

Sulfur-Containing Polymers: Effect of Composition on Melting Behavior and Crystallization Kinetics of Poly(butylene terephthalate)

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ABSTRACT: The melting behavior and crystallization kinetics of poly(butylene terephthalate/thiodipropionate) (PBT) copolymers were investigated using the differential scanning calorimetry technique. Multiple endotherms typical of PBT were observed in the copolymers under investigation and were found to be influenced both by crystallization temperature (T_c) and composition. Wide-angle X-ray diffraction measurements permitted the identification of the crystalline structure of PBT in all the copolymers investigated. By applying the Hoffman–Weeks method, the equilibrium melting temperature of the copolymers was derived. Isothermal crystallization kinetics were analyzed according to Avrami's treatment. Values of the exponent n close to 3 were obtained, independent of T_c and composition, results in agreement with it being a crystallization process originat-

ing from predetermined nuclei and characterized by three-dimensional spherulitic growth. The introduction of butylene thiodipropionate units was found to decrease the PBT crystallization rate. The heat of fusion (ΔH_m) was correlated to the specific heat increment (Δc_p) of samples of different degrees of crystallinity, and the results were interpreted based on there being an interphase, whose amount was found to increase as the sulfur-containing unit content was increased. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2003–2009, 2003

Key words: poly(butylene terephthalate); random copolymers; sulfur-containing units; melting behavior; crystallization kinetics

INTRODUCTION

Studies of the isothermal crystallization of polymers commonly have been used to investigate the specific mechanisms of the crystallization process and from a technical standpoint are relevant to optimizing process conditions. In fact, most of the physical and mechanical properties of polymeric products are controlled by the crystallization process, and as a consequence, the crystallization kinetics of polymers has been widely investigated.

Copolymerization is now becoming more and more attractive, both for industrial applications and academic interests. In fact, it is a more convenient way to develop new materials than is the method of starting from the synthesis of a specific monomer and its subsequent polymerization. Moreover, copolymerization can improve the properties and processability of existing polymers and reduce the cost of achieving a good balance between performance and price.

Among polyesters, poly(butylene terephthalate) (PBT), a widely used semicrystalline polymer, is one of the toughest and most versatile of all engineering thermoplastics. Nevertheless, some it is too brittle for some applications necessitating improvement of its flexibility. Along these lines, recently, some of us prepared a series of random poly(butylene terephthalate/thiodipropionate) copolymers (PB-T/TDP) by the usual bulk polycondensation method and investigated the effect of introducing flexible aliphatic sulfur-containing units along the PBT chains on the thermal properties, with special attention paid to the glass transition as well as the melting process of samples not subjected to isothermal treatments.¹ In the present study attention was focused on correlations between the melting behavior, kinetics parameters and copolymer composition.

EXPERIMENTAL

Materials

Poly(butylene terephthalate/thiodipropionate) copolymers of various compositions were synthesized according to the well-known two-stage polycondensation procedure, as previously reported.¹ The comonomeric units are:

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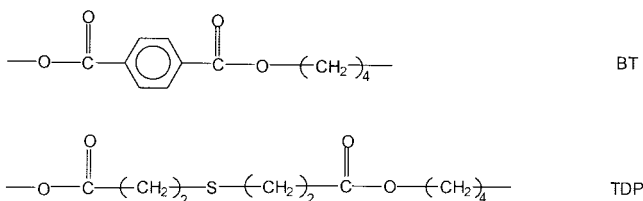
TABLE I
Molecular and Thermal Characterization Data for PB-T/TDP Copolymers¹

Copolymer	Mole fraction of BT units ^a	M_n^b	T_g (°C) ^c	T_m (°C) ^c	$T_{m,co}^o$ (°C)
PB-95T/5TDP	0.95	9,900	32	217	231
PB-90T/10TDP	0.91	6,800	23	209	225
PB-80T/20TDP	0.81	9,000	6	194	208
PB-50T/50TDP	0.51	7,000	-38	123	—

^a By ¹H-NMR spectroscopy.

^b By gel permeation chromatography.

^c By DSC scan after quenching in liquid nitrogen outside the calorimeter.



