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DILUTE SOLUTION AND THERMAL BEHAVIOUR OF RANDOM POLY(BUTYLENE ISOPHTHALATE/TEREPHTHALATE) COPOLYMERS

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Abstract—Random poly(butylene isophthalate/terephthalate) (PBI/PBT) copolymers of various compositions and different molecular weights were synthesized and characterized by vapour pressure osmometry and viscosity measurements in $CHCl_3$. The Stockmayer–Fixman procedure was applied to viscometric data in order to obtain information on the composition dependence of the unperturbed dimensions. The extrapolated K_θ values were found to decrease with increasing content of isophthalate units. Thermal characterization in the solid state was carried out by means of a differential scanning calorimeter on PBI/PBT copolymers as well as on PBI and PBT homopolymers. Minima for melting temperature and heat of fusion were observed for the copolymer with 60/40 PBI/PBT molar composition. Amorphous samples in the 40–100% PBI concentration range were obtained by quenching from the melt, characterized by a monotonic decrease of the glass transition temperature T_g and by a constant value of the specific heat increment Δc_p. The Fox equation was found to describe quite well the T_g-composition data and permitted calculation of the T_g of wholly amorphous PBT.

INTRODUCTION

Copolymers have become more and more important in the industrial field, since their physical properties can be tailored to fit specific applications more easily then homopolymers themselves. Physical properties strongly depend on copolymer composition, structural arrangement of molecular units, sample crystallinity, etc. Detailed knowledge of the relationship between polymer structure and properties opens up the possibility of controlled modification and optimization of polymer properties. In spite of this, relatively few data are reported in the literature on the dependence of dilute solution and thermal behaviour of copolyesters on composition and on the kind of monomeric units existing in the chain. The present paper deals with an investigation of such properties in a series of random poly(butylene isophthalate/terephthalate) (PBI/PBT) copolymers, which have been proposed in recent years as secondary coating materials for optical fibers [1], and whose homopolymers, especially PBT, have found large applications as thermoplastic materials.

EXPERIMENTAL PROCEDURES

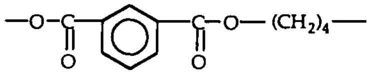
Products

Dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), 1,4-butanediol (BD) and $Ti(OBu)_4$ were reagent grade products and were used either as supplied or distilled before use.

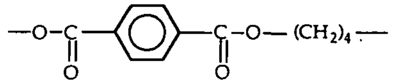
Synthesis of polymers

Poly(butylene isophthalate-co-butylene terephthalate) samples were synthesized starting from DMT, DMI and BD, with $Ti(OBu)_4$ [*ca* 0.7 g/kg of (DMT + DMI)] as catalyst, employing various amounts of DMT and DMI in order to obtain copolymers with different composition (from 20 to 80 mol% of isophthalate units).

The syntheses were carried out in a 1.8 l. stainless steel reactor according to the usual two-stage polycondensation procedure. In the first stage, at atmospheric pressure, the temperature was raised from 150 to 210° and maintained there until 90% of the methanol was distilled off. In the second stage the pressure was reduced to about 0.5 mbar and the temperature was kept in the range 240–250°. During each run, samples were taken from the bottom of the reactor at different times, in order to obtain samples with the same composition but different weights. The polymers obtained, because of the use of $Ti(OBu)_4$ as catalyst and the high reaction temperature which favour redistribution reactions [2], are essentially statistical, and the monomeric units constituting the copolymers are:



(I)



(II)

with $M_I = M_{II} = 220.2$.

Vapour pressure osmometry (VPO)

Number-average molecular weight ($\bar{M}_n$) was measured by means of a Wescan 233 vapour pressure osmometer, at 35° using $CHCl_3$ as solvent. The calibration constant was de-

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Table 1. Molecular and dilute solution characterization data for PBI/PBT copolymers

