

RANDOM COPOLYMERS OF POLY(BUTYLENE TEREPHTHALATE)

Effect of thiodiethylene terephthalate units on melting behaviour and crystallization kinetics

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Abstract

The melting behavior and the crystallization kinetics of poly(butylene terephthalate/thiodiethylene terephthalate) copolymers were investigated by DSC technique. The multiple endotherms were influenced both by T_c and composition. By applying the Hoffman–Weeks' method, the T_m^0 of the copolymers was derived. The isothermal crystallization kinetics was analyzed according to the Avrami's treatment. Values of the exponent n close to 3 were obtained, independently of T_c and composition. The introduction of thiodiethylene terephthalate units decreased the PBT crystallization rate. ΔH_m was correlated to Δc_p for samples with different degree of crystallinity and the results were interpreted on the basis of the existence of an interphase.

Keywords: crystallization kinetics, melting behavior, poly(butylene terephthalate), random copolymers

Introduction

Recently, the synthesis and the molecular and thermal characterization of poly(butylene terephthalate) (PBT), poly(thiodiethylene terephthalate) (PTDET) and random copolymers poly(butylene terephthalate/thiodiethylene terephthalate) (PBT/TDET) have been described [1]. As far as the thermal behavior is concerned, special attention has been focused on the effect of the introduction of thiodiethylene terephthalate units along PBT chains on the glass transition as well as the melting process of samples not subjected to isothermal treatments. It has to be emphasized that the behavior of polymers during isothermal crystallization from the melt has a relevant technological importance in order to optimize process conditions and control the properties of the final products. In fact, the

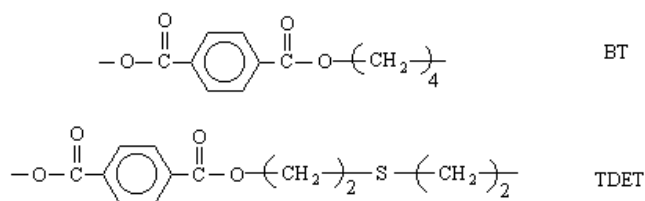
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morphological structure (size, shape, perfection, orientation of crystallites), which is formed by crystallization from the molten state, influences strongly the properties of a polymer. As a consequence, the thermal behavior of PBT has been accurately studied both under isothermal and non-isothermal conditions [2–15]. On the contrary, to our knowledge, up to now no papers have appeared in the literature on the crystallization kinetics of PBT/TDET copolymers. In this view, herein, we report the results of a detailed investigation about the influence of the introduction of the thiodiethylene terephthalate comonomeric units on the isothermal crystallization kinetics of PBT, carried out in order to obtain information on the kinetic and thermodynamic parameters which control the crystalline growth of these new copolymers.

Experimental

Materials

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



For all the copolymeric samples, the chemical structure and composition were investigated by means of $^1\text{H-NMR}$ spectroscopy, and their molecular masses were determined by GPC [1]. The copolymers obtained are statistical both in composition and molecular mass distribution, because of the use of $\text{Ti}(\text{OBu})_4$ as catalyst and the high reaction temperature, which favour the redistribution reactions [16]. The main molecular characterization data are reported in Table 1 along with the results of a thermal characterization carried out previously [1].

Table 1 Molecular and thermal characterization data for PBT/TDET copolymers [1]

| Copolymer | Mole fraction of BT units ^a | M_n^b | $T_g / ^\circ\text{C}^c$ | $T_m / ^\circ\text{C}^d$ | $T_{m,co}^0 / ^\circ\text{C}$ |
|------------|--|---------|--------------------------|--------------------------|-------------------------------|
| PBT/TDET10 | 0.90 | 17.700 | 37 | 209 | 225 |
| PBT/TDET20 | 0.80 | 13.300 | 34 | 189 | 210 |
| PBT/TDET30 | 0.70 | 17.200 | 31 | 178 | 197 |

^a by $^1\text{H-NMR}$ spectroscopy

^b by gel permeation chromatography

^c 2nd scan on samples quenched from the melt

^d 1st scan on samples annealed at room temperature

Calorimetric measurements

The isothermal crystallization kinetics and the melting behavior were investigated by 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 the oxidative degradation. The instrument was calibrated with high-purity standards (indium and cyclohexane) for melting temperature and heat of fusion. Relatively small sample sizes (5 mg) were used to minimize the effect of thermal conductivity of polymers; a fresh specimen was used for each run.

