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Random terephthalate polyesters based on 1,4-butanediol and bis(hydroxyethyl ether) of bisphenol A: thermal properties and crystallization kinetics

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Abstract

The thermal behavior of poly(butylene-*co*-2,2-bis[4-(ethylenoxy)-1,4-phenylene]propane terephthalate) copolymers (PBT/BHEEBT) was investigated by thermogravimetric analysis and differential scanning calorimetry. A good thermal stability was found for all the samples. The thermal analysis carried out using DSC technique showed that the T_m of the copolymers decreased with increasing BHEEBT unit content, different from that of T_g, which on the contrary increased. Wide-angle X-ray diffraction measurements permitted to identify the kind of crystalline structure of PBT in all the semi-crystalline samples. The multiple endotherms typical of PBT were also evidenced in the PBT/BHEEBT samples, due to melting and recrystallization processes. By applying the Hoffman–Weeks' method, the T_m° of the copolymers was derived. The isothermal crystallization kinetics was analyzed according to the Avrami's treatment. The introduction of BHEEBT units decreased the PBT crystallization rate. Values of the exponent n close to 3 were obtained, independently of T_c and composition. Furthermore, the presence of a crystal–amorphous interphase was evidenced.
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Keywords: Poly(butylene terephthalate); Random copolymers; Thermal properties

1. Introduction

As well known, poly(butylene terephthalate) (PBT) is a semi-crystalline polymer widely used in many industrial applications as thermoplastic material, because of its good thermal and mechanical properties, and high chemical resistance. Nevertheless, its drawback lies in the low impact resistance, especially at low temperatures. One of the most common ways of varying the properties of polymeric materials is represented by copolymerization. In fact, many characteristics of copolymers depend strongly on the kind, relative amount and distribution of the comonomeric units along the chain. In order to improve the impact resistance of PBT, recently, some of us prepared, by reactive blending, a series of poly(butylene-*co*-2,2-bis[4-(ethylenoxy)-1,4-phenylene]propane terephthalate) copolymers (PBT/BHEEBT), which have been accurately characterized by the molecular point of view. In addition, a preliminary investigation on the thermal behavior has been carried out [1].

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 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 widely studied both under isothermal and non-isothermal conditions by several authors [2–15]. On the contrary, to our knowledge, up till now no papers have appeared in the literature on the crystallization kinetics of PBT/BHEEBT copolymers. In this view, herein, we report the results of a detailed investigation about the influence of the introduction of the 2,2-bis[4-(ethylenoxy)-1,4-phenylene]propane terephthalate comonomeric units on the thermal behavior and crystallization kinetics of PBT, carried out in order to obtain information on the kinetic and

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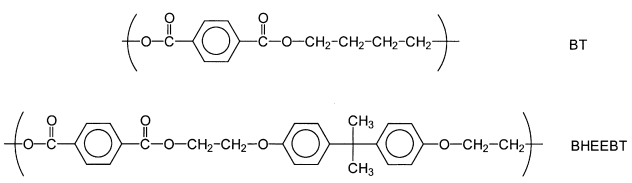
thermodynamic parameters which control the crystalline growth of these new copolymers.

2. Experimental

2.1. Materials

Poly(butylene-*co*-2,2-bis[4-(ethylenoxy)-1,4-phenylene]-propane terephthalate) copolymers of various compositions were synthesized by reactive blending, starting from PBT, BHEEB monomer and $Ti(OBu)_4$, as previously reported [1]. The comonomeric units present in the polymeric chains are:



Before molecular characterization, all the samples were purified by dissolution in 1,1,1,3,3,3-hexafluoro-2-propanol and precipitation in methanol: the chemical structure and composition were investigated by means of ^1H NMR spectroscopy, and their molecular weights were determined by GPC [1]. The copolymers obtained are statistical both in composition and molecular weight distribution, because of the use of $Ti(OBu)_4$ as catalyst and the high reaction temperature, which favor the redistribution reactions [16]. The main molecular characterization data are reported in Table 1.

2.2. Thermogravimetric measurements

Thermogravimetric curves were obtained 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.

2.3. Calorimetric measurements

Calorimetric measurements were carried out by means of a Perkin Elmer DSC7 instrument equipped with a liquid sub-ambient accessory and calibrated with high purity standards (indium and cyclohexane). The external block temperature control was set at −60 °C. With the aim of measuring the glass transition and the melting temperatures of the polymers under investigation, weighed samples (ca. 10 mg) were encapsulated in aluminum pans and heated up to 250 °C at a rate of 20 °C/min (first scan) and then rapidly quenched to −10 °C. Finally, they were reheated from −10 to 250 °C 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) and the crystallization temperature (T_c) were determined as the peak value of the endothermal and exothermal phenomenon in the DSC curve, respectively. 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 and the heat of crystallization of the crystal phase were calculated from the area of the DSC endotherm and exotherm, respectively. Repeated measurements on each sample showed excellent reproducibility.

In order to determine the crystallization rate under non-isothermal conditions, the samples were heated to about 30 °C above fusion temperature at 20 °C/min, kept there for 1 min and then cooled at 10 °C/min. The temperature corresponding to the maximum of the exothermic peak in the DSC cooling-curve (T_{cc}) was taken as indicative of the crystallization rate.

With the aim of studying the crystallization kinetics of the samples under isothermal conditions, the measurements were carried out under a nitrogen atmosphere, by using a fresh specimen (ca. 5 mg) for each run, employing the following standard procedure. The samples were heated to about 30 °C above fusion temperature, then quickly cooled by liquid nitrogen to the crystallization temperature T_c. The T_c range was chosen in order to avoid crystallization during the cooling step and to obtain crystallization times no longer

Table 1
Molecular and thermal characterization data of PBT/BHEEBT random copolymers

Polymer	BHEEBT (mol%)		M_n	T_g (°C)	Δc_p (J/g °C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	T_{cc} (°C)
	Feed	^1H NMR								
PBT	0	0	47700	40	0.088	50	11	223	56	190
PBT/BHEEBT3	3	2.9	47500	42	0.129	52	29	213	51	181
PBT/BHEEBT 6	6	5.5	41600	44	0.280	59	30	207	43	176
PBT/BHEEBT12	12	10.8	44200	47	0.345	77	29	194	31	151
PBT/BHEEBT24	24	22.5	40500	54	0.340	109	24	174	24	126
PBT/BHEEBT50	50	48.4	42700	68	0.347	–	–	–	–	–
PBHEEBT	100	100	33300	83	0.351	–	–	–	–	–

Data of composition and M_n from Ref. 1.

