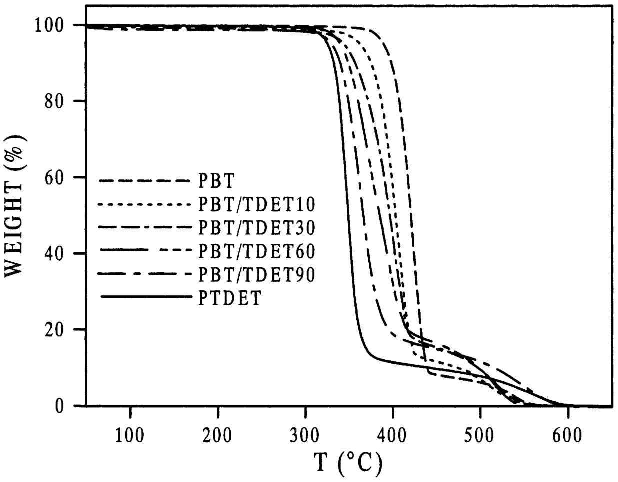


Fig. 2. TGA curves of PBT, PTDET and some PBT/TDET random copolymers in air at 10 °/min.

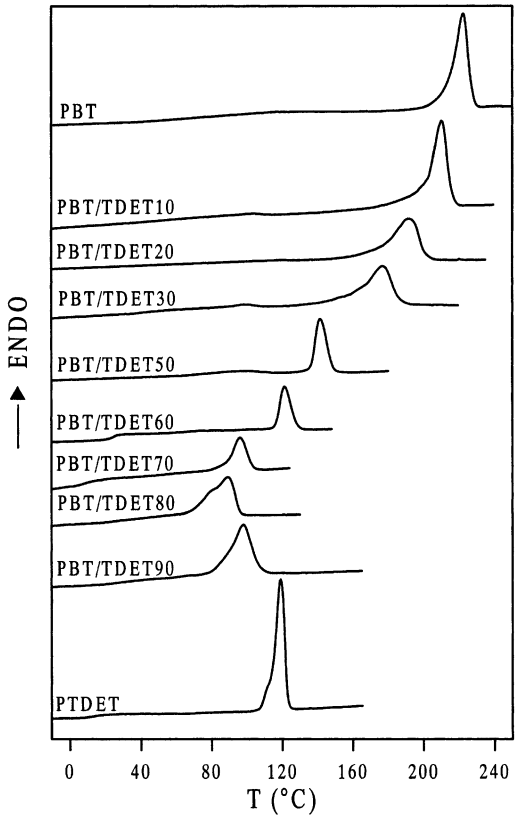


Fig. 3. Calorimetric curves of samples annealed at 60 °C.

As far as the calorimetric results are concerned, being well established that the melting behavior of a polymer is affected by its previous thermal history, in order to provide the same heat treatment to all the samples investigated, prior to thermal analysis the specimens were annealed at 60 °C for 8 days in an oven under vacuum. The DSC traces of such samples are reported in Fig. 3 and the data obtained in Table 3. In all cases, a glass transition and a melting endotherm are evident. In the copolymers, peak location appears to depend on composition; furthermore, the increase in the amount of comonomer added to PBT or to PTDET chains leads to a marked reduction of the heat of fusion, indicating a reduced

