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Preparation and thermal behavior of random copolyesters of thiodipropionic acid

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Abstract

Poly(butylene terephthalate/thiodipropionate) and poly(butylene terephthalate/azelate/thiodipropionate) random copolymers of various compositions were synthesized in bulk and characterized in terms of chemical structure and molecular weight. The thermal behavior was examined by thermogravimetric analysis and differential scanning calorimetry. The copolymers containing low amounts of thiodipropionate units showed a good thermal stability, similar to that of PBT, however decreasing with increasing sulfur atom content. All the samples synthesized appear as semicrystalline materials, with fusion temperatures well correlated to composition by Flory's equation. The T_m^0 and ΔH_u values for the completely crystalline homopolymers poly(butylene terephthalate) and poly(butylene azelate) derived using Flory's treatment are in good agreement with those reported elsewhere. Due to the high crystallization rate, the glass transition phenomenon can be detected only for some copolymers with intermediate compositions. As the introduction of S-atoms in the polymeric chain gives rise to a more flexible structure, a decrease of T_g was observed. © 2000 Elsevier Science Ltd. All rights reserved.

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]. The polyesters, mainly based on thiodipropionic, thiodiisobutyric, dithiodibutyric, dithiodibenzoic or dithiodiacetic acid, have been claimed to be plasticizers for poly(vinyl chloride) or rubber modifiers; they can also be used with the addition of elemental sulfur: by heating a mixture of sulfur and thiopolyesters caulking compounds or plastics useful as highways marking stripes are obtained. Moreover, it is well known that the presence of sulfur atoms in a polymeric chain can improve some important properties, such as refractive index, biodegradability, etc. As a consequence, several copolyesters containing sulfur atoms in the main chain or in side chains were recently prepared and studied [3–8]. In addition, polyesters based on thiodipropionic acid were also synthesized and the solid or semi-solid electrolytes obtained by dissolving appropriate lithium salts in them were studied [9–12]. These electrolytes showed rather good characteristics for use in rechargeable lithium batteries.

In view of this, and due to the widespread use of poly(butylene terephthalate) (PBT) and its copolymers, mostly thermoplastic materials with good properties for an ever growing number of applications, we decided to carry out an investigation on the effect of thiodipropionate units on some important characteristics of PBT and poly(butylene terephthalate/azelate) copolymers. These latter were previously studied by

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some of us, with the aim of elucidating the effect of the molecular structure mainly on the melting behavior [13], since in the patent literature copolyesters based on azelaic acid have been claimed as biodegradable polymers [14].

The present paper collects the results of an investigation of the effect of S-containing comonomeric units on the thermal behavior of random copolyesters, which were prepared in our laboratories, based on terephthalic acid and 1,4-butanediol and containing thiodipropionate and for some of them azelate comonomeric units.

2. Experimental

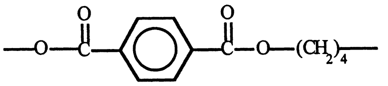
2.1. Products

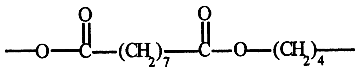
Dimethylterephthalate (DMT), azelaic acid (AA), 1,4-butanediol (BD) and dimethylthiodipropionate (DMTDP) (Aldrich) were reagent grade products and used as supplied.

2.2. Synthesis of polymer samples

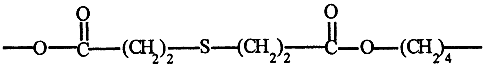
Poly(butylene terephthalate/thiodipropionate) (PB-T/TDP) and poly(butylene terephthalate/azelate/thiodipropionate) (PB-T/Az/TDP) copolymers were synthesized in bulk starting from different amounts of AA, DMT, DMTDP and from BD, employing $Ti(OBu)_4$ as catalyst (about 0.2 g of $Ti(OBu)_4$/kg of polymer). 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 to 200°C and maintained there for about 3 h. In the second stage the pressure was reduced, in order to facilitate the removal of BD in excess, and the temperature was kept in the range 200–240°C (according to the initial composition of the reaction system) for about 2 h. The copolymers obtained, because of the use of $Ti(OBu)_4$ as catalyst and the high temperature which favour redistribution reactions [15], are statistical both in composition and molecular weight distribution. In all cases a molar ratio of 1 : 1.4 between diesters/diacid mixture and BD was employed. Syntheses carried out starting from terephthalic acid (instead of DMT) showed no significant differences in the characteristics of the copolymers obtained.