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, for each isothermal scan a blank run was 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 °C/min.

The melting enthalpy of samples with different crystallinity degree was measured with the aim 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 immersion in liquid nitrogen with different speed of transfer, below the glass transition temperature, and reheated at 20 °C/min.

2.4. Wide-angle X-ray measurements

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. Cu anode was used as X-ray source ($\lambda_1 = 0.15406$ nm, $\lambda_2 = 0.15443$ nm). Data were collected in the range 5–80° (2θ) using a 0.1° step and a counting time of 3 s.

3. Results and discussion

The investigation on the thermal stability was carried out both in air and under nitrogen atmosphere. Some typical weight-loss curves as a function of temperature under nitrogen atmosphere are shown in Fig. 1a. As can be observed, PBT/BHEEBT6 sample shows a thermal stability similar to that of pure PBT, whereas in the case of the copolymers containing from 12 to 50 mol% of BHEEBT units, the thermal stability appears to depend on composition, being higher as 2,2-bis[4-(ethylenoxy)-1,4-phenylene]propane terephthalate) content is increased. Furthermore, it can be noted that for PBT and the copolymers containing up to 50 mol% of BHEEBT units, the weight loss takes place practically in one-step; on the contrary, the TGA curve of pure PBHEEBT shows two weight-loss steps. Lastly, the TGA curve of PBT is characterized by a very little char residue (5%), whereas that of pure PBHEEBT shows the highest char residue among all the samples under investigation (30%). As far as the copolymers are concerned, the char residue appears to depend on composition, regularly increasing as the amount of BHEEBT co-units is increased. A similar thermal

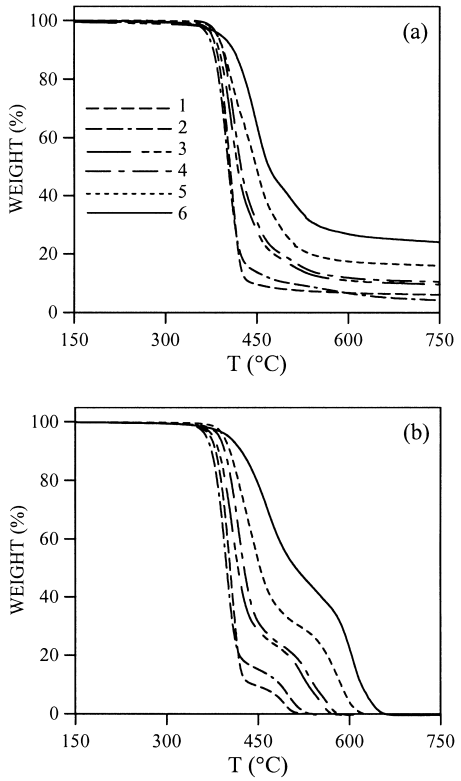


Fig. 1. TGA curves of (1) PBT, (2) PBT/BHEEBT6, (3) PBT/BHEEBT12, (4) PBT/BHEEBT24, (5) PBT/BHEEBT50 and (6) PBHEEBT at 10 °C/min in: (a) nitrogen, (b) air.

stability is observed in air (see Fig. 1b), however being all the samples characterized by a weight-loss of 100% and the thermal degradation process taking place always in two separate steps, the latter one being as more evident as higher is the amount of BHEEBT unit in the polymeric chain. The improved thermal stability of PBT by introduction of 2,2-bis[4-(ethylenoxy)-1,4-phenylene]propane terephthalate units along the polymeric chain may be explained as due to the steric hindrance and high stiffness of these co-units, which prevent thermal degradation reactions, which usually occur in polyesters when heated [17–23]. This hypothesis will be checked in a following paper, concerning the investigation of the thermal degradation mechanism.

As regards calorimetric results, an influence of molecular weight on the glass transition and melting of the polymers synthesized cannot be analyzed, not being available copolymers with the same composition and different molecular weights. However, being the samples characterized by high and similar M_n, such effect can be neglected.

It is well established that the thermal behavior of a polymer is affected by its previous thermal history and therefore, in order to erase it and provide the same heat treatment to all samples, the specimens were subjected to the thermal cycle described in Experimental. Moreover, it is known that a partially crystalline material usually exhibits a different glass transition behavior than completely amorphous. Although some conflicting results are reported in the

literature [24], crystallinity usually acts like crosslinking and raises T_g through its restrictive effect on segmental motion of amorphous polymer chains. Therefore, 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 to obtain polymers in a completely amorphous condition. The quenching procedure adopted consists of cooling the sample outside the calorimeter by immersion in liquid nitrogen as quickly as possible. As a matter of fact, such method permits a quicker cooling of the sample with respect to that obtained inside the DSC equipment. The DSC curves are shown in Fig. 2: in all cases, except for pure PBHEEBT and PBT/BHEEBT50 copolymer, the calorimetric traces show a glass transition followed by an exothermal 'cold crystallization' peak and a melting endotherm at higher temperature. As concern PBT and the PBT/BHEEBT copolymers poor in BHEEBT units (up to 6 mol%), the enthalpy associated with the crystallization phenomenon is lower than that of fusion endotherm, indicating that these copolymers cannot be frozen into a completely amorphous state by quenching. Nevertheless, a portion of amorphous material, once T_g is exceeded, acquires enough mobility to rearrange and crystallize. The DSC curves of such samples are therefore typical of partially crystalline polymers. 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 [6]. In the case of PBT/BHEEBT12 and PBT/BHEEBT24 copolymers the enthalpy of crystallization very well compares with the corresponding heat of fusion, indicating that the polymers are completely amorphous. As regards the calorimetric curves of pure PBHEEBT and PBT/BHEEBT50 copolymer, only an intense endothermal baseline deviation associated with the glass transition is observed. Therefore, the DSC scans indicate a quite different thermal behavior of PBHEEBT and PBT homopolymers: the former is completely amorphous, whereas the latter is partially crystalline. Moreover, the phase behavior of PBT/BHEEBT copolymers depends on composition: semi-crystalline samples are exclusively obtained at high PBT content. As can be seen in Fig. 2 and from the data collected in Table 1, the glass transition temperature is markedly influenced by the amount of BHEEBT 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. 3 as a function of BT unit content. The values of T_g and of Δc_p of partially crystalline PBT and PBT/BHEEBT copolymers containing 3 and 6 mol% of BHEEBT units do not follow the same composition dependence as that of the amorphous copolymers (BHEEBT unit content from 12 to 100 mol%): in fact these last samples show a rather constant Δc_p value (about 0.35 J/g °C), whereas the magnitude of the heat capacity change is considerably lower for PBT and the copolymers poor in BHEEBT units. This is an obvious consequence of the crystallinity of the samples, which reduces the amorphous phase undergoing the transition. Moreover, the measured glass transition temperature value is slightly 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 increase as BHEEBT unit content is increased, due to the stiffening effect of the moieties deriving from bisphenol A in the polymeric chain.