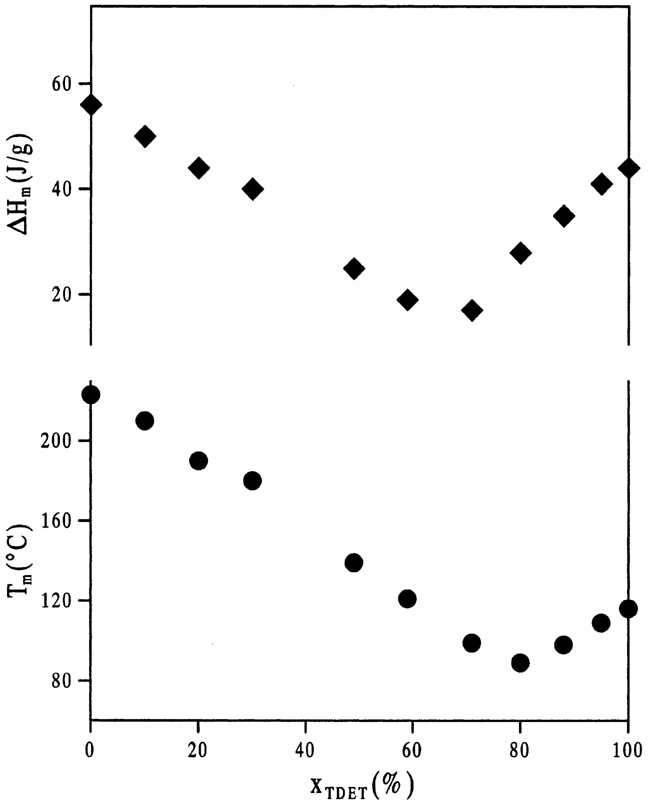


Fig. 4. Composition dependence of T_m (●) and ΔH_m (◆) for PBT/TDET random copolymers.

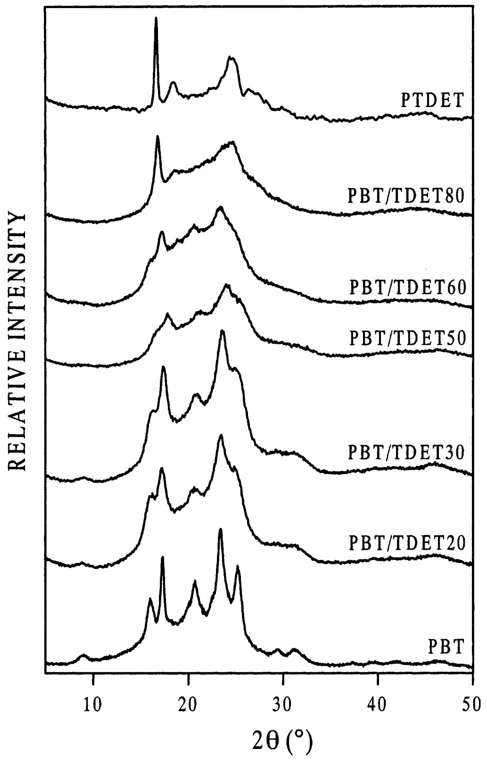


Fig. 5. Wide-angle X-ray spectra of PBT, PTDET and some PBT/TDET random copolymers.

level of crystallinity in the copolymers with respect to the homopolymers. Furthermore, in the copolymers the endotherm region is broader, suggesting the presence of a larger distribution of crystallites with different degree of perfection. The ΔH_m and T_m values are plotted in Fig. 4 as a function of TDET unit content. Both the minimum in the heat of fusion and the melting point-composition dependence are typical of random copolymers, with both comonomers able to crystallize, regardless of whether the comonomer units present in minor amount are completely rejected from the crystalline phase or partially incorporated in it [13,14]. As the repeating unit of PTDET has a similar chemical structure to that of PBT, except for the presence of a sulfur atom between two methylene groups, theoretically co-crystallization cannot be excluded. In order to check the nature of the crystalline phase present in the polymers under investigation, X-ray analysis was performed. The diffraction curves for PBT, PTDET and PBT/TDET copolymers are reported in Fig. 5. PBT and PTDET homopolymers show well-defined and different sets of crystalline diffraction peaks. Furthermore, PBT/TDET10, PBT/TDET20 and