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

The T_c range was chosen in order to avoid crystallization on 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 levelling of the DSC trace. For a better definition of the starting time (t_{start}), for each isothermal scan blank runs were also performed with the same sample, at a temperature above the melting point where no phase change occurred [15]. 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 exothermal curve. The isothermally crystallized samples were then heated directly from T_c up to melting at $10^{\circ}\text{C min}^{-1}$. The melting temperature (T_m) was taken as the peak value of the endothermic phenomenon of the DSC curve.

The melting enthalpy of samples with different crystallinity degree was measured in order to get information about the possible presence of a crystal-amorphous interphase. In order 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 immersing in liquid nitrogen with different speed of transfer below the glass transition temperature, and reheated at $20^{\circ}\text{C min}^{-1}$.

The specific heat increment Δc_p , 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.

Results and discussion

Melting behavior of isothermally crystallized samples

Some representative DSC traces of isothermally crystallized PBT/TDET copolymers are shown in Fig. 1. As can be seen, the DSC curves exhibit three endothermic peaks marked by I, II and III in order of increasing temperature. An analogous behavior was

previously found by some of us for PBT homopolymer [15]. The most common concepts invoked to explain the multiple melting behavior of semicrystalline polymers are: 1) melting of crystals of different stability [17–21], and 2) a melting-recrystallization-remelting process [22–24]. It is fair to state that this apparently universal behavior is not completely understood. Anyway, the multiple endotherm behavior observed in many of the best-studied polyesters [15, 25] has often been ascribed to a reorganization process taking place during the DSC scan, due to a mechanism based on melting and recrystallization of less perfect crystallites into thicker crystals, followed by a final melting process at higher temperature. As concern PBT/TDET copolymers, peak I, which always appears at about 10°C above the crystallization temperature can be considered as due to the melting of crystals formed during a secondary crystallization process [6]. Peak II, which is shifted to higher temperatures and whose intensity progressively increases as T_c increases, can be attributed to the fusion of crystals grown during primary crystallization at T_c . Thus, the melting temperature of the isothermally formed crystals can be estimated from the endothermic peak II. On the other hand, the peak III does not move with changing T_c , but its intensity decreases with increasing the crystallization temperature. Therefore, this peak can be attributed to the melting of crystals grown during the heating run. In order to investigate the nature of these multiple endotherms, the effect of the scanning rate on the melting behavior of PBT/TDET copolymers has been analyzed. It can be observed Fig. 2. that (i) the endotherm III moves to higher temperatures as the heating rate decreases and (ii) the ratio between the area of the second melting peak and the third one increases as the heating rate is increased, confirming that the multiple melting in the copolymers under investigation is due to a mechanism based on melting and recrystallization of less perfect crystallites into thicker crystals, followed by a final melting process at higher temperature. Some of us came previously to the same conclusions, investigating the multiple melting behavior of PBT [15].

Experimental melting temperatures ($T_{m,co}$) of the copolymers crystallized at different T_c s are commonly used to obtain information on the equilibrium melting temperature $T_{m,co}^0$ by means the Hoffman–Weeks' relationship [26]:

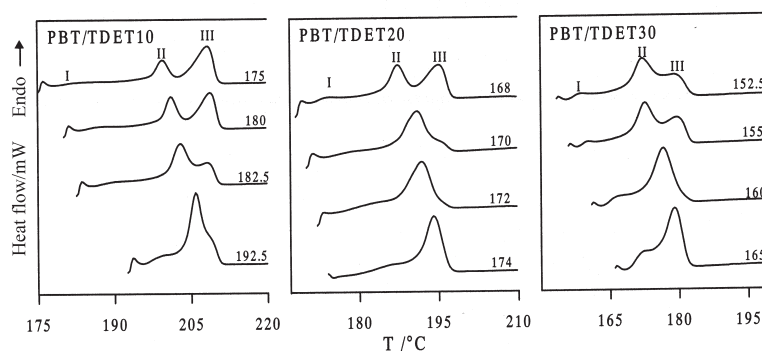


Fig. 1 DSC melting endotherms after isothermal crystallization at the indicated T_c s (heating rate 10°C min⁻¹)

$$T_{m,co} = T_{m,co}^0 (1 - 1/\gamma) + T_c/\gamma \quad (1)$$

where γ is a factor which depends on the lamellar thickness. More precisely $\gamma = l/l^*$ where l and l^* are the thickness of the grown crystallite and of the critical crystalline nucleus, respectively [27]. It has to be pointed out that Eq. (1) correctly represents experimental data only when γ is constant and the slope of the curve in a T_m vs. T_c plot is approximately equal to 0.5 [27].