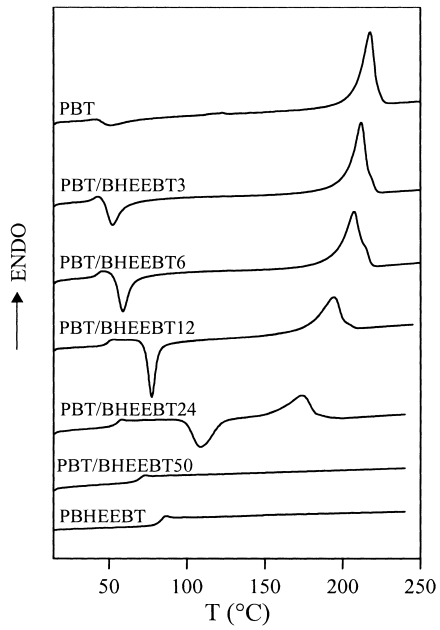


Fig. 2. Calorimetric curves of PBT and PBHEEBT homopolymers, and their random copolymers after melt quenching.

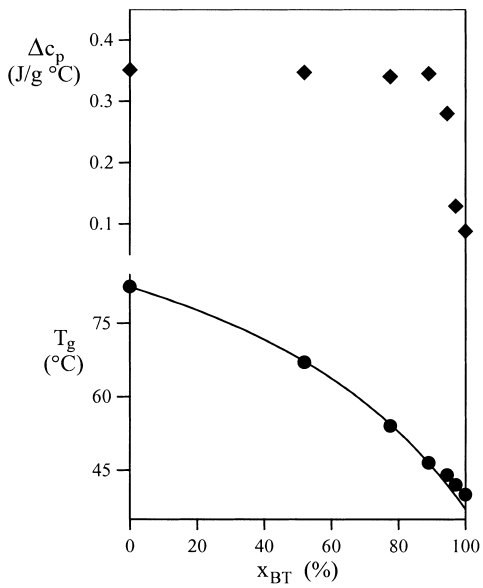


Fig. 3. Composition dependence of T_g (●) and Δc_p (◆) for PBT/BHEEBT random copolymers. Solid line: theoretical curve of T_g vs. composition calculated on the basis of Wood equation.

In amorphous random copolymers, T_g is usually a monotonic function of composition [25] and the most common relationship used to predict T_g as a function of comonomer content is the Fox equation [26]:

$$1/T_g = w_I/T_{gI} + w_{II}/T_{gII} \quad (1)$$

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.

The experimental T_g data of PBT/BHEEBT polymers in the amorphous state (BHEEBT unit content from 12 to 100 mol%) are in general higher than the predicted values, even though they follow the same trend, i.e. T_g increases with increasing the amount of BHEEBT units: this is not surprising, as the Fox equation is known to have limitations, since it does not account for factors like the differences in chemical structure and polymer chain mobility.

Among the various equations proposed to describe the composition dependence of the glass transition temperature in random copolymers, the Wood one is widely used [27]:

$$T_g = (w_I T_{gI} + k w_{II} T_{gII})/(w_I + k w_{II}) \quad (2)$$

where k is a constant parameter and w_I is the weight fraction of butylene terephtalate units.

As shown in Fig. 3, the equation fits well the experimental data (with the adjustable parameter k equal to 1.05), using for PBHEEBT the glass transition temperature experimentally measured by us, and fixing for PBT the value of 37 °C reported in literature [6].

As far as the melting phenomenon is concerned, the calorimetric results indicate that an increase in the amount of the comonomer BHEEBT leads to a reduction in the samples both of the melting temperature and the heat of fusion. Furthermore, in the copolymers the endotherm region is broader, suggesting the presence of a larger distribution of crystallites with different degree of perfection.

The kind of crystalline phase present in the polymers under investigation has been investigated by means of X-ray analysis. The diffraction curves for PBT, PBHEEBT and PBT/BHEEBT copolymers are reported in Fig. 4. PBT homopolymer shows well-defined set of crystalline diffraction peaks, differently from PHEEBT, which is characterized by X-ray spectrum typical of an amorphous material, showing in its WAXS profile no crystalline peaks. Moreover, as can be seen, all the copolymers, with the exception of PBT/BHEEBT50, 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 BHEEBT unit content. These results prove that the crystal structure, which develops in the above copolymers, corresponds to the characteristic lattice of PBT. On the contrary, PBT/BHEEBT50 copolymer appears to be completely amorphous, similarly to pure PBHEEBT.