The monomeric units are the following:


(1)


(2)

$$-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-$$


(3)

$$-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-S-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-$$

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 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 PB-T/Az/TDP and PB-T/TDP 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 case of copolymers rich in 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 5 m 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; higher concentrations were employed in the case of copolyesters containing low amount of aromatic units. A molecular weight calibration curve was obtained with several monodisperse polystyrene standards in the range of molecular weight 3000–100,000.

2.5. 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 −80°C. Finally, they were reheated from −80°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. Moreover, in order to erase the previous thermal history and provide the same heat treatment to all samples, the calorimetric results refer to second scans obtained after rapid quenching from the melt state.

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 PB-T/TDP and PB-T/Az/TDP copolyesters appear as hard or soft semicrystalline solids according to the amount of aliphatic units in the chain. The copolymers rich in aliphatic units are found to be well soluble in the most common organic solvents, i.e. chloroform, tetrachloroethane, methylene chloride, etc., whereas those rich in terephthalate units show a behavior similar to PBT. The copolymers synthesized are listed in Table 1, which also collects the number-average molecular weights (M_n) 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, while the C–H bending vibration of the CH_2–S group is located at 1422–1410 cm^{-1}; moreover, the absence is evident of the band centred at 3400 cm^{-1} corresponding to the stretching vibration of hydroxyl group of 1,4-butanediol, that has reacted or has been removed from the reaction system during the syntheses. The disappearance of most of the OH groups can be therefore considered as evidence of the fact that the polymerization reaction took place. In order to have an understanding into the chemical structure and copolymer composition, a ^{1}H-NMR investigation on the samples was made. The ^{1}H-NMR

Table 1
Molecular characterization data for PB-T/Az/TDP random copolymers

	Composition (feeding)			Composition (^{1}H-NMR)			
Polymer	X_T	X_{Az}	X_{TDP}	X_T	X_{Az}	X_{TDP}	$M_n \times 10^{-3}$
PBT[a]	1	–	–	1	–	–	11.4
PB-95T/5TDP	0.95	–	0.05	0.95	–	0.05	9.9
PB-90T/10TDP	0.90	–	0.10	0.91	–	0.09	6.8
PB-80T/20TDP	0.80	–	0.20	0.81	–	0.19	9.0
PB-50T/50TDP	0.50	–	0.50	0.51	–	0.49	7.0
PB-85T/10Az/5TDP	0.85	0.10	0.05	0.85	0.10	0.05	7.9
PB-75T/20Az/5TDP	0.75	0.20	0.05	0.73	0.22	0.05	12.3
PB-65T/30Az/5TDP	0.65	0.30	0.05	0.65	0.30	0.05	11.8
PB-55T/40Az/5TDP	0.55	0.40	0.05	0.55	0.40	0.05	12.8
PB-45T/50Az/5TDP	0.45	0.50	0.05	0.45	0.50	0.05	7.1
PB-35T/60Az/5TDP	0.35	0.60	0.05	0.35	0.60	0.05	7.3
PB-25T/70Az/5TDP	0.25	0.70	0.05	0.24	0.71	0.05	7.5
PB-15T/80Az/5TDP	0.15	0.80	0.05	0.14	0.81	0.05	8.6
PB-5T/90Az/5TDP	0.05	0.90	0.05	0.07	0.88	0.05	7.4
PB-95Az/5TDP	–	0.95	0.05	–	0.95	0.05	6.9
PB-60T/40Az[a]	0.60	0.40	–	0.60	0.40	-	8.9
PB-52T/38Az/10TDP	0.52	0.38	0.10	0.52	0.37	0.11	6.9
PB-46T/34Az/20TDP	0.46	0.34	0.20	0.47	0.33	0.20	7.2

[a] From Ref. [13].