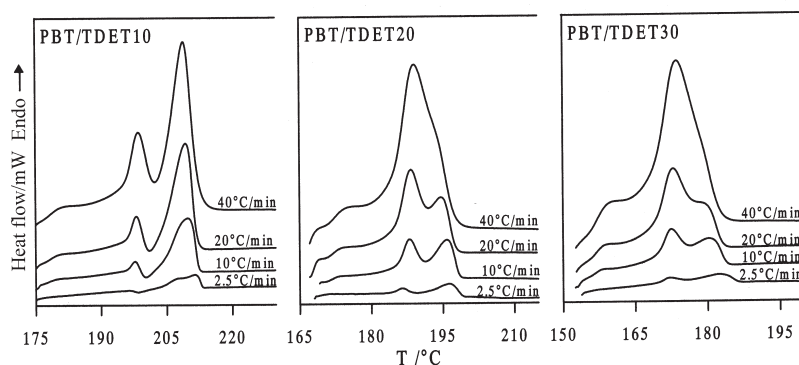


Fig. 2 DSC melting endotherms of PBT/TDET10, PBT/TDET20 and PBT/TDET30 scanned at the indicated heating rate after isothermal crystallization at 175, 168 and 152.5°C respectively. The curves have not been corrected for changes in the instrumental signal with heating rate

Although the concept of infinite lamellar thickness is appropriate only for homopolymers [27], the Hoffman–Weeks’ treatment is frequently applied to copolymers too [27–30] in order to obtain the driving force for crystallization (namely, the degree of undercooling $\Delta T = T_m^0 - T_c$). The extrapolated $T_{m,co}^0$ data can be also used with the aim of evaluating the melting point depression induced by the presence of the second non-crystallizable component [31]. In order to obtain the extrapolated $T_{m,co}^0$, if the thickening process is fast, it is recommended [27] to investigate samples with low levels of crystallinity. Consequently PBT/TDET copolymers were quenched from the melt to the desired crystallization temperature and maintained at T_c until the crystallization had proceeded to 10% of the overall process.

The peak temperatures of endotherm II as a function of T_c are plotted in Fig. 3 for all the copolymers under investigation. The melting temperatures $T_{m,co}^0$ obtained from the linear extrapolation of the experimental data are collected in Table 1 and plotted as a function of butylene terephthalate unit content in Fig. 4a, together with the equilibrium melting points-composition data concerning poly(butylene terephthalate-co-diethylene terephthalate) and poly(butylene terephthalate-co-triethylene terephthalate) copolymers (these last taken from [32]). As can be seen, $T_{m,co}^0$ decreases with increasing the co-unit content; moreover, the $T_{m,co}^0$ data of all the copolymeric systems examined appear to lie on the same curve. As $T_{m,co}^0$ depends ex-

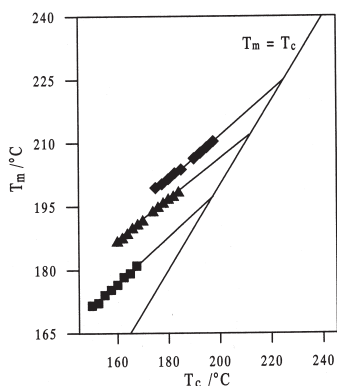


Fig. 3 Hoffman-Weeks plot of \diamond – PBT/TDET10, \blacktriangle – PBT/TDET20, \blacksquare – PBT/TDET30