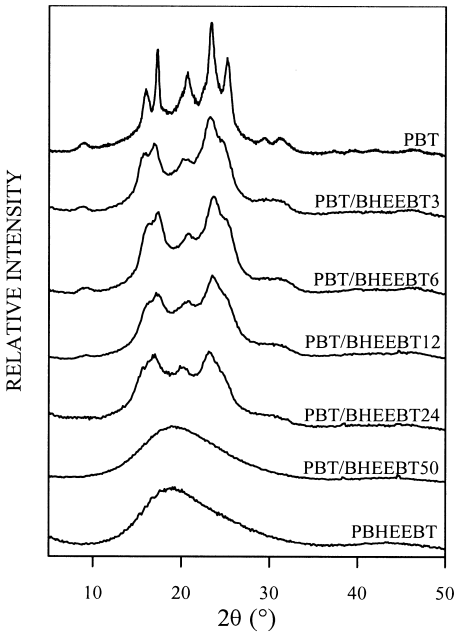


Fig. 4. Wide-angle X-ray spectra of PBT, PBHEEBT and PBT/BHEEBT random copolymers.

Lastly, in order to get preliminary results on the effect of composition on the crystallization rate of PBT, non-isothermal experiments were carried out, subjecting the samples to the thermal treatment described in Experimental. It is worth remembering that the half-time of primary crystallization in isothermal experiments correlates with the temperature corresponding to the maximum of the crystallization peaks in non-isothermal experiments (T_{cc}) [28], being this latter more easily obtainable. The exothermic crystallization peaks of the samples under investigation are reported in Fig. 5, with the exception of pure PBHEEBT and PBT/BHEEBT50 copolymer since both samples are not able to crystallize even though cooled from the melt at low rate (10 °C/min). It can be observed, as also shown in the inset, where the T_{cc} values are reported as a function of composition, that the temperature corresponding to the maximum of the exothermal crystallization peak regularly decreases as the BHEEBT unit content is increased. This trend indicates a decrement of the overall crystallization rate of PBT, due to the presence of non-crystallizable co-units which act as obstacles in the regular packing of polymer chains, being rejected from the crystalline phase of PBT.

3.1. Isothermally crystallized samples

3.1.1. Melting behavior

Some DSC traces of isothermally crystallized PBT/BHEEBT copolymers containing up to 24 mol% of BHEEBT unit are shown in Fig. 6. As can be seen, three endotherms appear in the thermograms of PBT/BHEEBT3 and PBT/BHEEBT6 on heating, which will be referred to as

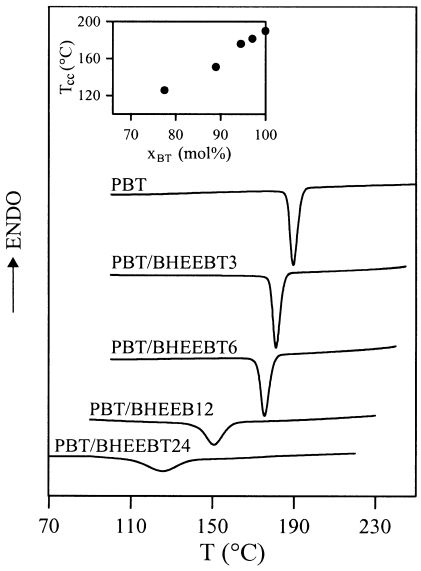


Fig. 5. DSC crystallization exotherms of PBT and PBT/BHEEBT random copolymers cooled from the melt at 10 °C/min. In the inset: cooling crystallization temperature as a function of butylene terephthalate unit content.

low, middle and high temperature melting peak, respectively. The most common concepts invoked to explain the multiple melting behavior of semi-crystalline polymers are: (1) melting of crystals of different stability or morphology [29–33], and (2) a melting–recrystallization–remelting process [34–36]. It is fair to state that this apparently universal behavior is not completely understood. Anyway, the multiple endotherm phenomenon observed in many of the best-studied polyesters [15,37] 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 regards PBT/BHEEBT copolymers, the low temperature melting peak, which appears at approximatively 10 °C above T_c, can be attributed to the melting of defective crystals formed during a secondary crystallization process (annealing peak). The middle-temperature melting peak is associated with the fusion of primary crystals formed during the isothermal crystallization. Its position and its area strongly depend on the crystallization temperature, the peak shifting to higher temperatures and the area increasing as T_c increases. In contrast to low and middle temperature peaks, the high temperature endotherm position is essentially independent of crystallization temperature and its area decreases with increasing T_c. Such result suggests that this peak is due to the melting of crystals of higher stability and perfection grown in consequence of recrystallization or reorganization of crystals initially formed during isothermal crystallization. A similar behavior was pointed out by some of us investigating the melting phenomena of PBT and different copolymers of phthalic acids [15,38–40]. In the case of PBT/BHEEBT12 and PBT/BHEEBT24 copolymers, one can observe that for all the T_cs investigated, besides the annealing peak only one broad endotherm is evident (see Fig. 6). The effect of the heating rate (5, 20, 40 and 80 °C/min) on the melting phenomenon was evaluated for the PBT/BHEEBT3 and PBT/BHEEBT6 copolymers in order to investigate deeply the nature of the multiple endotherms observed in these two cases. It can be observed (see Fig. 7) that the ratio between the area of the middle temperature melting peak and the high temperature 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. The effect of the scanning rate on the melting phenomenon of PBT/BHEEBT12 and PBT/BHEEBT24 samples was also analyzed. The shape of the endotherm turned out to be unchanged with the heating rate, this result suggesting that the recrystallization process is hindered by the presence of a relatively high content of non-crystallizable comonomeric units.