Table 3
Thermogravimetric and calorimetric data of PBT/TDET random copolymers

Polymer	T_{id} (°C)	T_{max} (°C)	1st scan		2nd scan					
			T_m (°C)	ΔH_m (J/g)	T_g (°C)	Δc_p (J/g °C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PBT	403	424	223	56	40	0.088	–	–	222	49
PBT/TDET10	380	411	210	50	37	0.111	–	–	209	42
PBT/TDET20	370	409	190	44	34	0.133	–	–	189	36
PBT/TDET30	367	403	180	40	31	0.156	–	–	178	31
PBT/TDET50	356	401	139	25	26	0.346	60	18	140	20
PBT/TDET60	343	380	121	19	24	0.352	86	8	121	8
PBT/TDET70	338	367	99	17	21	0.353	–	–	–	–
PBT/TDET80	338	362	89	28	19	0.356	–	–	–	–
PBT/TDET90	339	363	98	35	18	0.372	–	–	–	–
PBT/TDET95	339	352	109	41	16	0.377	–	–	–	–
PTDET	334	344	116	44	15	0.384	71	13	113	13

PBT/TDET30 copolymers are characterized by X-ray spectra which are very similar to that of PBT, the position of the reflections being essentially the same and no evidence of a variation in the unit cell volume being found. The only two differences are an increasing amount of amorphous portion and a reduced crystal size with increasing TDET unit content. These results prove that the crystal structure which develops in the above copolymers corresponds to the characteristic lattice of the PBT. On the contrary, in PBT/TDET95, PBT/TDET90 and PBT/TDET80 samples, the crystalline diffraction peaks match those of the PTDET crystal structure, indicating that the crystalline phase present is that of PTDET homopolymer. In the X-ray spectra of the copolymers with intermediate compositions, some characteristic diffraction peaks of both PBT and PTDET are observed and therefore the diffraction pattern is not strictly attributable to the former or the latter. The profile shape, even if more similar to PBT pattern, owing to its high complexity, can be explained either on the basis of the possible insertion of a number of TDET units in the crystalline lattice of PBT or the coexistence of a pure PBT crystalline phase with a small amount of PTDET crystals.

The melting temperature depression in a random copolymeric system can be expressed as a function of the composition as predicted by Flory [15], Baur [16], Sanchez and Eby [17], Helfand and Lauritizen [18] and others [19, 20]. In particular, when only one co-unit can crystallize, the second one being completely excluded from the crystals, the melting point reduction is commonly examined using Flory's equation:

$$1/T_m - 1/T_m{}^\circ = -(R/\Delta H_m{}^\circ)\ln x_C \tag{1}$$

where T_m is the melting temperature of a random copolymer with mole fraction x_C of the crystallizable comonomer C, $T_m{}^\circ$ and $\Delta H_m{}^\circ$ are the equilibrium melting temperature and the heat of fusion of the completely crystalline homopolymer C and R is the universal gas constant.

Taking into account the effect of the sequence length of crystallizable units which can crystallize only when their length corresponds to the crystals thickness, a modified exclusion theory as proposed by Baur leads to the equation:

$$1/T_m = 1/T_m{}^\circ - (R/\Delta H_m{}^\circ)(\ln x_C - 2x_C(1 - x_C)) \tag{2}$$

The melting temperatures of copolymers containing from 70 to 90 mol% of butylene terephthalate units are plotted as a function of BT unit content in Fig. 6a, together with the melting points-composition data concerning poly(butylene terephthalate-*co*-butylene isophthalate), poly(butylene terephthalate-*co*-diethylene terephthalate) and poly(butylene terephthalate-*co*-triethylene terephthalate) copolymers (these last taken from Refs. [10,21,22], respectively). As can be seen, T_m decreases with increasing the co-unit content; moreover, the T_m data of all the copolymeric systems examined appear to lie on the same curve. As T_m depends exclusively on the molar fraction of butylene terephthalate content and not on the specific chemical characteristics of the co-units, the total exclusion of these last from the crystalline lattice of PBT is confirmed, as well as the random nature of the copolymers investigated. Therefore, the above exclusion models can be applied to the experimental data reported in Fig. 6a. As commonly found for random copolymers, Flory's equation underestimates the melting point depression; on the contrary, Baur's equation fits well with our experimental data, as can be seen in Fig. 6b, where the T_m values are reciprocally plotted against $-[\ln x_C - 2x_C(1 - x_C)]$. As can be noted, the plot shows a good linearity and this result can be considered a further proof of the random nature of the