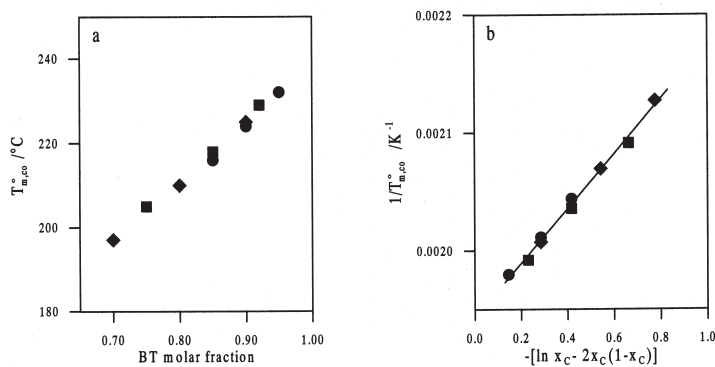


Fig. 4 a – Equilibrium melting temperatures ($T_{m,co}^0$) as a function of composition for \diamond – poly(butylene terephthalate/thiodiethylene terephthalate), \blacksquare – poly(butylene terephthalate/diethylene terephthalate) and \bullet – poly(butylene terephthalate), b – $1/T_{m,co}^0$ -composition plots according to Baur's equation

clusively 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. As a matter of fact, X-ray measurements carried out previously on PBT/TDET samples proved that the crystal structure which develops in the above copolymers corresponds to the characteristic lattice of the PBT [1]. Further on these data were analyzed by Baur's equation [33]:

$$1/T_{m,co}^0 = 1/T_m^0 - (R/\Delta H_m^0) (\ln x_C - 2x_C(1-x_C)) \quad (2)$$

where $T_{m,co}^0$ is the melting temperature of a random copolymer with mole fraction x_C of crystallizable comonomer C , T_m^0 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

$T_{m,co}^0$ s were reciprocally plotted vs. $-\ln x_C - 2x_C(1-x_C)$ in Fig. 4b and the equilibrium melting temperature for the crystallizable component was extrapolated. 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 copolymers investigated (and, among of these of PBT/TDET copolyesters). The estimated T_m^0 is found to be 241°C, in excellent agreement with the values reported in literature (where T_m^0 for PBT homopolymer ranges from 233 to 249°C [4, 6, 10, 13, 14]).

Thermodynamic parameter

In order 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 ratio was examined. The experimental enthalpy of fusion has been normalized for the linear butylene terephthalate mass fraction. The ΔH_m values obtained were plotted as a function of Δc_p in Fig. 5. The specific heat increment is seen to decrease regularly as the melting enthalpy increases and the experimental data are well represented by a straight line. A two-phase model has been 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 Fig. 4 for all the samples according to the equation:

$$\Delta c_p = w_A \Delta c_{p,A} + w_B (1 - \Delta H_m / \Delta H_m^0) \Delta c_{p,B} \tag{3}$$

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 mass fractions of A and B units, ΔH_m is the normalized melting enthalpy associated with the fusion of the crystallizable units, ΔH_m^0 is the equilibrium melting enthalpy of the crystallizable component. $\Delta c_{p,PTDET}$ was experimentally measured by us previously [1]; on the con-

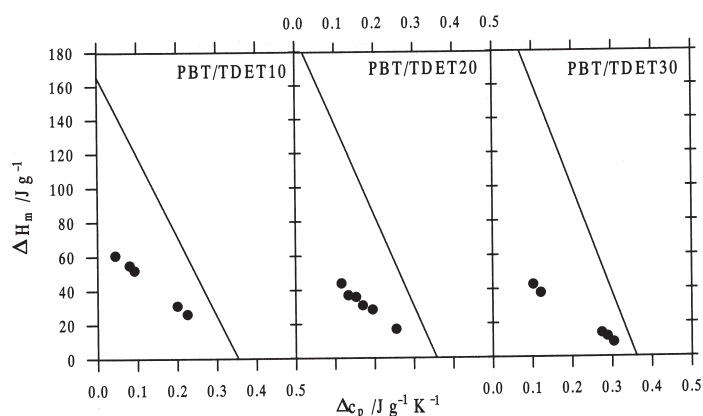


Fig. 5 Heat of fusion ΔH_m , as a function of the specific heat increment Δc_p at T_g . Solid lines were calculated on the basis of a two-phase model