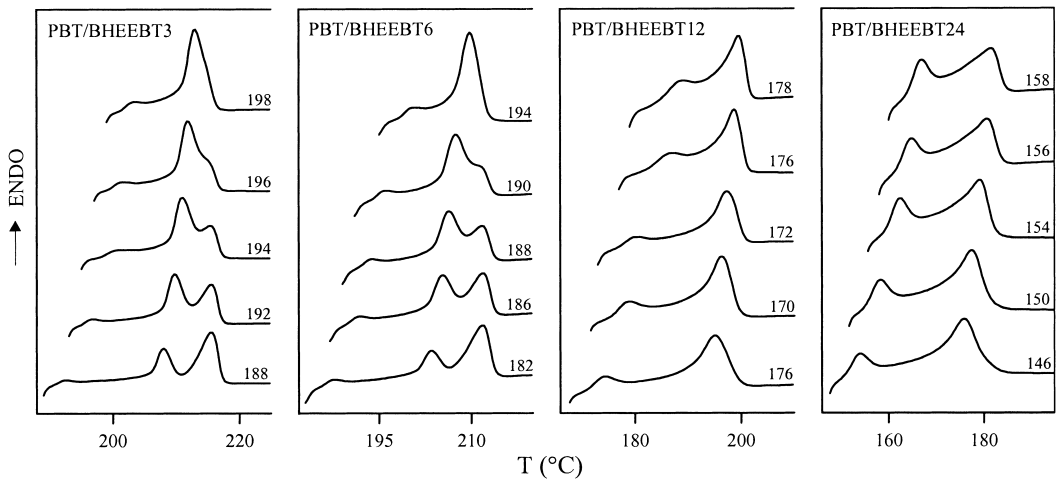


Fig. 6. DSC melting endotherms after isothermal crystallization at the indicated T_cs (heating rate: 10 °C/min).

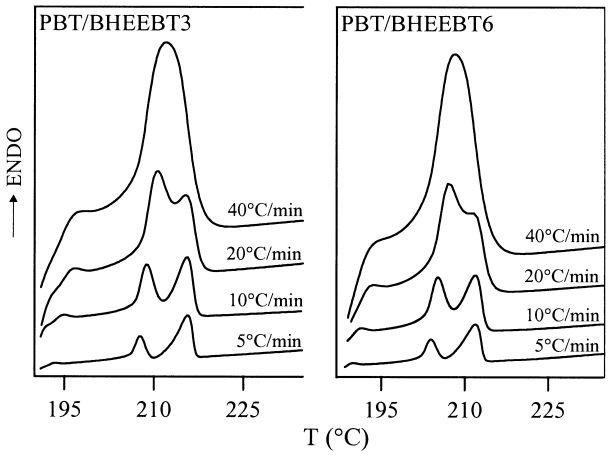


Fig. 7. DSC melting endotherms of PBT/BHEEBT3 and PBT/BHEEBT6 scanned at the indicated heating rate after isothermal crystallization at 190 and 186 °C, respectively. The curves have not been corrected for changes in the instrumental signal with heating rate.

The two most commonly used procedures in order to determine the equilibrium melting temperature of a polymer (T_m°) are the Gibbs–Thomson [41] and the Hoffman–Weeks' [42] methods. As well known, the first one is based upon a thermodynamic relationship, according to which the melting temperature depression ($T_m^\circ - T_m$) is proportional to the ratio of the crystal basal surface free energy to the lamellar thickness. Consequently, if the melting temperature is plotted as a function of the reciprocal of the crystal thickness, the intercept of the extrapolation of a linear regression of the plot gives T_m°. The Hoffman–Weeks' method results from a combination of the Gibbs–Thomson equation and an expression derived from the Lauritzen–Hoffman secondary nucleation theory, which relates the initial nucleus length to the undercooling degree ($\Delta T = T_m^\circ - T_c$). It is also based on the assumption that the difference between crystallization and observed melting temperatures is solely due to the thickening of lamellae formed at the crystallization temperature. The popularity of this approach stems from the need to measure only the experimental melting temperature of the crystallites formed at T_c. Nevertheless, as demonstrated by some results appeared in the literature [43–45], the method sometimes fails, not accounting for a significant contribution to the difference between melting and crystallization temperatures arising from both the temperature dependence of the fold surface free energy and the thickness increment above the minimum (thermodynamic) lamellar thickness. Neglecting this contribution can cause an underestimation of the equilibrium melting temperature and overestimation of the thickening coefficient. Moreover, in the case of copolymers, the concept of infinite lamellar thickness is not appropriate, even though this treatment is frequently applied to these systems [46–48], in order to obtain the driving force for crystallization (namely, the degree of undercooling $\Delta T = T_m^\circ - T_c$). The extrapolated data ($T_{m,co}^\circ$) are also used with the aim of evaluating the melting point depression induced by the presence of the second non-crystallizable component [49].

Notwithstanding the above limitations, the experimental melting temperatures ($T_{m,co}$) of the PBT/BHEEBT copolymers crystallized at different T_cs were used to obtain information on the extrapolated melting temperature $T_{m,co}^\circ$ by means the Hoffman–Weeks' relationship [42]:

$$T_{m,co} = T_{m,co}^\circ(1 - 1/\gamma) + T_c/\gamma \quad (3)$$

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 [46]. It has to be pointed out that Eq. (3) 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 [46]. In order to obtain the extrapolated $T_{m,co}^\circ$, if the thickening process is fast, it is recommended [46] to investigate samples with low levels of crystallinity. Consequently PBT/BHEEBT 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 values of the middle temperature endotherm as a function of T_c are plotted in Fig. 8 for all the copolymers under investigation. The deviation from linearity found at low T_c values is symptomatic of the fast reorganization process involving imperfect crystallites during the DSC heating. The melting temperatures $T_{m,co}^\circ$ obtained from the linear extrapolation of the experimental data are collected in Table 2 and plotted as a function of butylene terephthalate unit content in Fig. 9a: as can be seen, $T_{m,co}^\circ$ decreases with increasing the co-unit content. It is worth remembering that the melting point depression can be due to a reduction in the

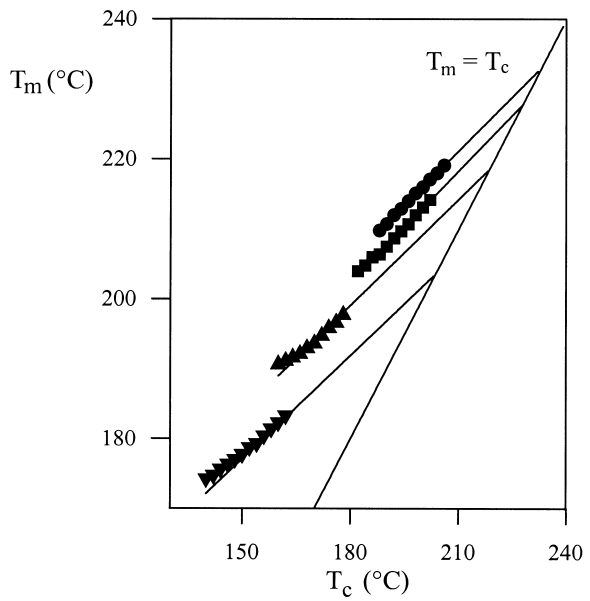


Fig. 8. Hoffman–Weeks' plot for: (●) PBT/BHEEBT3, (■) PBT/BHEEBT6, (▲); PBT/BHEEBT12 and (▼) PBT/BHEEBT24.