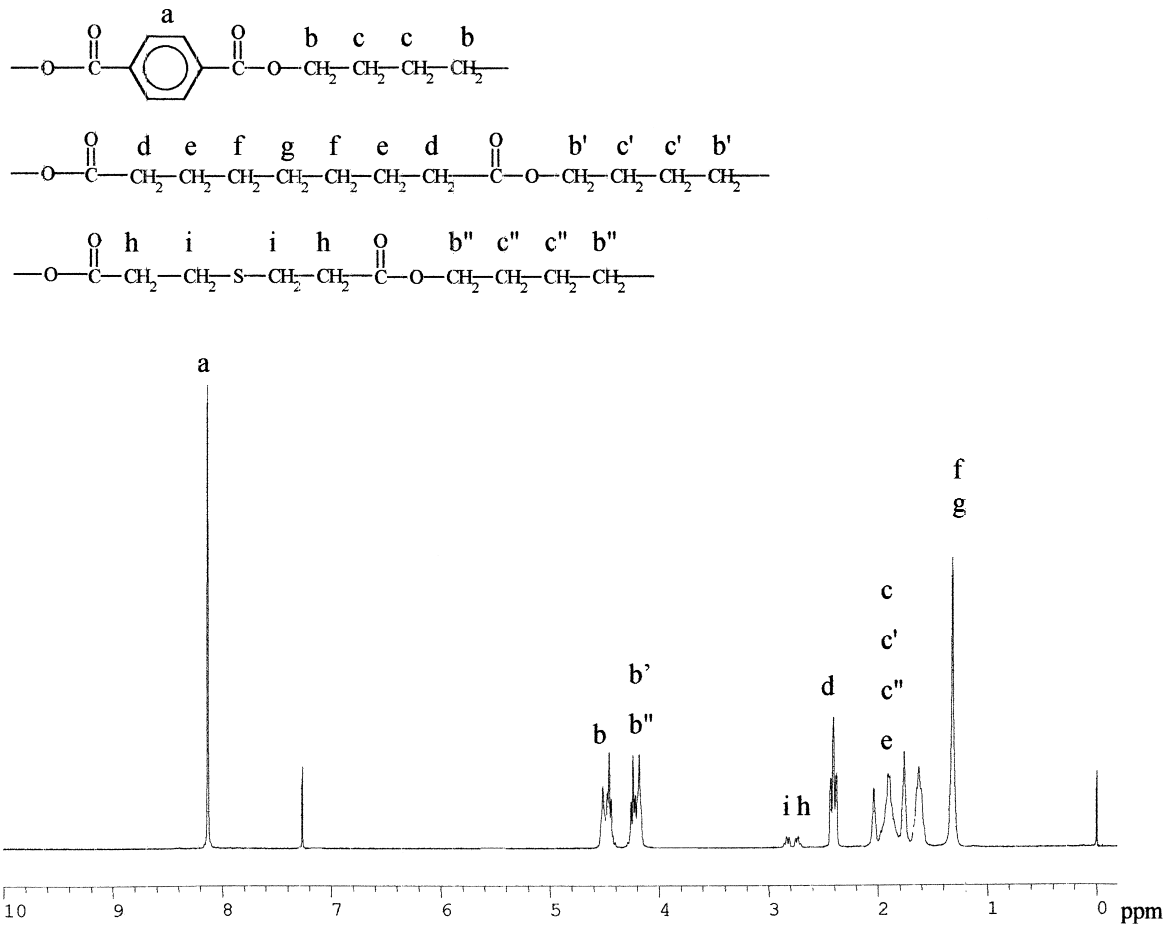


Fig. 1. ^{1}H-NMR spectrum of PB-45T/50Az/5TDP terpolymer.

spectra of all copolyesters are consistent with the expected structure. As an example, the ^{1}H-NMR spectrum of the PB-45T/50Az/5TDP terpolyester is shown in Fig. 1, together with the chemical shift assignments. The peaks chosen for the determination of the copolymer composition, which is collected in Table 1, were the one at 8.13 ppm for the terephthalate unit, that at 2.38 ppm for the azelate unit and finally at 2.70 ppm for the thiodipropionate 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.