Table 2 Kinetic parameters for the isothermal crystallization of PBT/TDET copolymers

| Sample | $T_c / ^\circ\text{C}$ | $t_{1/2} / \text{s}$ | n | k_n / s^{-n} |
|------------|------------------------|----------------------|-----|-----------------------|
| PBT/TDET10 | 185 | 121 | 2.9 | $1.5 \cdot 10^{-6}$ |
| | 187.5 | 188 | 2.9 | $3.1 \cdot 10^{-7}$ |
| | 190 | 231 | 2.9 | $1.2 \cdot 10^{-7}$ |
| | 192.5 | 291 | 3.0 | $6.2 \cdot 10^{-8}$ |
| | 195 | 434 | 2.9 | $2.1 \cdot 10^{-8}$ |
| | 197.5 | 780 | 3.0 | $3.8 \cdot 10^{-10}$ |
| | 168 | 95 | 2.9 | $5.7 \cdot 10^{-6}$ |
| PBT/TDET20 | 170 | 128 | 3.0 | $2.9 \cdot 10^{-6}$ |
| | 172 | 192 | 2.9 | $1.4 \cdot 10^{-6}$ |
| | 174 | 244 | 2.9 | $4.7 \cdot 10^{-7}$ |
| | 176 | 332 | 3.0 | $1.3 \cdot 10^{-7}$ |
| | 178 | 491 | 3.0 | $3.8 \cdot 10^{-8}$ |
| | 180 | 686 | 3.0 | $6.5 \cdot 10^{-9}$ |
| | 182 | 998 | 2.9 | $2.2 \cdot 10^{-9}$ |
| PBT/TDET30 | 150 | 91 | 2.8 | $9.9 \cdot 10^{-6}$ |
| | 152.5 | 98 | 2.8 | $4.8 \cdot 10^{-6}$ |
| | 155 | 137 | 3.0 | $8.4 \cdot 10^{-7}$ |
| | 157.5 | 176 | 2.9 | $4.3 \cdot 10^{-7}$ |
| | 160 | 244 | 3.0 | $2.6 \cdot 10^{-7}$ |
| | 162.5 | 376 | 2.9 | $5.0 \cdot 10^{-8}$ |
| | 165 | 716 | 2.8 | $1.5 \cdot 10^{-8}$ |
| | 167.5 | 1381 | 2.9 | $4.2 \cdot 10^{-9}$ |

trary, as PBT cannot be quenched to a fully amorphous state by adopting the procedure described in the experimental section, $\Delta c_{p,\text{PBT}}$ has been taken from literature [6], as well as the ΔH_m^0 [34]. It is clear from Fig. 5 that the two-phase prediction is not satisfied, since the experimental specific heat increments of semi-crystalline samples are considerably lower than expected for the full mobilization of the non-crystalline fraction. In addition, Fig. 5 clearly shows that the deviation from the two-phase model increases with increasing crystallinity and is greater for the sample with higher content of non-crystallizable component (i.e. of sulfur-containing units). This is a consequence of the fact that often in polymers there is not a sharp separation between crystalline and amorphous phase [26, 35, 36] and constraints imposed by the crystallites are expected on non-crystallizable units linked to crystal surfaces. Consequently, three distinguishable phases can coexist in a semicrystalline copolymer: (i) a crystalline phase, due to the crystallizable component, (ii) a ‘normal’ amorphous phase, (iii)

an interphase (or rigid amorphous phase) occurring in the vicinity of the crystallites. Interphase is defined as that portion of non-crystalline material which does not mobilize at the glass transition temperature and therefore does not contribute to the observed specific heat increment.

In order to determine the interphase content as a function of copolymer composition, the mass fractions of the crystalline phase (w_c), amorphous phase (w_a) and interphase (w_i) were calculated according to the following relationships:

$$w_c = (\Delta H_m w_{BT}) / \Delta H_m^0 \tag{4}$$

$$w_a = \Delta c_p / \Delta c_p^a \tag{5}$$

$$w_i = 1 - w_c - w_a \tag{6}$$

where Δc_p and Δc_p^a correspond to the experimental specific heat increments of the semicrystalline and fully amorphous copolymer respectively and w_{BT} is the mass fraction of butylene terephthalate units. The variation of the interphase mass fraction as a function of the copolymer composition can be analyzed for a given crystallinity degree of the crystallizable component $x_c = \Delta H_m / \Delta H_m^0$. The results are shown in Fig. 6 for $x_c = 0.10$ and 0.20 . The crystallinity, as expected, decreases with increasing the percentage of the non-crystallizable component, but also the amorphous content shows a reduction. As a matter of fact, an increase of the calculated interphase mass fraction results. As already mentioned, the non-crystallizable comonomer hinders the crystallization process, leading to small and imperfect crystallites. The crystalline phase turns out to be highly dispersed, and the increase in crystal surface results into