The chemical structure and composition of all copolymeric samples were investigated by ¹H-NMR spectroscopy, and their molecular weights were determined by gel permeation chromatography.¹ The copolymers obtained were statistical, both in composition and molecular weight distribution, because of the use of Ti(OBu)₄ as catalyst and because of the high reaction temperature, which favored the redistribution reactions.² The main molecular characterization data are reported in Table I, along with the results of a previous thermal characterization.¹

Calorimetric measurements

The isothermal crystallization kinetics and melting behavior were investigated using a Perkin-Elmer DSC7 calorimeter. The external block temperature control was set at -60°C. All the measurements were carried out under a nitrogen atmosphere to minimize oxidative degradation. The instrument was calibrated using high-purity standards (indium and cyclohexane) for melting temperature and heat of fusion. A relatively small sample size, 5 mg, was used to minimize the effect of the thermal conductivity of the polymers. A fresh specimen was used for each run.

To erase the previous thermal history, the samples were heated to about 40°C above their fusion temperature, held there for 3 min, and then rapidly cooled by liquid nitrogen to the predetermined crystallization temperature, T_c . Such short annealing did not lead to any significant thermal degradation of the copolymers.

The T_c range chosen was selected to avoid crystallization during the cooling step and to obtain crystallization times no longer than 60 min.

The heat flow evolving during the isothermal crystallization was recorded as a function of time, and the completion of the crystallization process was detected by the leveling of the differential scanning calorimetry (DSC) trace. To better define the starting time (t_{start}), for each isothermal scan, a blank run was also performed with the same sample at a temperature above the melting point at which no phase change occurred.³ The blank run was subtracted from the isothermal crystallization scan, and the start of the process was taken as the intersection of the extrapolated baseline and the resulting exothermic curve. The isothermally crystallized samples were then heated directly from T_c to melting at 10°C/min. The melting temperature (T_m) was taken as the peak value of the endothermic phenomenon of the DSC curve.

To obtain samples characterized by a different crystal/amorphous ratio, the copolymers were heated above their corresponding melting temperatures and quenched outside the calorimeter by immersion in liquid nitrogen with different transfer speeds below the glass-transition temperature and reheated at 20°C/min.

The specific heat increment, Δc_p , which is associated with the glass transition of the amorphous phase, was calculated from the vertical distance between the two extrapolated baselines at the glass-transition temperature. The heat of fusion of the crystal phase was calculated from the difference between the enthalpy associated with the melting endotherm and the cold-crystallization exotherm, whenever present.

Wide-angle X-ray scattering measurements

Wide-angle X-ray scattering (WAXS) measurements were carried out at room temperature with a Bragg/Brentano diffractometer system (Philips PW 1050/81-PW1710) equipped with a graphite monochromator in the diffracted beam. A Cu anode was used as the X-ray source ($\lambda_1 = 0.15406$ nm, $\lambda_2 = 0.15443$ nm). Data were collected in the range of 5°–80° (2θ) using a 0.1° step and a counting time of 3 s.

RESULTS AND DISCUSSION

Melting behavior of isothermally crystallized samples

Figure 1 shows some typical calorimetric traces of PB-T/TDP copolymers isothermally crystallized at various temperatures (T_c) according to the thermal treatment described in the Experimental section. The isothermal crystallization and the melting behavior of PB-50T/50TDP could not be investigated because of the rate of crystallization was too low. As can be seen, all the DSC curves obtained for the melt-crystallized PB-T/TDP samples are characterized by multiple endotherms, marked as I, II, and III in order of increasing temperature. An analogous behavior of the PBT homopolymer was previously found by some of us.³ In particular, it can be observed that endotherm I was present at a temperature just slightly higher than the crystallization temperature. The position and the area of endotherm II strongly depended on the crystallization temperature, the corresponding peak shifting to higher temperatures and the area increasing with increased T_c . In contrast to melting peaks I and II, the high-temperature endotherm position essentially was independent of crystallization temperature, and its area decreased with increasing T_c . Many crystalline polymers, including polyesters,^{3,4-8} have shown multiple melting peaks on heating, which generally have been ascribed to various crystal modifications⁹⁻¹³ or, alternatively, to the melting–recrystallization process occurring during the DSC scan.¹⁴⁻¹⁶