Table 2
Kinetic parameters and equilibrium melting temperatures for the isothermally crystallized PBT/BHEEBT copolymers

Sample	T_c (°C)	$t_{1/2}$ (s)	n	k_n (s^{-n})	T_m° (°C)
PBT/BHEEBT3	188	72	2.9	1.1×10^{-5}	232
	190	91	3.0	3.6×10^{-6}	
	192	121	3.0	1.6×10^{-6}	
	194	160	3.0	5.2×10^{-7}	
	196	237	2.9	1.7×10^{-7}	
	198	370	3.0	2.0×10^{-8}	
	200	630	3.0	2.3×10^{-9}	
	202	1123	2.9	7.5×10^{-10}	
PBT/BHEEBT6	182	75	2.8	1.9×10^{-5}	228
	184	89	2.9	5.8×10^{-6}	
	186	117	3.0	1.9×10^{-6}	
	188	160	2.9	7.8×10^{-7}	
	190	229	2.9	2.8×10^{-7}	
	192	336	3.0	3.4×10^{-8}	
	194	555	2.9	1.7×10^{-8}	
	196	883	2.9	2.7×10^{-9}	
	198	1251	2.8	9.4×10^{-10}	
PBT/BHEEBT12	156	49	2.9	$8.7\ 10^{-6}$	218
	158	63	2.9	4.2×10^{-6}	
	160	77	2.9	2.3×10^{-6}	
	162	106	2.9	9.3×10^{-7}	
	164	132	2.9	4.9×10^{-7}	
	166	180	3.0	1.2×10^{-7}	
	168	238	2.9	8.9×10^{-8}	
	170	280	2.9	5.5×10^{-8}	
	172	360	2.8	4.8×10^{-8}	
	174	485	2.9	1.1×10^{-8}	
	176	635	2.9	5.2×10^{-9}	
	178	780	2.9	2.8×10^{-9}	
	180	1201	2.9	8.2×10^{-10}	
PBT/BHEEBT24	136	150	2.9	$6.4\ 10^{-7}$	202
	138	160	2.9	3.9×10^{-7}	
	140	168	2.9	2.4×10^{-7}	
	142	187	2.9	2.1×10^{-7}	
	144	228	2.9	1.8×10^{-7}	
	146	253	2.9	1.2×10^{-7}	
	148	277	2.9	7.7×10^{-8}	
	150	328	2.9	5.2×10^{-8}	
	152	424	2.9	1.7×10^{-8}	
	154	497	2.9	1.4×10^{-8}	
	156	584	2.9	1.1×10^{-8}	
	158	718	2.9	8.2×10^{-9}	
	160	945	2.9	2.6×10^{-9}	
	162	1292	2.8	1.5×10^{-9}	

thickness of lamellar crystals as well as an increase in the level of crystal imperfection.

Further on, the data also were analyzed by Baur's equation [50]:

$$1/T_{m,co}^\circ = 1/T_m^\circ - (R/\Delta H_m^\circ)(\ln x_C - 2x_C(1 - x_C)) \quad (4)$$

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. (4) the $T_{m,co}^\circ$s were reciprocally plotted against $-[\ln x_C - 2x_C(1 - x_C)]$ in Fig. 9b and the equilibrium melting temperature and the 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 a 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 literature [4,6,10,13–15].

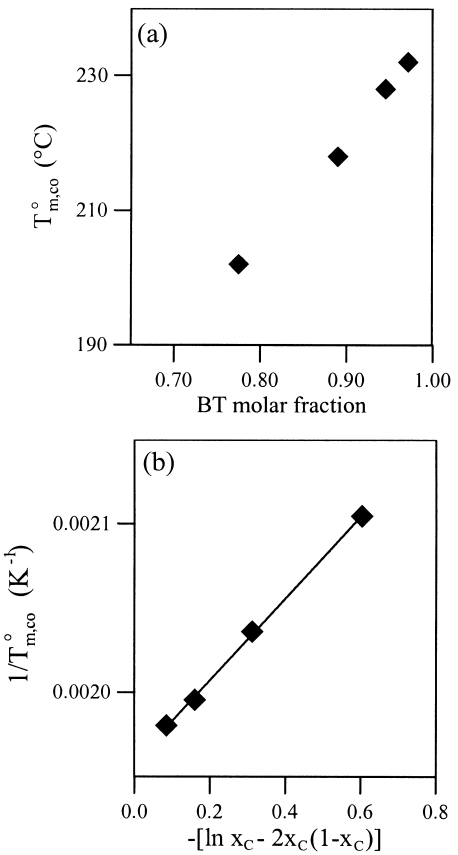


Fig. 9. (a) Equilibrium melting temperatures ($T_{m,co}^\circ$) as a function of composition; (b) $1/T_{m,co}^\circ$-composition plot according to Baur's equation.

3.2. Crystallization kinetics

The analysis of the isothermal crystallization kinetics can be carried out on the basis of the Avrami equation [51]:

$$X_t = 1 - \exp[-k_n(t - t_{start})^n] \quad (5)$$

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 Experimental, 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 relationship:

$$k_n = \ln 2/t_{1/2}^n \quad (6)$$

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. 5 is usually applied to the experimental data in the linearized form, by plotting $\ln[-\ln(1 - X_t)]$ as a function of $\ln(t - t_{start})$, permitting the determination of n and k_n from the slope and the intercept, respectively. In Fig. 10, typical linearized Avrami plots for PBT/BHEEBT3, PBT/BHEEBT6, PBT/BHEEBT12 and PBT/BHEEBT24 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 in the case of polymers and attributed to a primary crystallization followed by a secondary crystallization process [51]. 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 ($\Delta T = T_m^\circ - T_c$) in Fig. 11 together with the data concerning homopolymer PBT [15]: a marked increase in $t_{1/2}$ is observed as the content of BHEEBT 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 BHEEBT unit content can be considered as due to the rejection from the crystalline phase of these units, which makes more difficult the regular packing of PBT polymer chains.

