

Melting Behavior and Crystallization Kinetics of Poly(butylene terephthalate-*co*-diethylene terephthalate) and Poly(butylene terephthalate-*co*-triethylene terephthalate) Copolyesters

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ABSTRACT: The melting behavior of poly(butylene terephthalate-*co*-diethylene terephthalate) and poly(butylene terephthalate-*co*-triethylene terephthalate) copolymers was investigated by differential scanning calorimetry after isothermal crystallization from the melt. Multiple endotherms were found for all the samples, and attributed to the melting and recrystallization processes. By applying the Hoffman-Weeks' method, the equilibrium melting temperatures of the copolymers under investigation were obtained. Two distinct peaks in the crystallization exothermic curve were observed for all the samples. Both of them appeared at higher times than that of PBT, indicating that the introduction of a comonomer decreased the crystallization rate. The observed dependence of this latter on composition was explained on the basis of the content of ether-oxygen atoms in diethylene and triethylene terephthalate units, and of the different sizes of these units. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3545–3551, 2001

Key words: melting behavior; crystallization kinetics; poly(butylene terephthalate) copolymers

INTRODUCTION

Among semicrystalline polymers, poly(butylene terephthalate) (PBT) nowadays has gained great importance, being used as thermoplastic material for a large number of applications. The crystallinity and crystallization rate are factors that markedly affect most of the properties of the final prod-

uct. In this view, copolymerization represents a common way to favorably modify the crystallization behavior and the crystallinity degree, these physical properties being strongly influenced by composition, kind, and arrangement of structural units in the chain.

Recently, we synthesized a series of semicrystalline poly(butylene terephthalate-*co*-diethylene terephthalate) and poly(butylene terephthalate-*co*-triethylene terephthalate) copolymers that have been characterized from the point of view of molecular and rheological properties in the melt. The thermal behavior has also been investigated,

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Table I Molecular and Thermal Characterization Data for PBTDEG and PBTTEG Copolymers

Sample	Mol Fraction of DET or TET Units (Feed)	Mol Fraction of DET or TET Units (NMR)	N^a	M_w^b	T_m^c (°C)
PBT10DEG	0.10	0.08	8	44,000	229
PBT20DEG	0.20	0.15	15	39,500	218
PBT30DEG	0.30	0.25	25	37,300	205
PBT5TEG	0.05	0.05	10	34,200	232
PBT10TEG	0.10	0.10	20	40,100	224
PBT15TEG	0.15	0.15	30	42,600	216

^a Mean number of ether-oxygen atoms per 100 repeating units.

^b Calculated by end-group content, assuming "the most probable" molecular weight distribution.^{1,2}

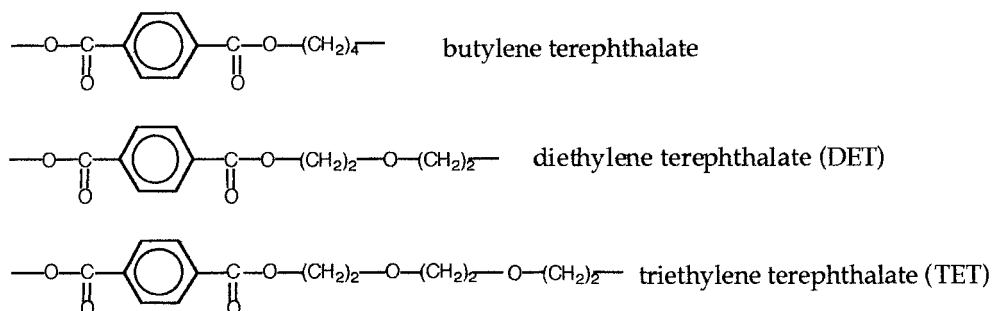
with special attention to the effect of composition on the glass transition temperature as well as on the melting process of samples not subjected to isothermal treatments.^{1,2}

The present article reports the results of an investigation about the influence of diethylene terephthalate and triethylene terephthalate units on the isothermal crystallization of PBT, carried out to obtain informations on the kinetic and thermodynamic parameters that control the crystalline phase growth in these copolymers.