In the current study, based on the trends observed, the small melting endotherm I can be attributed to the melting of defective crystals formed during a secondary crystallization process (annealing peak). Endotherm II can be ascribed to the fusion of the crystals grown by normal primary crystallization during the isothermal period at T_c , and the observed dependence on the crystallization temperature, in both peak position and area, suggests that thicker crystalline lamellae developed with increasing T_c . The high-temperature melting peak (III) can be explained by the melting of more stable, more perfect crystals grown during the heating run as a consequence of the recrystallization

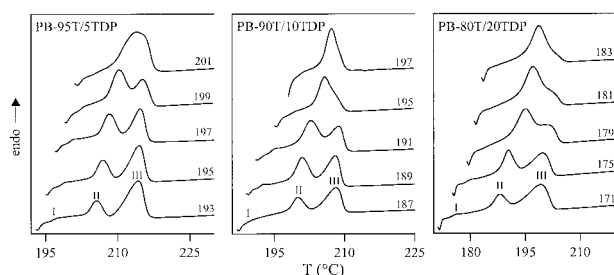


Figure 1 DSC melting endotherms after isothermal crystallization at the indicated T_c s (heating rate: 10°C/min).

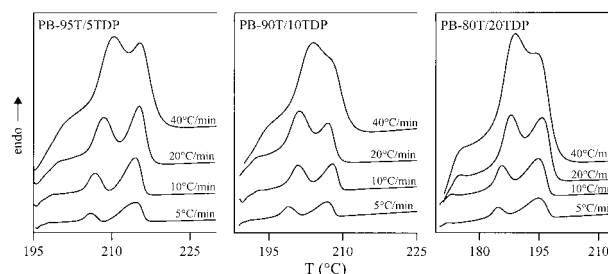


Figure 2 DSC melting endotherms of PB-95T/5TDP, PB-90T/10TDP, and PB-80T/20TDP scanned at the indicated heating rate after isothermal crystallization at 195°C, 189°C, and 170°C, respectively (curves not corrected for changes in instrumental signal with heating rate).

or reorganization of crystals initially formed during isothermal crystallization.

To confirm the hypothesis of the melting–recrystallization processes, the effect of the heating rate on the melting phenomenon was analyzed. As shown in Figure 2, the magnitude of endotherm II increased as the heating rate was increased, contrary to the high-temperature melting peak (III), whose intensity regularly decreased with the heating rate. The higher value of the heat of fusion of endotherm II at the faster heating rates indicates that the crystals formed at T_c did not have enough time to melt and recrystallize, thus confirming a mechanism based on melting and recrystallization of less perfect crystallites into thicker crystals melting at a higher temperature. Some of us previously came to the same conclusions, investigating the multiple melting behavior of PBT.³

The kind of crystalline phase present in the copolymers under investigation was investigated by X-ray analysis. The diffraction curves for the PBT and PB-T/TDP copolymers are reported in Figure 3. As is well known, the PBT homopolymer has a well-defined set of crystalline diffraction peaks. Moreover, as can be seen, all the copolymers are characterized by X-ray spectra very similar to that of PBT, with the position of the reflections essentially the same and no evidence of a variation in the unit cell volume. Only two differences were found: an increasing amount of the amorphous portion and a reduced crystal size with increasing TDP unit content. These results prove that the crystal structure that developed in the above copolymers corresponds to the characteristic lattice of the PBT.

One of the most commonly used procedures to determine the equilibrium melting temperature (T_m^0) of a polymer is the Hoffman–Weeks method. The approach is popular because of the need to measure only the experimental melting temperature of the crystallites formed at T_c . Nevertheless, as some results reported in the literature show,¹⁷⁻¹⁹ the method sometimes fails, as it does not account for a significant

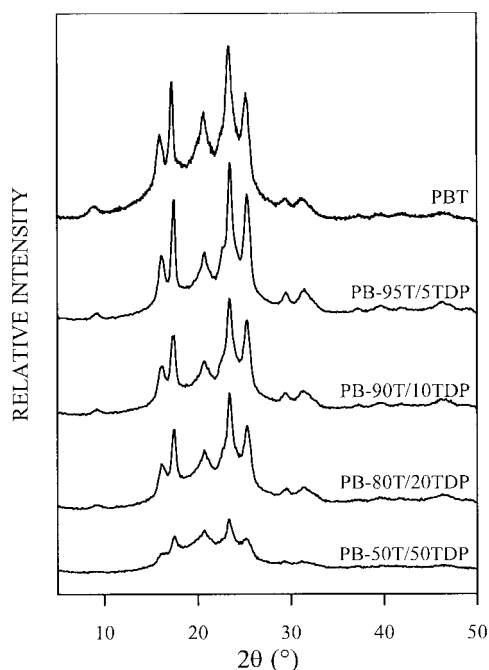


Figure 3 Wide-angle X-ray spectra for PBT and PB-T/TDP random copolymers.