4. Thermal properties

4.1. PB-T/TDP copolymers

The copolyesters were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The investigation of the thermal stability of PB-T/TDP copolymers was carried out both in air and under nitrogen atmosphere. Fig. 2 shows the ther-

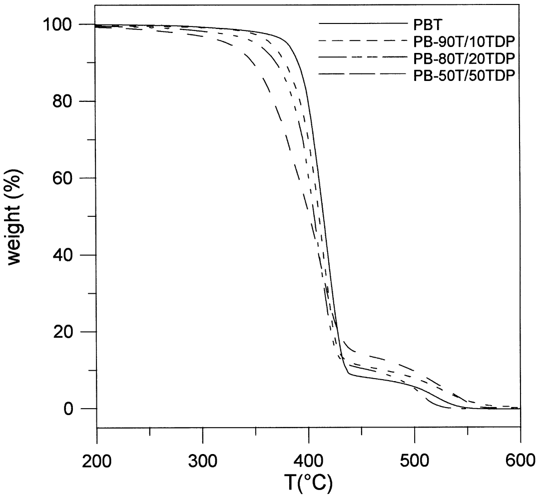


Fig. 2. TGA curves of PB-T/TDP copolymers in air at 10°C/min.

mogravimetric curves in air, from which the temperature of initial decomposition (T_{id}), the temperature corresponding to the maximum weight loss rate (T_{max}) and the weight loss % at T_{id}, collected in Table 2, were determined. 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 TDP content increases; an analogous behavior was found by other authors for a different kind of sulfur-containing polymers [16]. Anyway, it has to be noted that the thermal stability stays good if the amount of TDP units is not too high. Similar results were obtained when the TGA measurements were carried out under nitrogen atmosphere.

As far as the calorimetric results are concerned, the DSC traces of PBT and PB-T/TDP copolymers are reported in Fig. 3 and the data in Table 3. In all cases, a melting endotherm is evident, whose peak location and width depend on composition. In the copolymers the endotherm region is broader with respect to the homopolymer, suggesting the presence of a larger distribution of crystallites with different degree of perfection. Furthermore, the increase in the amount of comonomer added to PBT leads to a marked reduction of the heat of fusion, indicating a reduced level of crystallinity in the copolymers with respect to the homopolymer. The thermogram of the copolymer containing 50 mol% of TDP units also shows a glass transition phenomenon, due to the segmental motion of amorphous chains. For this copolymer, even if the crystallization rate stays high, rapid quenching from the melt makes it possible to obtain a sufficiently amorphous sample to detect the transition.

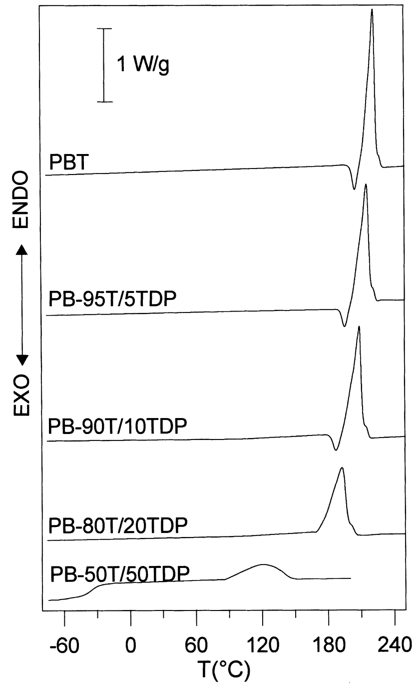


Fig. 3. Calorimetric curves of PBT homopolymer and PB-T/TDP copolymers after melt quenching.

Table 2
Thermogravimetric data of PB-T/Az/TDP random copolymers (in air at 10°C/min)

Polymer	T_{id} (°C)	T_{max} (°C)	Weight loss at T_{id} (%)
PBT[a]	395	423	1.0
PB-95T/5TDP	396	415	0.5
PB-90T/10TDP	391	414	1.0
PB-80T/20TDP	384	408	2.0
PB-50T/50TDP	358	403	1.8
PB-85T/10Az/5TDP	387	413	1.0
PB-75T/20Az/5TDP	390	412	0.8
PB-65T/30Az/5TDP	387	413	1.3
PB-55T/40Az/5TDP	389	415	2.0
PB-45T/50Az/5TDP	388	414	2.2
PB-35T/60Az/5TDP	395	419	3.0
PB-25T/70Az/5TDP	393	418	2.5
PB-15T/80Az/5TDP	393	420	3.1
PB-5T/90Az/5TDP	395	420	3.7
PB-95Az/5TDP	389	418	4.5
PB-60T/40Az[a]	398	419	2.5
PB-52T/38Az/10TDP	395	410	2.6
PB-46T/34Az/20TDP	392	405	2.5

[a] From Ref. [13].