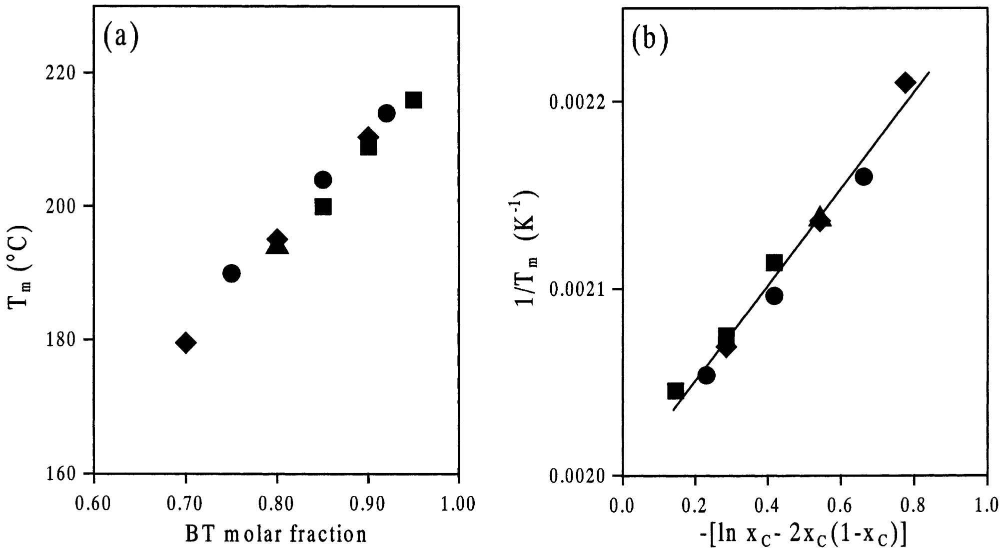


Fig. 6. (a) Melting temperature (T_m) as a function of composition for PBT/TDET random copolymers (◆), poly(butylene terephthalate/butylene isophthalate) (▲), poly(butylene terephthalate/diethylene terephthalate) (●) and poly(butylene terephthalate/triethylene terephthalate) (■) copolymers rich in BT units; (b) $1/T_m$-composition plot according to Baur's equation.

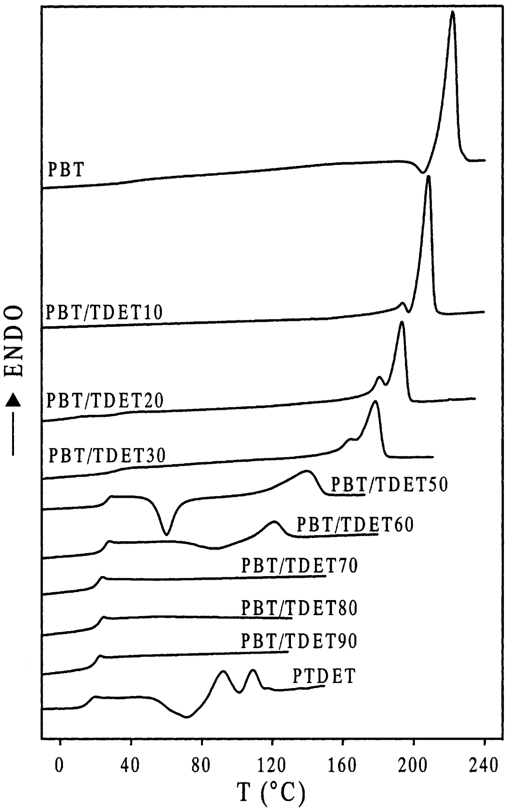


Fig. 7. Calorimetric curves of PBT, PTDET homopolymers and their random copolymers after melt quenching.

copolymers investigated (and, among these, of PBT/TDET copolyesters). The $T_m°$ and $\Delta H_m°$ values estimated on the basis of Baur's equation were found to be 227 °C and 146 J/g, respectively, in good agreement with those previously reported [21–23].