contribution from both the temperature dependence of the fold surface free energy and the thickness increment above the minimum (thermodynamic) lamellar thickness to the difference between the melting and crystallization temperatures. In fact, neglecting this contribution can cause an underestimation of the equilibrium melting temperature and an overestimation of the thickening coefficient. Moreover, for copolymers, the concept of infinite lamellar thickness is not appropriate, even though this treatment is frequently applied to these systems^{20–22} to obtain the driving force for crystallization (namely, the degree of undercooling, $\Delta T = T_m^\circ - T_c$). Extrapolated data ($T_{m,co}^\circ$) also have been used with the aim of evaluating the melting point depression induced by the presence of the second noncrystallizable component.²²

Notwithstanding the above limitations, the experimental melting temperatures ($T_{m,co}$) of the PB-T/TDP copolymers crystallized at different crystallization temperatures were used to obtain information on the equilibrium melting temperature of the copolymers, $T_{m,co}^\circ$, using the Hoffman–Weeks relationship²³:

$$T_{m,co} = T_{m,co}^\circ(1 - 1/\gamma) + T_c/\gamma \quad (1)$$

where γ is a factor which depends on the lamellar thickness. More precisely, $\gamma = l/l^*$, where l and l^* are the thicknesses of the grown crystallite and of the critical crystalline nucleus, respectively.²⁴ Note that eq. (1) correctly represents experimental data only when γ is constant and the slope of the curve in a plot of T_m versus T_c is approximately equal to 0.5.²⁴ If the

thickening process is fast, to obtain the extrapolated $T_{m,co}^\circ$, it is recommended²⁴ that samples with low crystallinity being investigated. Consequently, PB-T/TDP copolymers were quenched from the melt to the desired crystallization temperature and maintained at T_c until crystallization had proceeded to 10% of the overall process.

The peak values of the middle-temperature endotherm as a function of T_c are plotted in Figure 4 for all copolymers under investigation. The melting temperatures ($T_{m,co}^\circ$) obtained from the linear extrapolation of the experimental data are collected in Table I and plotted as a function of butylene terephthalate unit content in Figure 5(a). As can be seen, $T_{m,co}^\circ$ decreased with increasing co-unit content.

Further on, the data were also analyzed by Baur's equation.²⁵

$$1/T_{m,co}^\circ = 1/T_m^\circ - (R/\Delta H_m^\circ)(\ln x_c - 2x_c(1 - x_c)) \quad (2)$$

where $T_{m,co}^\circ$ is the melting temperature of a random copolymer with mole fraction, x_c , of crystallizable comonomer C, T_m° is the equilibrium melting temperature of the homopolymer (in this case, PBT), and R is the gas constant. On the basis of eq. (2) the $T_{m,co}^\circ$ values were reciprocally plotted against $-\ln x_c - 2x_c(1 - x_c)$, shown in Figure 5(b), and the equilibrium melting temperature and heat of fusion for the completely crystalline PBT were extrapolated. As can be noted, the plot shows a good linearity, and this result can be considered further proof of the random nature of the copolymers investigated. The estimated T_m° and ΔH_m° were found to be 237°C and 157 J/g, respectively, in excellent agreement with the values reported in the literature.^{3,26–28}

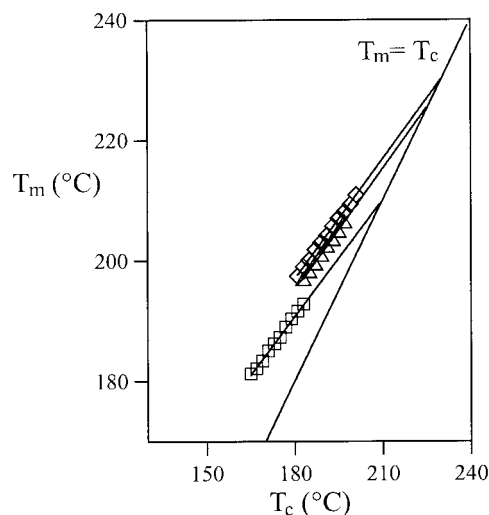


Figure 4 Hoffman–Weeks plots of: (\diamond) PB-95T/5TDP, (Δ) PB-90T/10TDP, and (\square) PB-80T/20TDP.