With the aim of evaluating if the constitutional irregularity affects the amount of crystallinity developed

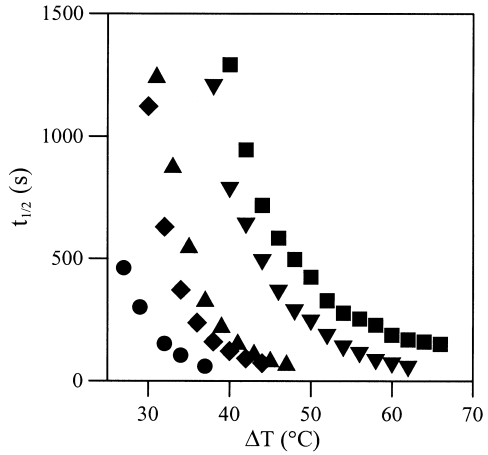


Fig. 11. Crystallization half-time ($t_{1/2}$) vs. undercooling degree ($\Delta T = T_m^\circ - T_c$) for: (●) PBT (from Ref. [15]); (◆) PBT/BHEEBT3; (▲) PBT/BHEEBT6; (▼) PBT/BHEEBT12; (■) PBT/BHEEBT24.

during the isothermal crystallization, for all the samples investigated, the enthalpy of fusion has been calculated. It has been found that ΔH_m is essentially independent of T_c, but strongly dependent on composition, being 46, 43, 39 and 35 J/g for PBT/BHEEBT3, PBT/BHEEBT6, PBT/BHEEBT12 and PBT/BHEEBT24 respectively, after normalization for the butylene terephthalate units content. As a matter of fact, a value of 48 J/g was previously found for the homopolymer PBT by some of us [15]. Therefore, the random incorporation of amounts of non-crystallizable units into the PBT backbone influences the total crystallinity degree of PBT, which crystallizes in the copolymer in minor percentage as in the pure state. As far as the Avrami exponent n is concerned, for all the isothermally crystallized copolymers, it turned out to be close to 3 for all the crystallization temperatures investigated (see Table 2), indicating that the crystallization process originates from predeterminated nuclei and is characterized by three-dimensional spherulitic growth. Values of Avrami exponents very close to 3 were found previously by some of us also in the case of PBT homopolymer [15].

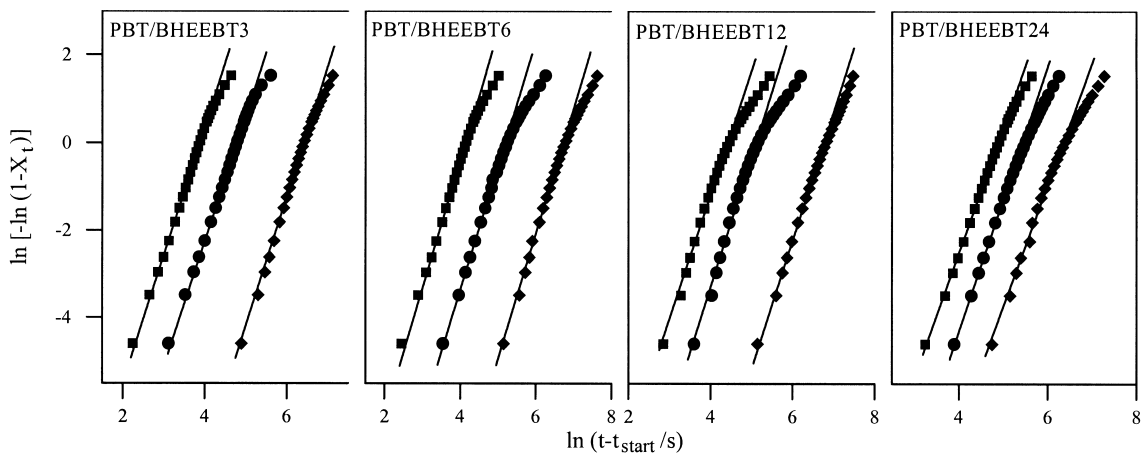


Fig. 10. Avrami plots for PBT/BHEEBT3 at T_c: (■) 188 °C, (●) 194 °C, (◆) 200 °C; PBT/BHEEBT6 at T_c: (■)184 °C, (●) 190 °C, (◆) 196 °C; PBT/BHEEBT12 at T_c: (■) 158 °C, (●) 164 °C, (◆) 176 °C; PBT/BHEEBT24 at T_c: (■ 136 °C, (●) 146 °C, (◆) 156 °C.

3.3. Thermodynamic parameter

In a previous paper, a rigid amorphous fraction (interphase) for PBT was hypothesized [52]. 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. Therefore, three distinguishable phases can be hypothesized to exist in semi-crystalline polymers: (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.