Table 3
Calorimetric data of PB-T/Az/TDP random copolymers (second DSC scan, after rapid quenching from the melt)

Polymer	T_m (°C)	ΔH_m (J/g)	T_g (°C)	Δc_p (J/g °C)
PBT[a]	229	44	–	–
PB-95T/5TDP	217	43	–	–
PB-90T/10TDP	209	41	–	–
PB-80T/20TDP	194	37	–	–
PB-50T/50TDP	123	22	−38	0.295
PB-85T/10Az/5TDP	200	40	–	–
PB-75T/20Az/5TDP	182	35	–	–
PB-65T/30Az/5TDP	160	30	−28	0.150
PB-55T/40Az/5TDP	133	25	−42	0.200
PB-45T/50Az/5TDP	9–104	21	−47	0.260
PB-25T/70Az/5TDP	30	44	−56	0.130
PB-15T/80Az/5TDP	34	59	–	–
PB-5T/90Az/5TDP	43	66	–	–
PB-95Az/5TDP	50	77	–	–
PB-60T/40Az[a]	142	27	−39	0.189
PB-52T/38AZ/10TDP	121	23	−48	0.214
PB-46T/34AZ/20TDP	108	17	−54	0.325

[a] From Ref. [13].

Applying Flory's theory [17], the melting temperature and the heat of fusion of completely crystalline PBT can be determined from the copolymer melting points. According to this theory, in a copolymer consisting of two units (A and B) occurring in random sequence along the chain, of which only A units are able to crystallize under the chosen experimental conditions, the B units, rejected from the crystal lattice, should depress the melting point according to the following relationship:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\left(\frac{R}{\Delta H_u}\right)\ln X_A$$

where T_m^0 and ΔH_u are the melting temperature and the heat of fusion per repeating unit of the completely crystalline homopolymer A, respectively, T_m the melting point of the copolymer, and X_A the molar fraction of the A comonomer. From the slope and the intercept of the $1/T_m$ vs. $-\ln X_A$ plot, $R/\Delta H_u$ and $1/T_m^0$ values were calculated for PBT. The ΔH_u and T_m^0 values obtained (48 J/g and 229°C, respectively) are in good agreement with those previously determined by some of us investigating other copolymeric systems [13,18].

4.2. PB-T/Az/TDP terpolymers

In order to investigate the effect of thiodipropionate units on the characteristics of poly(butylene terephthalate/azelate) copolymers, whose thermal properties were studied previously [13], two series of terpolymers were prepared, one containing a fixed amount of thiodipropionate units (5 mol%) and variable quantity of terephthalate and azelate ones, and another characterized by a constant ratio between these two units and different TDP content. Both series were subjected to thermogravimetric and calorimetric analyses.

As far as the terpolymers containing 5 mol% of thiodipropionate units are concerned, the TGA measurements carried out in air or under nitrogen atmosphere lead to similar results: For all samples synthesized the thermal decomposition takes place practically in one step and is 100%. The T_{id}, T_{max} and weight loss % at T_{id} in air are reported in Table 2. All samples show good thermal stability and relatively high temperature of decomposition with only slight differences relative to PBT. As far as the weight loss % at T_{id} is concerned, it can be seen that it increases slightly as the content of the azelate units is increased, as already found for the copolymers of terephthalic and azelaic acids and 1,4-butanediol [13].

As regards the DSC measurements, the calorimetric data of PBT and PB-T/Az/5TDP terpolymers are collected in Table 3. All samples appear as partially crystalline materials, exhibiting one or two melting endotherms. In particular, the copolymers containing up to 25 mol% of azelate unit show multiple endotherms due to a complex pattern of melting–recrystallization processes which take place during the thermal scanning and lead to the formation of crystals with different degrees of perfection. A similar behavior, typical of many polyesters [19,20], was pointed out by some of us in investigating the thermal properties of copolymers of terephthalic and azelaic acid with 1,4-butanediol [13]. Therefore, the T_m values reported in Table 3 are those corresponding to the fusion process taking place at the highest temperature. The ΔH_m and T_m data are also plotted in Fig. 4 as a function of the molar fraction of PBT: these values decrease at first and then increase again with increasing terephthalate unit content. This behavior is typical of random copolymers in which each comonomer can crystallize when present in major amount [21,22]. On the contrary, PB-45T/50Az/5TDP copolymer shows two distinct melting phenomena (T_m = 9 and 104°C) which presumably has to be attributed to the fusion of the crystalline phases of the two homopolymers, PBT and poly(butylene azelate) (PBAz), as previously observed for similar copolyesters [13,23]. As far as its ΔH_m value is concerned, the datum reported in Table 3 is the sum of the heats of fusion associated with the two distinct melting phenomena.