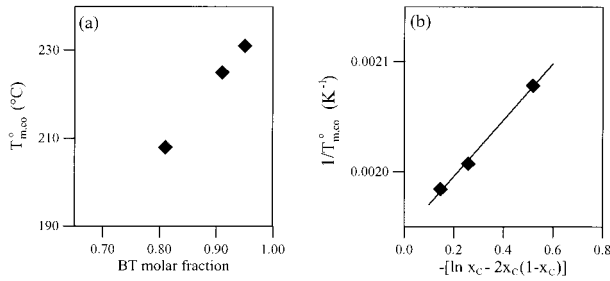


Figure 5 (a) Equilibrium melting temperatures ($T_{m,co}^{\circ}$) as a function of composition for poly(butylene terephthalate/thiodipropionate) copolymers; (b) $1/T_{m,co}^{\circ}$ composition plots according to Baur's equation.

Crystallization kinetics

Analysis of the isothermal crystallization kinetics was carried out on the basis of the Avrami equation²⁹:

$$X_t = 1 - \exp[-k_n(t - t_{\text{start}})^n] \quad (3)$$

where X_t is the fraction of polymer crystallized at time t ; k_n is the overall kinetic constant; t is the time of the isothermal step measured from the achievement of the temperature control; t_{start} is the initial time of the crystallization process, as described in the experimental section; and n is the Avrami exponent, which was correlated with the nucleation mechanism and the morphology of the growing crystallites. X_t can be calculated as the ratio between the area of the exothermic peak at time t and the total measured area of crystallization. The value of the kinetic constant, k_n , is also frequently obtained using the following relationship:

$$k_n = \ln 2 / t_{1/2}^n \quad (4)$$

where $t_{1/2}$ is the crystallization half-time, defined as the time required to reach $X_t = 0.5$.

It is likewise worth remembering that eq. (3) is usually applied to experimental data in the linearized form by plotting $[\ln(-\ln(1 - X_t))]$ as a function of $\ln(t - t_{\text{start}})$, permitting the determination of n and k_n from the slope and the intercept, respectively. In Figure 6 typical linearized Avrami plots for PB-95T/5TDP, PB-90T/10TDP, and PB-80T/20TDP are shown for a selected set of crystallization temperatures. The presence in the curves of two zones with different slopes is evident: $\ln[-\ln(1 - X_t)]$ varies linearly with a higher slope at the early stage and with a lower one at the later stage. This trend is usually observed for polymers and attributed to a primary crystallization followed by a secondary crystallization process.²⁹ The values for crystallization half-time, $t_{1/2}$, the parameter n , and the kinetic constant, k_n , are collected in Table II: as can be seen, for all copolymers under investigation, the overall kinetic constant, k_n , regularly decreased

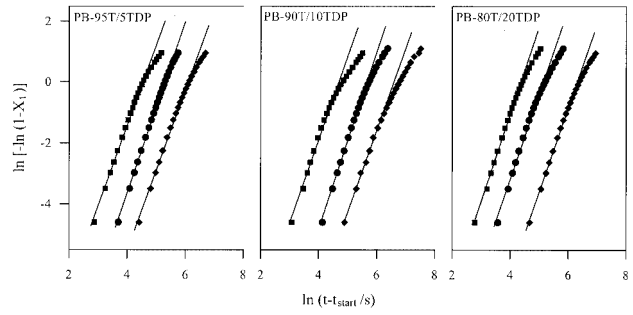


Figure 6 Avrami plots of PB-95T/5TDP at T_c of: (■) 185°C, (●) 191°C, (◆) 199°C; PB-90T/10TDP at T_c of: (■) 181°C, (●) 185°C, (◆) 193°C; and PB-80T/20TDP at T_c of: (■) 160°C, (●) 164°C, (◆) 172°C.