As mentioned above, X-ray measurements carried out on PTDET and PBT/TDET copolymers containing from 80 to 95 mol% of thiodiethylene terephthalate units showed that the crystal phase which develops in the copolymers is related to the characteristic lattice of PTDET. Baur's equation can be therefore applied to the few available experimental data: the T_m values fit very well onto a straight line and from the slope a value of $\Delta H_m° = 91$ J/g can be obtained, whereas from the intercept a $T_m° = 117$ °C was determined. To our knowledge, up to now, no data are available in the literature on PTDET for comparison.

In Fig. 7, the calorimetric curves of the samples after rapid quenching from the molten state are collected; a double melting peak can be noted in the DSC trace of PTDET homopolymer. The most common concepts invoked to explain the multiple melting behavior of semicrystalline polymers are: (1) melting of crystals of different stability [24,25], and (2) a melting–recrystallization–remelting process [26,27]. In the case of PTDET, different kinds of experiments carried out previously by us by means of DSC and X-ray equipments [28] permitted to explain the double melting peak as due to a coexistence of two groups of crystals with different stability.

As well known, a partially crystalline material is expected to exhibit different glass transition behavior than completely amorphous. Although some conflicting results are reported in the literature [29], crystallinity usually acts like crosslinking and raises T_g through its restrictive effect on segmental motion of amorphous polymer chains. In order to study the influence of chemical structure on the glass transition of random copolymers, the phenomenon should be examined in the total absence of crystallinity. Rapid cooling (quenching) from the melt is the method commonly used to prevent crystallization and obtain polymers in a completely amorphous condition. Most of the DSC curves obtained after rapid cooling from the melt are shown in Fig. 7: the calorimetric traces concerning PBT and the PBT/TDET copolymers poor in sulfur-containing units (up to 30 mol% of TDET units) are typical of a partially crystalline polymer, being characterized by a glass transition phenomenon followed by a considerable melting endotherm. As a matter of fact, it is well known that PBT cannot be easily frozen in an amorphous glassy state due to its high rate of crystallization [30]. The DSC traces of PBT/TDET50 and PBT/TDET60 show an intense glass transition followed by an exothermal 'cold crystallization' peak and a melting endotherm at higher temperature. The enthalpy associated with the crystallization exotherm very well compares with the corresponding heat of fusion, indicating that the polymer was completely vitrified into the amorphous state by quenching and that, once T_g is exceeded, the amorphous chains acquire enough mobility to rearrange and crystallize. The same thermal behavior is shown by pure PTDET homopolymer. As regards the calorimetric curves of PBT/TDET copolymers where TDET unit content varies from 70 to 95 mol%, only an intense endothermal baseline deviation associated with the glass transition is observed. The DSC scans, obtained after rapid cooling from the molten state, indicate therefore a quite different thermal behavior of PTDET and PBT homopolymers: the former is completely amorphous, whereas the latter is partially crystalline. Moreover, the phase behavior of PBT/TDET copolymers depends on composition: amorphous or semicrystalline samples are obtained at high PTDET or high PBT content, respectively. As can be seen in Fig. 7 and from the data collected in Table 3, the glass transition temperature is markedly influenced by the amount of sulfur-containing units in the chain: the values of T_g and of the specific heat increment Δc_p associated with the glass transition are plotted in Fig. 8 as a function of TDET unit content. The values of T_g and of Δc_p of partially crystalline PBT, PBT/TDET copolymer containing from 0 to 30 mol% of thiodiethylene terephthalate units do not follow the same composition dependence as that of the amorphous polymers (TDET unit content from 50 to 100 mol%). Amorphous samples show a rather constant Δc_p value (about 0.37 J/g °C), whereas the magnitude of the heat capacity change is