EXPERIMENTAL

Synthesis

Poly(butylene terephthalate-*co*-diethylene terephthalate) (PBTDEG) and poly(butylene terephthalate-*co*-triethylene terephthalate) (PBTTEG) copolymers of various compositions and molecular weights were synthesized following the two-stage polycondensation procedure previously reported.^{1,2} The comonomeric units are:



The copolymers were found to be statistic. The molecular characterization data, obtained by ¹H-NMR spectroscopy and end-group analysis, are reported in Table I.

Calorimetric Measurements

The isothermal crystallization behavior of PBT-DEG and PBTTEG copolymers was 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. The instrument was calibrated in temperature and energy with high-purity standards (indium and cyclohex-

ane). The sample weight was approximately 5 mg for higher precision in the evaluation of the crystallization heats; a fresh specimen was used for each run.

The following procedure was employed: the samples were heated to about 40°C above their fusion temperature and kept at this temperature for 3 min to erase the previous thermal history. Such a short annealing does not lead to any significant thermal degradation of the copolymers, as previously reported.^{1,2} Subsequently, the samples were quickly quenched by liquid nitrogen to the crystallization temperature T_c . The T_c range was chosen to avoid crystallization during the

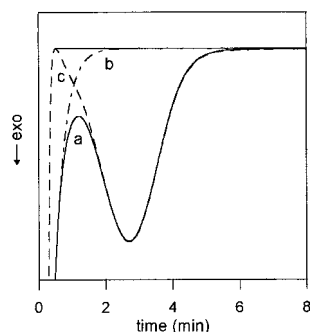


Figure 1 Typical DSC isothermal crystallization curve: (a) experimental run; (b) blank run; (c) corrected curve (see text).

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 DSC trace. Due to the high crystallization rate of the samples, the beginning of the process was in some cases masked by the initial transient signal that is observed after a sudden change of the scanning rate. For a better definition of the starting time, 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.³ The blank runs were 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 (Fig. 1).

The isothermally crystallized samples were then heated directly from T_c up to melting. The melting temperature (T_m) was taken as the peak value of the endothermic phenomenon of the DSC curve.

Wide-Angle X-ray Measurements

WAXS measurements were carried out with a Philips PW1050/81 diffractometer controlled by a PW1710 unit, using a graphite monochromatized Cu K radiation ($\lambda = 0.1542$ nm; 40 kV; 40 mA).

RESULTS AND DISCUSSION

Melting Behavior

Figure 2 shows the DSC heating curves of PBT-DEG and PBTTEG copolymers after isothermal

crystallization from the melt. As can be seen, all the copolymers display multiple endotherms, whose peaks have been labelled with Roman numbers (I to III) in order of increasing temperature. It is well known that in many cases semi-crystalline polymers as well as their copolymers show multiple endothermic peaks.³⁻⁶ There has been much discussion in the literature as to the possible origin of the phenomenon: multiple endotherms could be due to the presence of two or more groups of crystals with different morphologies or lamellar thickness,⁴ or they can be ascribed to a recrystallization process occurring during the DSC scan.^{3,5} In addition, both processes could operate at different undercooling degrees.⁶ The multiple endotherm behavior is typical of many polyesters, for the best-studied of which the phenomenon has always been ascribed to a reorganization process taking place during the DSC scan.^{3,5} In particular, endotherm I, which appears as a small peak at about 10°C above T_c , is usually attributed to the melting of crystals formed during a secondary crystallization process.⁷ Endotherm II is ascribed to the fusion of the crystal population grown during the isothermal period at T_c . It exhibits a strong dependence on crystallization temperature, in terms of both peak position and area, i.e., the endotherm appears at higher temperatures and its area progressively increases as T_c is risen. Such an increase suggests that thicker crystalline lamellae develop with increasing T_c . In contrast