with increasing T_c , similar to PBT,³ as is usual at low undercooling, where crystal formation is controlled by nucleation. To evaluate the effect of composition on crystallization rate, the half-crystallization time, $t_{1/2}$, was plotted as a function of degree of undercooling ($\Delta T = T_m^{\circ} - T_c$), shown in Figure 7 together with the data concerning homopolymer PBT.³ An increase in $t_{1/2}$ can be observed with increasing TDP unit content. As the crystallization of a single component in copolymers involves segregation of the co-units, the observed decrease in the crystallization rate with increasing TDP unit content can be considered a result of the rejection from the crystalline phase of these

TABLE II
Kinetic Parameters for Isothermal Crystallization of PB-T/TDP Copolymers

Sample	T_c (°C)	$t_{1/2}$ (s)	n	k_n (s ⁻ⁿ)
PB-95T/5TDP	185	49	2.7	1.9×10^{-5}
	187	62	2.7	1.0×10^{-5}
	189	81	2.8	3.3×10^{-6}
	191	99	2.8	1.7×10^{-6}
	193	155	2.9	3.1×10^{-7}
	195	200	2.9	1.5×10^{-7}
	197	318	2.8	6.8×10^{-8}
	199	459	2.7	2.4×10^{-8}
	201	764	3.0	1.6×10^{-9}
	PB-90T/10TDP	179	65	2.8
181		83	2.8	1.2×10^{-6}
183		101	2.9	6.8×10^{-7}
185		125	2.9	3.1×10^{-7}
187		196	2.7	9.6×10^{-8}
189		301	2.7	2.4×10^{-8}
191		444	2.7	7.9×10^{-9}
193		858	2.8	1.0×10^{-9}
PB-80T/20TDP	160	67	2.9	2.1×10^{-6}
	162	83	2.7	1.1×10^{-6}
	164	105	2.8	6.0×10^{-7}
	166	157	2.9	1.8×10^{-7}
	168	183	2.7	1.2×10^{-7}
	170	213	2.6	7.2×10^{-8}
	172	290	2.8	2.8×10^{-8}
	174	491	2.7	5.8×10^{-9}
	176	880	2.9	9.7×10^{-10}

units, which the regular packing of PBT polymer chains makes more difficult. However, it has to be noted that the co-units did not affect the amount of crystallinity that developed during isothermal crystallization, the enthalpy of fusion (normalized for the butylene terephthalate unit content) being approximately 48 J/g for all copolymers investigated, corresponding to 33% crystallinity, with the assumption that the heat of fusion of the perfect crystal was 145 J/g for PBT.³⁰ For all the isothermally crystallized copolymers, the Avrami exponent, n , was found to be close to 3, independent of the crystallization temperatures investigated (see Table II), indicating that the crystallization process originated from predetermined nuclei and was characterized by three-dimensional spherulitic growth. Values of Avrami exponents very close to 3 were found previously by some of us also for the PBT homopolymer.³

Thermodynamic parameter

To evaluate the heat of fusion of completely crystalline samples, the relationship between the specific heat increment at T_g and the heat of fusion of samples with different crystal/amorphous ratios was examined, with the experimental enthalpy of fusion normalized for the butylene terephthalate weight fraction. The thermal treatment, described in the Experimental section, allowed us to obtain samples with various proportions of crystalline and amorphous phases in all cases except for PB-95T/5TDP. In fact, all the samples of this copolymer crystallized at the same degree independent of the speed of transfer in liquid nitrogen. This behavior can be ascribed to its high crystallization rate (higher than the maximum speed of transfer).

The ΔH_m values obtained were plotted as a function of the corresponding Δc_p , shown in Figure 8: the spe-

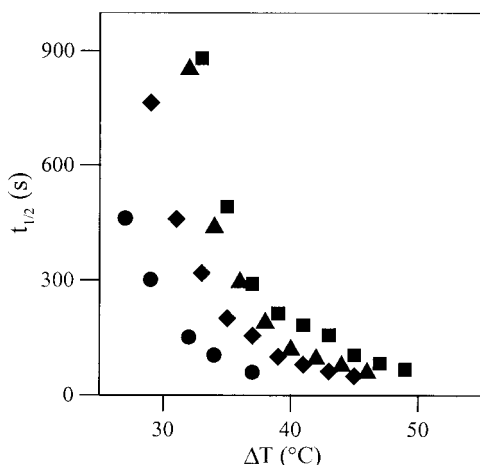


Figure 7 Crystallization half-time ($t_{1/2}$) versus undercooling degree ($\Delta T = T_m^\circ - T_c$) for (●) PBT³, (◆) PB-95T/5TDP, (▲) PB-90T/10TDP, (■) PB-80T/20TDP.