Sample	Isophthalate unit (mol%)	$[\eta]$ (dl/g)	$\bar{M}_n \times 10^{-3}$	p	$\bar{M}_w \times 10^{-3}$	q_w	$K \times 10^4$ (dl/g)	a
20PBIPBT1	20	0.670	14.6	0.9849	29.0	0.943	5.46	0.70
20PBIPBT2	20	0.745	16.4	0.9866	32.6	0.943		
20PBIPBT3	20	0.780	18.1	0.9878	36.0	0.943		
20PBIPBT4	20	0.815	19.1	0.9885	38.0	0.943		
40PBIPBT1	40	0.550	12.7	0.9827	25.2	0.949	2.94	0.75
40PBIPBT2	40	0.680	16.7	0.9868	33.2	0.949		
40PBIPBT3	40	0.780	18.8	0.9883	37.4	0.949		
40PBIPBT4	40	0.800	21.4	0.9897	42.6	0.949		
60PBIPBT1	60	0.495	12.0	0.9817	23.8	0.952	2.29	0.77
60PBIPBT2	60	0.680	18.1	0.9878	36.0	0.952		
60PBIPBT3	60	0.710	19.9	0.9889	39.6	0.952		
60PBIPBT4	60	0.780	20.9	0.9895	41.6	0.952		
80PBIPBT1	80	0.422	10.2	0.9784	20.2	0.958	1.35	0.81
80PBIPBT2	80	0.550	15.1	0.9854	30.0	0.958		
80PBIPBT3	80	0.705	18.5	0.9881	36.8	0.958		
80PBIPBT4	80	0.765	21.7	0.9899	43.2	0.958		

rived using several monodisperse polystyrene standards of molecular weights in the range 5000–11600. For each sample several measurements were made in order to obtain reliable results.

Viscometry

Dilute solution viscosity was measured using Ubbelohde dilution viscometers; measurements were made in $CHCl_3$ at $30.0 \pm 0.1°$ at four polymer concentrations in the range 0.5–1.0 g/dl. Intrinsic viscosity $[\eta]$ was obtained using both Huggins and Kramer plots, i.e. by extrapolating η_{sp}/c and $(\ln \eta_r)/c$ to zero concentration.

Thermal analysis

Calorimetric measurements were carried out by means of a Perkin–Elmer DSC7 instrument equipped with a liquid subambient accessory and calibrated with high-purity standards. The DSC curves were recorded at a scanning rate of 20°/min, over the temperature range $-50/250°$. The glass transition temperature T_g was taken as the midpoint of the specific heat increment Δc_p associated with the transition. The melting (T_m) and crystallization (T_c) temperatures were taken as the peak values of the endo- and exo-thermal phenomena in the DSC curve respectively. In the presence of multiple endotherms, the highest peak temperature was taken as T_m. Repeated measurements on each sample showed excellent reproducibility. No significant influence of the molecular weight parameter on the calorimetric results was found in the range of molecular weights investigated.

SOLUTION PROPERTIES

Evaluation of Mark–Houwink–Sakurada parameters

The behaviour of polymers in solution is described by the well-known Mark–Houwink–Sakurada (MHS) equation:

$$[\eta] = KM^a \tag{1}$$

which holds for monodisperse samples over a wide range of molecular weights.

In order to allow for the effect of polydispersity, the following extension of equation (1) was proposed [3] by some authors:

$$[\eta] = Kq_w\bar{M}_w^a \tag{2}$$

where:

$$q_w = (\bar{M}_w/\bar{M}_n)^b(\bar{M}_z/\bar{M}_w)^c \tag{3}$$

$\bar{M}_w$ and $\bar{M}_z$ are the weight-average and the z-average molecular weights respectively, b and c are parameters depending on a and, for b only, on the ratio $\bar{M}_z/\bar{M}_w$ [3]. Equation (2) proved to apply to a very large number of polymers having different molecular weight distributions, provided that $\bar{M}_z/\bar{M}_w$ is not too high.