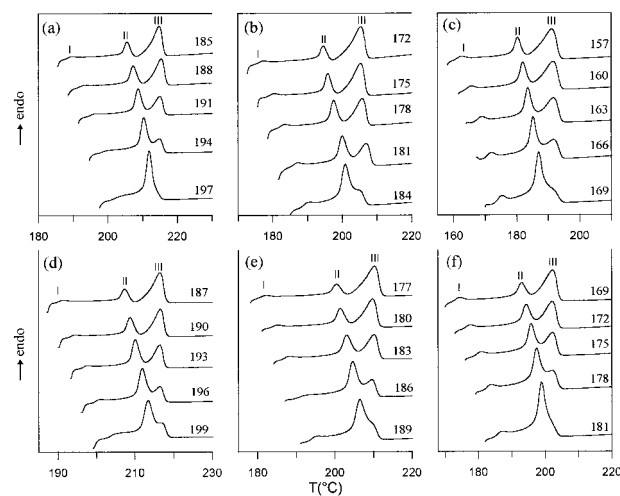


Figure 2 DSC melting endotherms after isothermal crystallization at the indicated T_c s (heating rate: 10°C/min); (a) PBT10DEG; (b) PTB20DEG; (c) PBT30DEG; (d) PBT5TEG; (e) PBT10TEG; (f) PBT15TEG.

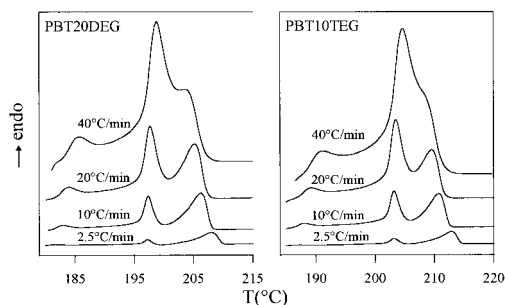


Figure 3 DSC melting endotherms of PBT20DEG and PBT10TEG scanned at the indicated heating rate after isothermal crystallization at 178 and 183°C, respectively. The curves have not been corrected for changes in the instrumental signal with heating rate.

to endotherms I and II, the location of the highest temperature melting endotherm (III), whose intensity decreases with increasing T_c , shows no dependence on the crystallization temperature. To deeply investigate the nature of these multiple endotherms, the effect of the scanning rate on the melting behavior of PBTDEG and PBTTEG copolymers has been analyzed. As an example, Figure 3 shows the DSC heating curves for PBT20DEG and PBT10TEG. It can be observed that (a) the endotherm III moves to higher temperatures as the heating rate decreases, and (b) the ratio of the area of the second melting peak to the third one increases as the heating rate is increased, confirming that the multiple melting in PBTDEG and PBTTEG copolymers 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.

Experimental melting temperatures of the copolymers crystallized at different T_c s are commonly used to obtain information on the equilibrium melting temperature T_m° by means the Hoffman-Weeks' relationship:⁸

$$T_m = T_m^\circ(1 - 1/\gamma) + T_c/\gamma \quad (1)$$

where γ is a factor that 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.⁹ 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 approximatively equal to 0.5.⁹

Although the concept of infinite lamellar thickness is appropriate only for homopolymers,⁹ the

Hoffman-Weeks' treatment is frequently applied to copolymers also,^{10–12} to obtain the driving force for crystallization (namely, the degree of undercooling ($T = T_m^\circ - T_c$)). The extrapolated T_m° data can be also used with the aim of evaluating the melting point depression induced by the presence of the second noncrystallizable component.¹³ To obtain the extrapolated T_m° , if the thickening process is fast, it is recommended⁹ to investigate samples with low levels of crystallinity. Consequently, PBTDEG as well as PBTTEG 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 identification of the unit cell structure of the crystalline phase in the samples was performed by using the wide-angle X-ray diffractometry technique. The diffraction curves for PBT, PBT30DEG, and PBT15TEG are reported in Figure 4. The PBT homopolymer shows a well-defined set of crystalline diffraction peaks,¹⁴ whose position is the same in the copolymer X-ray spectra. These results prove that the crystal structure that develops in PBTDEG as well as in PBTTEG copolymers corresponds to the characteristic lattice of the homopolymer PBT.