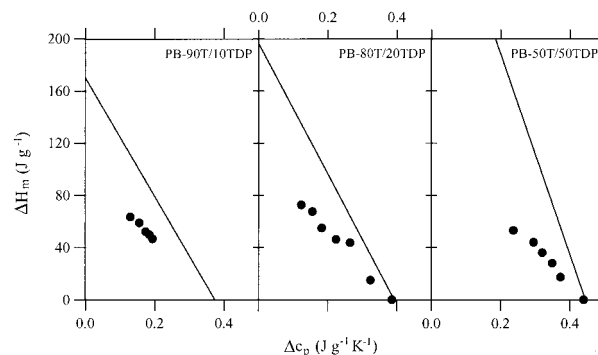


Figure 8 Heat of fusion, ΔH_m , as a function of the specific heat increment Δc_p at T_g (solid lines calculated on basis of a two-phase model).

cific heat increment can be seen to decrease regularly as the melting enthalpy increased. A two-phase model was applied to the copolymers under investigation, and the $\Delta H_m - \Delta c_p$ dependence (solid line), calculated on the basis of this model and the additivity of the specific heat increments, is reported in Figure 8 for all the samples according to the equation:

$$\Delta c_p = w_A \Delta c_{p,A} + w_B (1 - \Delta H_m / \Delta H_m^\circ) \Delta c_{p,B} \quad (5)$$

where Δc_p , $\Delta c_{p,A}$, and $\Delta c_{p,B}$ are the specific heat increments of copolymer and homopolymers A and B, respectively, w_A and w_B are the weight fractions of A and B units, ΔH_m is the normalized melting enthalpy associated with the fusion of the crystallizable units, ΔH_m° is the equilibrium melting enthalpy of the crystallizable component. The Δc_p of both the poly(butylene terephthalate) and poly(butylene thiodipropionate) homopolymers were calculated using the approach of Bicerano,³¹ whereas the way of calculating the ΔH_m° value for PBT was taken from the literature.³⁰ It is clear from Figure 8 that the two-phase prediction was not satisfied because the experimental specific heat increments of semicrystalline samples were considerably lower than expected for the full mobilization of the noncrystalline fraction. In addition, Figure 8 shows that the deviation from the two-phase model increased with increasing crystallinity and was greater for the sample with a higher content of the noncrystallizable component. The results obtained can be interpreted on the basis of the existence of an interphase, defined as that portion of noncrystalline material that does not mobilize at the glass-transition temperature and therefore does not contribute to the observed specific heat increment, originating from the constraints imposed by the crystallites on noncrystallizable units linked to crystal surfaces.

CONCLUSIONS

The investigations carried out on the PB-T/TDP random copolymers led to some interesting results on the

effect of butylene thiodipropionate units on the thermal properties of PBT.

As for the melting phenomenon, multiple endotherms after isothermal crystallization from the melt were found in all the copolymers, similar to PBT, as proved by the calorimetric measurements, performed at different heating rates on the samples isothermally crystallized. Such behavior can be ascribed to a reorganization process occurring during the DSC scan. For each copolymer the Hoffman–Weeks relationship was applied to calculate the equilibrium melting point, T_m° . The extrapolated values appear to be well correlated to composition by Baur's equation, permitting the determination of T_m° for the completely crystalline homopolymer PBT. The applicability of this equation is further evidence of the random nature of the copolymers under investigation.

Concerning the crystallization kinetics, a decrease in the overall crystallization rate in the copolymers was found because of the rejection from the crystalline phase of the noncrystallizable sulfur-containing units, making the regular packing of the PBT polymer chains more difficult. The values of the Avrami exponent, close to 3 for all samples under investigation, indicate a spherulitic morphology in isothermally crystallized samples. Last, the presence of a crystal/amorphous interphase was evidenced in all the copolymers, the interphase amount increasing as the butylene thiodipropionate unit content was increased, because of a highly dispersed crystalline phase. In fact, the noncrystallizable sulfur-containing comonomeric units hindered the crystallization process, leading to small and imperfect crystallites.

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