The application of Flory's equation to the T_m values of PB-T/Az/TDP terpolymers permits the determination of T_m^0 and ΔH_u for PBT and PBAz. The values calculated (234°C and 46 J/g for PBT and 52°C and 50 J/g for PBAz) agree well with those determined by some of us and reported elsewhere [13]. Furthermore, as far as the PBT data are concerned, they are in good

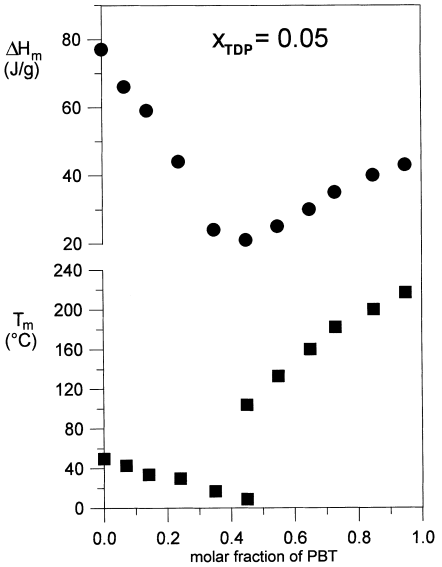


Fig. 4. Composition dependence of T_m (■) and ΔH_m (●) for PB-T/Az/5TDP terpolymers.

agreement with those found using the T_m values of PB-T/TDP copolymers.

As can be seen from the data of Table 3, copolymers having intermediate composition (25–65 mol% of terephatalate units) exhibit a glass transition phenomenon whose temperature (T_g) increases as the content of terephthalate units is increased. This increment is due to the well known stiffening effect of aromatic groups. Since the quenching procedure adopted did not permit us to obtain completely amorphous polymers, any theoretical equation proposed in the literature cannot be applied to correlate T_g values with the composition.

In addition to the above copolyesters, all containing the same percent of thiodipropionate units, copolymers characterized by a constant ratio terephthalate/azelate and different content of thiodipropionate units were prepared. First of all, the thermal stability of the polymers was investigated. The results of the thermogravimetric analysis in air are collected in Table 2; similar results were obtained when TGA analyses were carried out under nitrogen atmosphere. From the data reported, one can observe that increasing amounts of thiodipropionate units lead to less thermally stable polymers, as found for PB-T/TDP copolymers.

The DSC measurements, whose results are collected in Table 3, indicate that the samples are partially crystalline, being characterized by a glass transition followed by a melting process at higher temperature. The calorimetric data are also reported in Fig. 5 as a function of composition. Fig. 5a shows that the fusion temperature and the enthalpy of fusion decrease with increasing TDP unit content. Such behavior is typical of random copolymers whose crystalline phase is composed of only one crystallizable unit [22] (owing to the amount of terephthalate units present in the copolymers synthesized, the crystalline lattice is that of PBT), the depression of T_m and ΔH_m being indicative of a lower level of crystallinity in the copolymers with respect to the homopolymer. The glass transition temperature T_g and the heat capacity increment Δc_p are shown in Fig. 5b: T_g values decrease as thiodipropionate content is increasing. The reason for this decrement in T_g derives from the introduction in the chain of flexible S-containing units; on the contrary, the Δc_p increases as the content of TDP units is increased, and this is a further evidence of the reduced degree of crystallinity in the copolymers with respect to PBT. Taking into account that all quenched samples maintain a partially crystalline character, in this case as well as for the systems investigated above, the theoretical and semiempirical expressions derived to describe the glass transition temperature of amorphous systems as a function of composition cannot be applied.