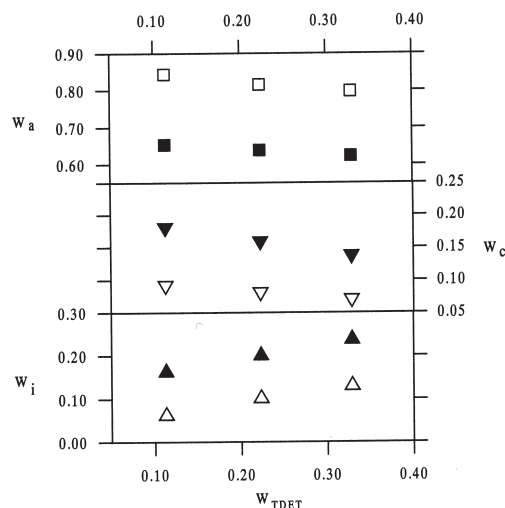


Fig. 6 Mass fractions of amorphous phase (w_a), crystalline phase (w_c), and interphase (w_i), as a function of sulfur-containing units mass fraction (open symbols: $x_c=0.10$, full symbols: $x_c=0.20$)

extensive constraints on the amorphous phase. In the report by Cheng *et al.* a rigid amorphous fraction for PBT was also hypothesized [6].

Crystallization kinetics

The analysis of the isothermal crystallization kinetics can be carried out on the basis of the Avrami equation [37]:

$$X_t = 1 - \exp[-k_n (t - t_{\text{start}})^n] \quad (7)$$

where X_t is the fraction of polymer crystallized at time t , k_n the overall kinetic constant, t is the time of the isothermal step measured from the achievement of the temperature control, t_{start} the initial time of the crystallization process, as described in the experimental section, and n the Avrami exponent, which is 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 by means of the following relation:

$$k_n = \ln 2 / t_{1/2}^n \quad (8)$$

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. (7) is usually applied to the 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 Fig. 7, typical linearized Avrami plots for PBT/TDET10, PBT/TDET20 and PBT/TDET30 are shown for a selected set of crystallization temperatures. The presence in the curves of two zones with different slopes is evident:

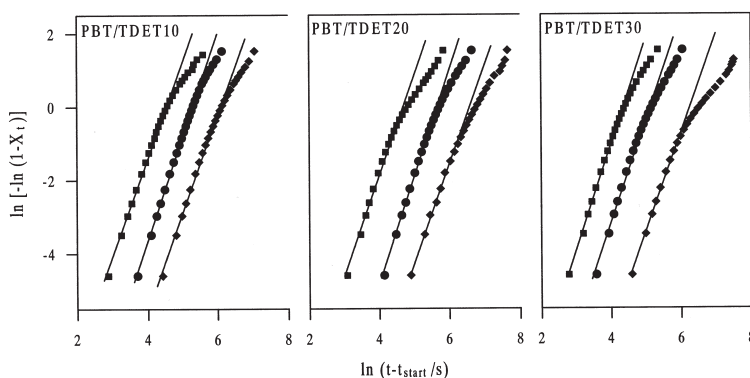


Fig. 7 Avrami plots for PBT/TDET10 at T_c : ■ – 180°C, ● – 185°C, ◆ – 195°C; PBT/TDET20 at T_c : ■ – 170°C, ● – 176°C, ◆ – 182°C; PBT/TDET30 at T_c : ■ – 152.5°C, ● – 160°C, ◆ – 165°C