The peak temperatures of endotherm II as a function of T_c are plotted in Figure 5 for both PBTDEG and PBTTEG copolymeric systems. The melting temperatures T_m° 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 6. As can be seen, T_m° decreases with increasing diethylene terephthalate or triethylene terephthalate content. Moreover, the T_m° data of the two copolymeric systems are found to lie on the same curve. As T_m° depends exclusively on

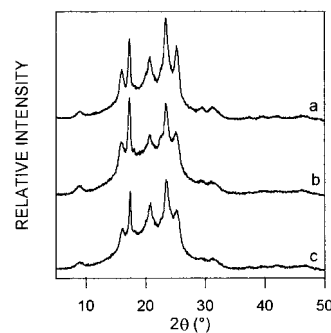


Figure 4 Wide-angle X-ray spectra of: (a) PBT; (b) PBT30DEG; (c) PBT15TEG.

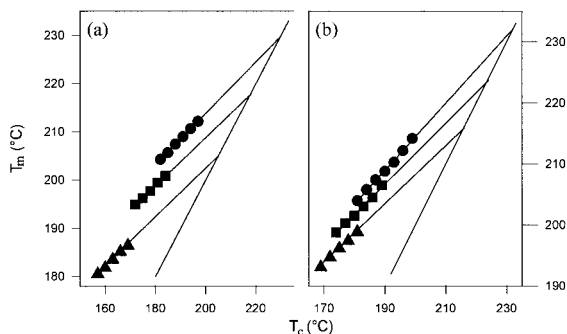


Figure 5 Hoffman-Weeks plot of (a) (●) PBT10DEG; (■) PBT20DEG; (▲) PBT30DEG; (b) (●) PBT5EG, (■) PBT10TEG, (▲) PBT15TEG.

the molar fraction of butylene terephthalate content and not on the specific chemical characteristics of the counts, the exclusion of diethylene and triethylene terephthalate units from the crystalline lattice is confirmed, as well as the random nature of the copolymer investigated.

Crystallization Kinetics

As an example, Figure 7 shows the crystallization curve of PBT15TEG copolymer at $T_c = 175^\circ\text{C}$ after subtraction of a blank run, as previously described in the experimental section. One can observe two partially overlapped peaks in the crystallization exotherm, a phenomenon that is common to all the PBTDEG and PBTTEG systems. The position of the two peaks depends on the crystallization temperature, both of them being observed at shorter times as T_c is decreased.

The appearance of two separate peaks leads to postulate a complex crystallization process for PBTDEG as well as PBTTEG copolymers. Further information can be derived from the Avrami

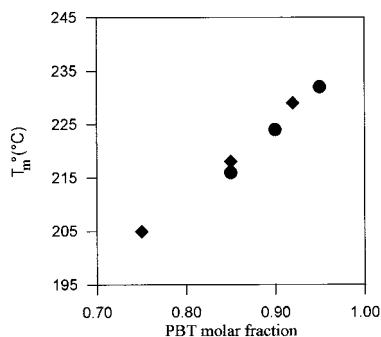


Figure 6 Equilibrium melting temperatures (T_m) as a function of composition for: (◆) PBTDEG and (●) PBTTEG copolymers.

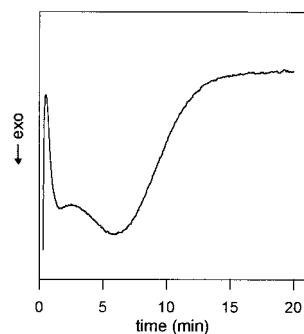


Figure 7 Isothermal crystallization curve of PBT15TEG at $T_c = 175^\circ\text{C}$.

analysis.¹⁵ The Avrami treatment is usually employed to study the isothermal crystallization kinetics, and is based on the following equation:

$$X_t = 1 - \exp[-k_n(t - t_{\text{start}})^n] \quad (2)$$

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 (see 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 Avrami equation is usually applied to the experimental data in the linearized form, by plotting $[\ln(-\ln(1-X_t))]$ as a function of $\ln(t - t_{\text{start}})$. In Figure 8 linearized Avrami plots for PBT20DEG and PBT15TEG copolymeric systems are shown for the highest crystallization temper-