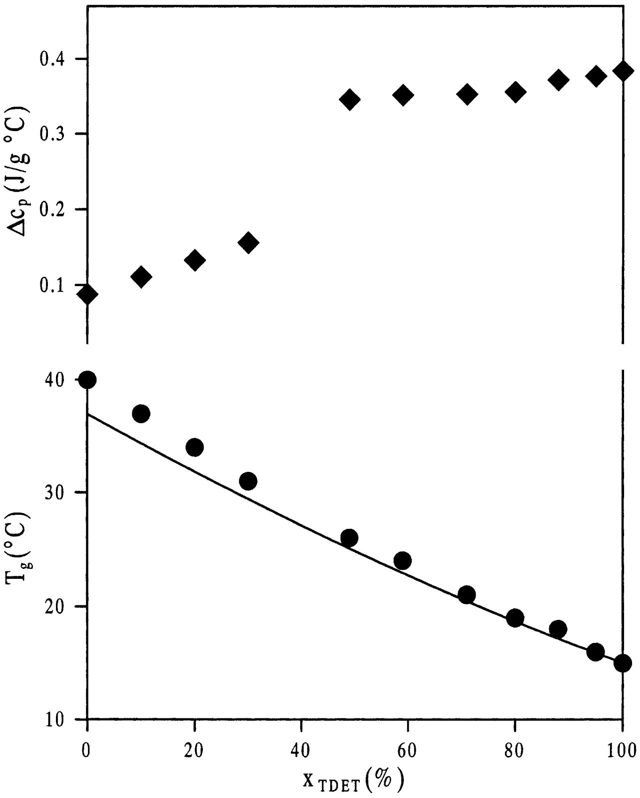


Fig. 8. Composition dependence of T_g (●) and Δc_p (◆) for PBT/TDET random copolymers. Solid line: theoretical curve of T_g vs. composition calculated on the basis of Fox equation.

considerably lower for the copolymers poor in TDET units. This is an obvious consequence of the crystallinity present in these samples, which reduces the amorphous phase undergoing the transition. Moreover, the measured glass transition temperature value is higher than expected, the crystallites hindering the motion of the amorphous chains. As far as the trend of the glass transition temperature with the composition is concerned, one can observe that T_g values decrease as thiodiethylene terephthalate unit content is increased, due to the effect of flexible C–S–C bonds in the polymeric chain.

It is well known that in amorphous random copolymers, T_g is usually a monotonic function of composition [31]; the most common relationship used to predict T_g as a function of comonomer concentration is the Fox equation [32]:

$$1/T_g = w_I/T_{gI} + w_{II}/T_{gII} \tag{3}$$

where T_{gI} and T_{gII} are the glass transition temperatures of the pure homopolymers and w_I and w_{II} the respective weight fractions. As shown in Fig. 8, the equation fits well the experimental data, using for PTDET the glass transition temperature experimentally measured by us, and fixing for PBT the value of 37 °C reported in literature [30].

4. Conclusions

The investigations carried out on the poly(butylene-*co*-diethylene terephthalate) copolymers lead to some interesting results on the effect of sulfur-containing comonomeric units on the thermal properties of PBT. Composition appears to be the prominent parameter in determining the characteristics of the polymeric materials. As far as the thermal stability is concerned, it was found to be good and similar to that of PBT for all the copolymers, but decreasing with increasing sulfur atom content. At room temperature, all the samples synthesized appear as semicrystalline materials with crystal structures strongly depending on composition. The pure crystalline phase of PBT or PTDET was observed in the copolymers with high content of butylene terephthalate or tiodiethylene terephthalate units, respectively; on the contrary, in the copolymers characterized by intermediate compositions, co-crystallization or the co-existence of the two crystalline phases have to be hypothesized in order to explain the experimental results obtained by X-ray measurements. The T_m-composition plots are typical of statistical copolymers, and the application of Baur's equation to the data concerning the samples characterized by the presence of a pure crystalline phase permitted to calculate the melting temperature (T_m°) and the heat of fusion (ΔH_m°) of both completely crystalline homopolymers. The DSC scans, performed after rapid cooling from the molten state, indicate a quite different thermal behavior of PTDET and PBT homopolymers, the former being completely amorphous, the latter partially crystalline. As far as the copolymers are concerned, their behavior appears to be strongly affected by composition, amorphous or semicrystalline samples being obtained at high PTDET or high PBT content, respectively. Lastly, amorphous samples showed a monotonic decrease of the glass transition temperature as the amount of sulfur-containing units is increased, due to the flexible C–S–C bonds in the polymeric chain.

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