Finally, we collected all the melting points and heats of fusion-composition data concerning PB-T/TDP, PB-T/Az/TDP and PB-T/Az copolymers (these last taken from Ref. [13]) on the same diagram; in Fig. 6a the T_m and ΔH_m data of the copolymers rich in azelate units are considered as a function of the molar fraction of butylene azelate, whereas in Fig. 6b the melting data of the copolymers rich in terephthalate units are plotted against the molar fraction of PBT. As can be seen in each figure, the T_m values lie on a common curve, and so do ΔH_m values. This behavior, i.e. with the T_m and ΔH_m values depending exclusively on the molar fraction of the crystallizable unit and not on the specific chemical characteristics of the other units in the polymer chain, confirms the random nature of the copolymers investigated and can be considered a further proof that the crystalline lattice is that of PBT or of PBAz, according to the composition.

5. Conclusions

The renewed interest in sulfur-containing polyesters

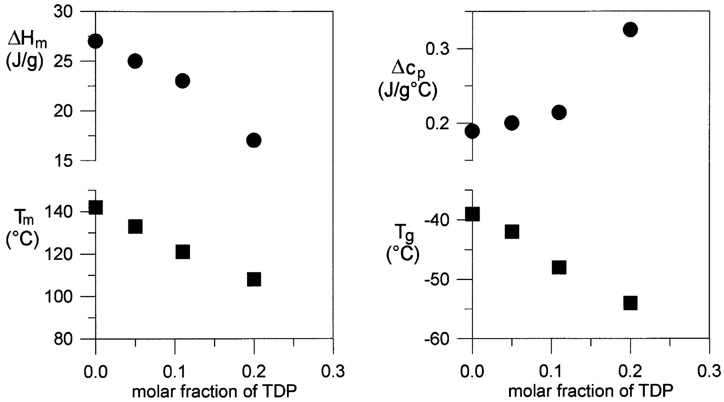


Fig. 5. Composition dependence of calorimetric data for PB-T/Az/TDP terpolymers with different TDP content: (a) T_m (■) and ΔH_m (●) as a function of molar fraction of TDP; (b) T_g (■) and Δc_p (●) as a function of molar fraction of TDP.

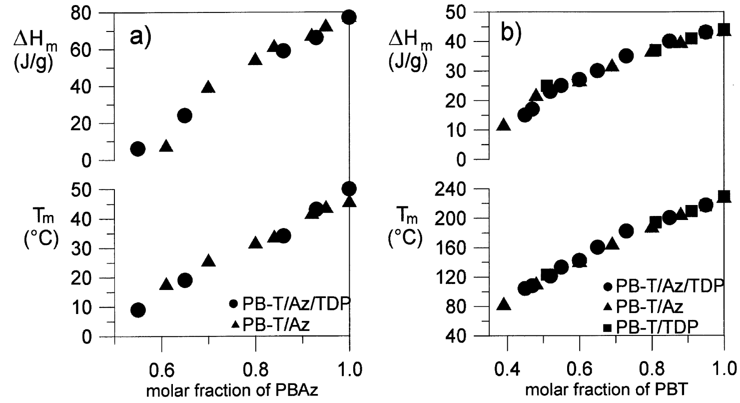


Fig. 6. Melting points (T_m) and heats of fusion (ΔH_m) as a function of composition: (a) vs. molar fraction of PBAz; (b) vs. molar fraction of PBT.

prompted us to investigate the effect of the presence of thiodipropionate units on the thermal properties of PBT as well as PBT/Az copolymers, whose fusion behavior was studied previously. PB-T/TDP and PB-T/Az/TDP random copolymers of various compositions were prepared in bulk with the usual two-stage polycondensation procedure; they proved to be semicrystalline materials, with a good thermal stability that decreases as the content of TDP units is increased. As far as the results of the calorimetric characterization are concerned, due to the high crystallization rate, it was not possible to obtain by rapid quenching from the melt state a sufficiently amorphous sample to detect a glass transition phenomenon; exceptions are represented by a few samples with intermediate compositions. Flory's equation, whose applicability is evidence of the random nature of the copolymers, proved to correlate the fusion temperatures well to composition both of PB-T/TDP and PB-T/Az/TDP copolymers, and permitted calculation of the values of T_m^0 and ΔH_u for the completely crystalline homopolymers PBT and PBAz. The results are in good agreement with data previously reported. Furthermore, for copolymers rich in terephthalate units, the calorimetric results confirm the presence in all cases of the crystalline structure of PBT only, whereas for those rich in azelate units only the PBAz crystal lattice is found.

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