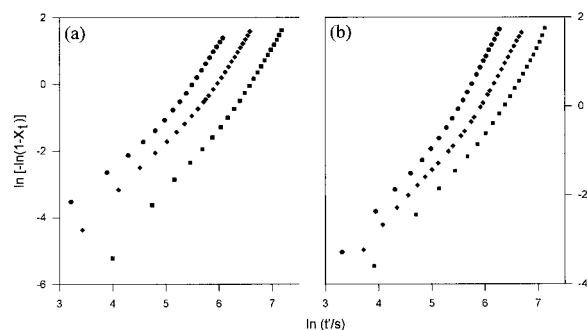


Figure 8 Avrami plots for: (a) PBT20DEG at T_c : (●) 178°C , (◆) 181°C , (■) 184°C ; (b) PBT15TEG at T_c : (●) 172°C , (◆) 175°C , (■) 178°C , $t' = t - t_{\text{start}}$.

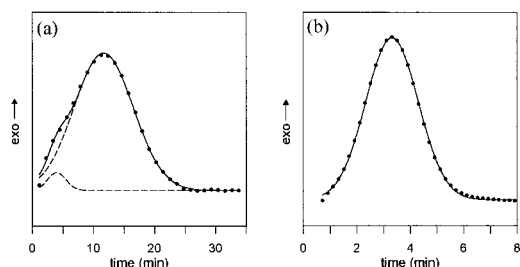


Figure 9 Nonlinear curve fitting for the isothermal crystallization curve: (a) PBT20DEG at $T_c = 184^\circ\text{C}$: (●) experimental data; (---) resolved curves; (—) sum of the resolved curves; (b) PBT at $T_c = 200^\circ\text{C}$: (●) experimental data; (—) Gaussian fitting.

atures investigated. One can observe that the curves shift towards longer times as T_c is increased, indicating that the crystallization rate decreases with increasing the crystallization temperature. This fact proves that the crystallization occurs by a nucleation-controlled mechanism.¹⁶ Analogous trends are observed for the other copolymers. The presence in the curves of two zones with different slopes is evident in all cases: $[\ln(-\ln(1-X_t))]$ varies linearly with a lower slope at the early stage and with a higher slope at the later stage. An opposite trend, i.e., a linear variation followed by a second one with lower slope, is often observed, and is attributed to a primary crystallization followed by a secondary crystallization process.¹⁷ Clearly, such a mechanism cannot explain the crystallization in PBTDEG and PBTTEG copolymers, which on the whole is a more complex event. Therefore, the Avrami treatment, used to estimate the crystallization rate constant k_n and the exponent n , cannot be applied. Nevertheless, informations on the crystallization kinetics can be obtained by using the value of the peak time (t_p) in the DSC curve, which is defined as the time at which the maximum of the crystallization rate occurs. As reported above, two partially overlapped exothermic peaks were found for all the copolymers. To separate the peaks and calculate with accuracy the corresponding t_p values, a nonlinear fitting was performed with multiple Gaussian curves.¹⁸ Figure 9(a) shows an example of the resolved exothermic curves; for comparison in Figure 9(b) the crystallization trace of homopolymer PBT at $T_c = 200^\circ\text{C}$ is reported together with the Gaussian fitting. It can be noted that the Gaussian function perfectly describes the crystallization exothermic curve of PBT. Considering that the

crystalline structure that develops in PBTDEG and PBTTEG copolymers corresponds to that of the homopolymer PBT, it can be deduced that the Gaussian function is a correct model for the copolymers also.