$[\ln(-\ln(1-X_t))]$ varies linearly with a higher slope at the early stage and with a lower one at the later stage. This trend is usually observed in the case of polymers and attributed to a primary crystallization followed by a secondary crystallization process [37]. The crystallization half-time $t_{1/2}$, the parameter n , and the kinetic constants k_n are collected in Table 2. As can be seen, for all the copolymers under investigation, the overall kinetic constant k_n regularly decreases with increasing T_c , similarly to PBT [15], as usual at low undercooling where the crystal formation is controlled by nucleation. In order to evaluate the effect of composition on crystallization rate, the half-crystallization time $t_{1/2}$ was plotted as a function of undercooling degree ($\Delta T = T_m^0 - T_c$) in Fig. 8 together with the data concerning homopolymer PBT [15]. A marked increase in $t_{1/2}$ is observed as the content of thiodiethylene terephthalate units is increased. As the crystallization of a single component in copolymers involves segregation of the co-units, the observed decrease of the crystallization rate with increasing sulfur-containing unit content is due to the rejection from the crystalline phase of these units, which makes more difficult the regular packing of PBT polymer chains. However, it has to be noted that the co-units do not affect the amount of crystallinity developed during the isothermal crystallization, the enthalpy of fusion (normalized for the butylene terephthalate units content) being approximately 48 J g^{-1} for all the copolymers investigated, which corresponds to 33% of crystallinity, with the assumption that the heat of fusion of the perfect crystal is 145 J g^{-1} for PBT [34]. As far as the Avrami exponent n is concerned, for PBT/TDET10, PBT/TDET20 and PBT/TDET30 copolymers it turned out to be close to 3 for all the crystallization temperatures investigated (Table 2), indicating that the crystallization process originates from predetermined nuclei and is characterized by three-dimensional spherulitic growth. Indeed, some optical microscopy observations carried out by us have revealed a spherulitic morphology in isothermally crystallized PBT/TDET copolymers. Values of Avrami exponents very close to 3 were also found for PBT homopolymer by some of us [15].

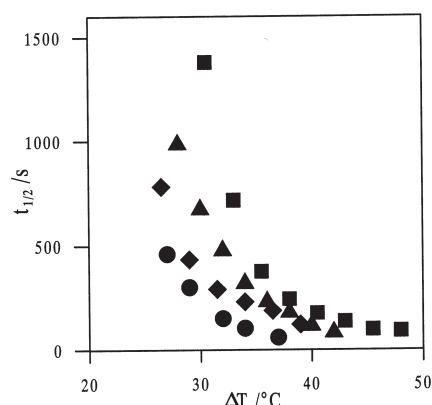


Fig. 8 Crystallization half-time ($t_{1/2}$) vs. undercooling degree ($\Delta T = T_m^0 - T_c$) for ● – PBT (from Ref. [15]); ◆ – PBT/TDET10; ▲ – PBT/TDET20; ■ – PBT/TDET30

Conclusions

The investigations carried out on PBT/TDET samples lead to some interesting results on the effect of the presence of thiodiethylene terephthalate units on the thermal properties of PBT.

As far as the melting phenomenon is concerned, multiple endotherms after isothermal crystallization from the melt were found in all the copolymers, similarly to PBT; as proved by the calorimetric measurements, which show the effect of the scanning rate on the melting peaks of the samples isothermally crystallized, such behavior can be ascribed to a reorganization process occurring during the DSC scan. For each copolymer, the Hoffmann–Weeks' relationship was applied to calculate the equilibrium melting point T_m^0 . The extrapolated values appear to be well correlated to composition by Baur's equation, permitting the determination of T_m^0 for the completely crystalline homopolymer PBT. The applicability of this equation is a further evidence of the random nature of the copolymers under investigation.

Concerning the crystallization kinetics, a marked decrement of the overall crystallization rate in the copolymers was found, due to the rejection from the crystalline phase of the non-crystallizable sulfur-containing units, which makes more difficult the regular packing of PBT polymer chains. The values of Avrami exponent close to three for all the samples under investigation indicate a spherulitic morphology in isothermally crystallized samples. Lastly, the presence of a crystal-amorphous interphase was evidenced in all the copolymers, the interphase amount increasing as the thiodiethylene terephthalate unit content was increased, due to a highly dispersed crystalline phase. As a matter of fact, the non-crystallizable sulfur-containing comonomeric units hinder the crystallization process, leading to small and imperfect crystallites.

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