In order to evaluate the existence of a crystal–amorphous interphase in the copolymers under investigation, 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 being normalized for the butylene terephthalate weight fraction. The ΔH_m values obtained were plotted as a function of the corresponding Δc_p in Fig. 12: the specific heat increment is seen to decrease regularly as the melting enthalpy increases. 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. 12 for all the samples according to the equation:

$$\Delta c_p = w_A \Delta c_{p,A} + w_B(1 - \Delta H_m/\Delta H_m^\circ)\Delta c_{p,B} \quad (7)$$

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. $\Delta c_{p,BHEEBT}$ has been experimentally measured by us (see above); on the contrary, as PBT cannot be quenched to a fully amorphous state by adopting the procedure described in Experimental, $\Delta c_{p,PBT}$ has been taken from literature [52], as well as the ΔH_m° value [53]. It is clear from Fig. 12 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. 12 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. The results obtained can be interpreted on the basis of the existence of an interphase, originating from the constraints imposed by the crystallites on non-crystallizable units linked to crystal surfaces. In order to determine the interphase content as a function of copolymer composition, the weight fractions of the crystalline phase (w_c), amorphous phase (w_a) and interphase (w_i) were calculated according to the following relationships:

$$w_c = (\Delta H_m w_{BT})/\Delta H_m^\circ \quad (8)$$

$$w_a = \Delta c_p/\Delta c_p^a \quad (9)$$

$$w_i = 1 - w_c - w_a \quad (10)$$

where Δc_p and Δc_p^a correspond to the experimental specific heat increments of the semi-crystalline and fully amorphous copolymer, respectively, and w_{BT} is the weight fraction of butylene terephthalate units. The variation of the interphase weight fraction as a function of the copolymer composition can be analyzed for a given crystallinity degree of the crystallizable component $x_c = \Delta H_m/\Delta H_m^\circ$. The results are shown in Fig. 13 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, examining the data concerning the interphase weight fraction, its increase with increasing BHEEBT units weight fraction

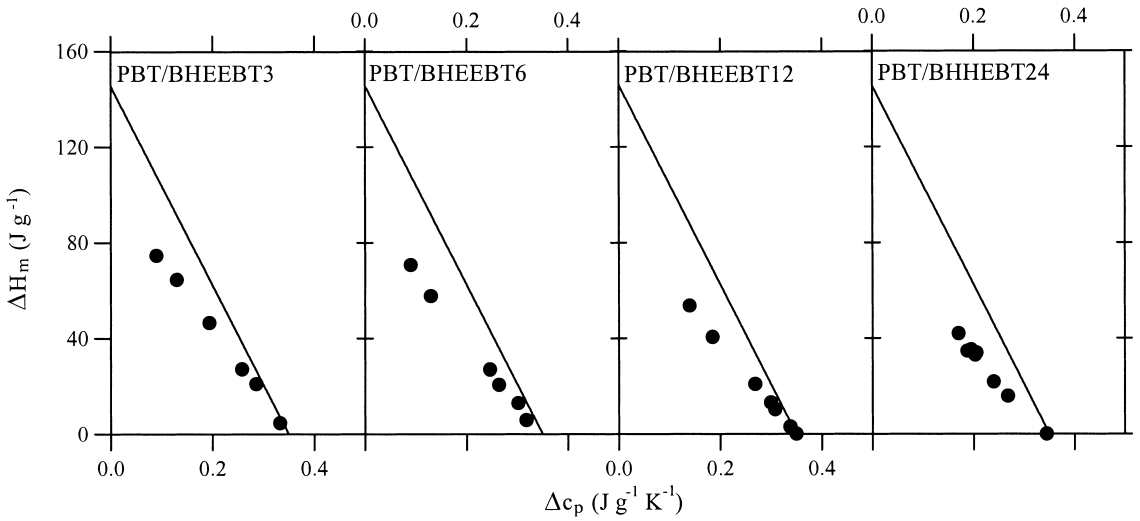


Fig. 12. Heat of fusion ΔH_m, as a function of the specific heat increment Δc_p at T_g. Solid lines were calculated on the basis of a two-phase model.

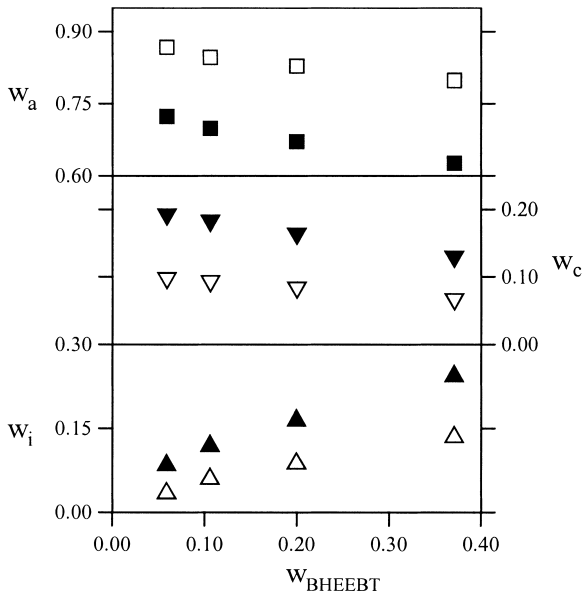


Fig. 13. Weight fractions of amorphous phase (w_a), crystalline phase (w_c), and interphase (w_i), as a function of BHEEBT unit weight fraction (open symbols: $x_c = 0.10$, full symbols: $x_c = 0.20$).

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 extensive constraints on the amorphous phase.

4. Conclusions

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

As regards the thermal stability of PBT, it was found to be improved by the insertion along its polymeric chain of BHEEBT co-units, these latter preventing with their high stiffness and steric hindrance the well-known thermal degradation reactions occurring in the homopolymer. The higher thermal stability of the copolymers with respect to pure PBT can be considered an important result, being this property crucial during the processing of a polymeric material.

At room temperature, the samples containing up to 24 mol% of BHEEBT unit appear as semi-crystalline materials with the same crystal structure of PBT homopolymer, however the crystallinity degree regularly decreasing as the content of co-units is increased. Amorphous samples, obtained after melt-quenching, showed a monotonic increment of the glass transition temperature as the amount of BHEEBT units is increased, due to the higher content of stiff and hindering moieties deriving from bisphenol A along the polymeric chain. As far as the melting phenomenon is concerned, multiple endotherms after isothermal crystallization from the melt were found, similarly to PBT; such behavior has to 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°. The extrapolated values appear to be well correlated to composition by Baur's equation, permitting the determination of T_m° and ΔH_m° for the completely crystalline homopolymer PBT; moreover, 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 BHEEBT units, which makes more difficult the regular packing of PBT polymer chains. The values of Avrami exponent close to three for all the copolymers 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 BHEEBT unit content was increased, due to a highly dispersed crystalline phase. As a matter of fact, the non-crystallizable comonomeric units hinder the crystallization process, leading to small and imperfect crystallites.

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