The t_p values of the two peaks are plotted in Figure 10 as a function of the undercooling degree ($\Delta T = T_m^\circ - T_c$), together with the data relative to homopolymer PBT.³ For sake of clarity, the data concerning the peak occurring at the shorter times (t_{p1}) are indicated with the same symbol for both PBTDEG and PBTTEG copolymers, independently of composition. An analogous description was adopted for the second more intense peak. The most significant finding is that the t_{p1} data for the copolymers are slightly higher than the homopolymer PBT t_p values, whereas t_{p2} data are significantly higher, indicating that the crystallization rate is depressed by the presence of the comonomeric units. These results suggest a complex mechanism for the crystallization of the butylene terephthalate units in PBTDEG and PBTTEG copolymers. In fact, all the copolymers are rich in butylene terephthalate units, so that long crystallizable sequences of these units are expected to be present in the backbone of the chains. The peak occurring at the beginning of the crystallization event, characterized by the peak time t_{p1} , could be related to the crystallization of chain segments of practically pure PBT, the presence of the second comonomer affecting only weakly the crystallization rate. The second peak could be related to the crystallization of butylene terephthalate sequences bound to diethylene or triethylene terephthalate units. In this case, the second component should influence more markedly the crystallization rate, acting as hindrance to the diffusion of the crystallizable segments to the crystalline growth surface.

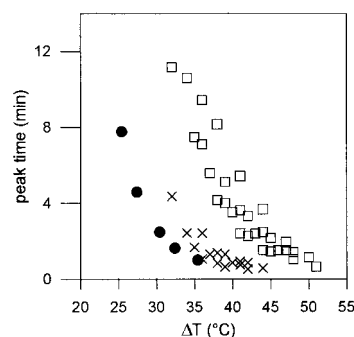


Figure 10 Peak time data vs. undercooling degree (●) t_p for PBT (from ref. 3); (×) t_{p1} and (□) t_{p2} for PBTDEG and PBTTEG copolymers.

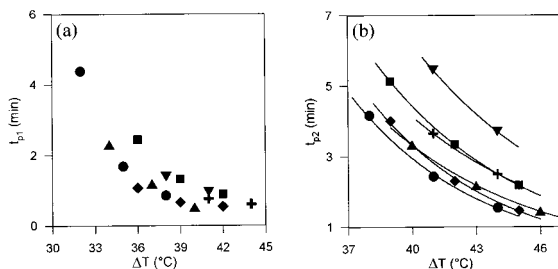


Figure 11 (a) t_{p1} , (b) t_{p2} data vs. undercooling degree for: (●) PBT10DEG; (▲) PBT20DEG; (■) PBT30DEG; (◆) PBT5TEG; (+) PBT10TEG; (▼) PBT15TEG.

Figure 11(a) and (b) provides t_{p1} and t_{p2} data, respectively, on more enlarged scales, to analyze the effect of composition on the crystallization kinetics. The t_{p1} values appear to be affected to a very little extent by copolymer composition; on the contrary, t_{p2} data show a marked dependence on the content of diethylene terephthalate or triethylene terephthalate units. Moreover, regarding each copolymeric series, the decrement in the crystallization rate turns out to be higher as the counit content is increased. From the comparison of t_{p2} of PBTDEG and PBTTEG copolymers with about the same molar composition (PBT20DEG, PBT15TEG), it can be seen that the crystallization rate depression is more remarkable when the comonomer is triethylene terephthalate. Because the crystallization of a single component in random copolymers involves the segregation of the counits, the finding that triethylene terephthalate segments reduces more markedly the rate of PBT lattice formation can be attributed to the larger dimensions of these counits with respect to diethylene terephthalate ones.

The t_{p2} data can also be discussed on the basis of the presence in the comonomeric units of ether-oxygen atoms. In this view, in Table I the mean number of ether-oxygen atoms per 100 repeating units is also reported for each copolymer. As can be seen in Figure 11(b), t_{p2} increases with increasing the oxygen content. This fact suggests that the presence of oxygen atoms hinders the diffusion of the crystallizable segments, because the increased polarity that characterizes the molecules with larger content of ether bonds produces an increase in the intermolecular interaction forces.

In conclusion, the lower crystallization rate of PBTDEG and PBTTEG copolymers with respect

to PBT homopolymer can be attributed to three factors: the content and the size of the noncrystallizable comonomeric units, and the presence of ether-oxygen atoms along the copolymeric chains.

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