In order to determine the correction factor q_w for the copolymers under investigation, $\bar{M}_w$ was calculated, assuming the "most probable" molecular weight distribution and the absence of cyclic molecules, by the following expression [4]:

$$\bar{M}_w = \bar{M}_0 + 2p\bar{M}_0/(1-p) \tag{4}$$

where $\bar{M}_0 = x_I M_I + x_{II} M_{II} = w_I M_I + w_{II} M_{II} = 220.2$ is the molecular weight of the repeating unit, x_I, x_{II}, w_I, w_{II} being the molar and the weight fractions of the two comonomeric units. From the experimental values of $\bar{M}_n$ (obtained by means of VPO), the conversion p was calculated with the following equation:

$$\bar{M}_n = \bar{M}_0/(1-p). \tag{5}$$

From the values of p, $\bar{M}_w$ was calculated by means of equation (4); for $\bar{M}_z$ the following expression [5] was applied:

$$\bar{M}_z = \bar{M}_w(1 + p^2 + 4p)/(1+p)^2 \tag{6}$$

which holds for statistical polymers.

The values of $[\eta]$ in $CHCl_3$ at 30° and of the various average-molecular weights reported in Table 1 were used to calculate, by means of a least square analysis associated with an iterative procedure (the correction factor q_w depending on a), q_w and the parameters a and K of equation (2) for PBI/PBT copolymers at different composition. The final MHS plots are shown in Fig. 1. As can be seen also in Fig. 2, a increases and K decreases, both monotonically, with increasing content of isophthalate units and their values are consistent with those for poly(butylene isophthalate) homopolymer [6, 7]; no data are available for PBT, since this polymer is not soluble in $CHCl_3$ at 30°.

Unperturbed dimensions

The conformational properties of flexible macromolecules in solution can be described by two independent parameters [8, 9] which separately take into account the two different kinds of interaction

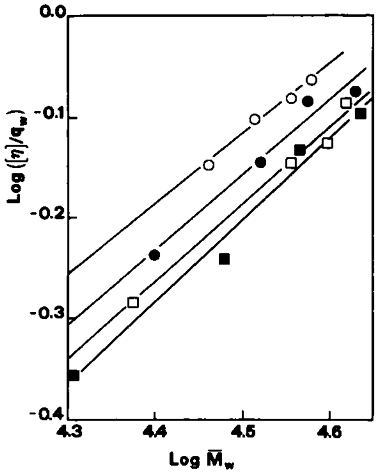

Fig. 1. MHS plots for: ○, 20PBIPBT; ●, 40PBIPBT; □, 60PBIPBT; and ■, 80PBIPBT copolymers in $CHCl_3$ at 30°.

between chain elements, the short-range (between atoms or groups separated by only a small number of bonds) and the long-range ones (between groups which are separated in the chain structure by many bonds). Under special temperature and solvent conditions, called Θ-conditions, the dimensions of the chain (unperturbed dimensions) are influenced only by short-range interactions and the MHS equation turns out to be:

$$[\eta]_\Theta = K_\Theta M^{1/2} \qquad (7)$$

where K_Θ is correlated with the unperturbed chain dimensions by the following expression [8]:

$$(K_\Theta/\Phi_0)^{1/3} = (\overline{R_0^2}/M)^{1/2} \qquad (8)$$

in which $\overline{R_0^2}$ is the mean square end-to-end distance of the chain in the unperturbed state and $\Phi_0 = 2.87 \times 10^{23}\ g^{-1}$ is the universal Flory constant. Evaluation of K_Θ allows estimation of the extension of the chain in the unperturbed state; unfortunately direct experimental determination of K_Θ is often difficult, as a Θ-solvent is not always readily available and in many cases polymers tend to crystallize out from "poor" solvents. To overcome these difficulties, many expressions based on the two-parameter theory have been developed [9–15], assuming different approximations in the mathematical procedure, in order to obtain K_Θ from measurements of intrinsic viscosity in good solvents. The most commonly applied is the so-called Stockmayer–Fixman equation [11]:

$$[\eta]/M^{1/2} = K_\Theta + 0.51 B\Phi_0 M^{1/2} \qquad (9)$$

where B is a parameter that takes into account long-range interactions. This equation is the simplest and most versatile and is generally applicable to polymer solutions both in "poor" and "good" solvents, provided that $\alpha_\eta < 1.4$, where α_η the expansion coefficient of viscosity is defined by:

$$\alpha_\eta = ([\eta]/[\eta]_\Theta)^{1/3}$$

On the basis of equation (9), a linear relationship is expected by plotting $[\eta]/M^{1/2}$ vs $M^{1/2}$, whose intercept gives the value of K_Θ.

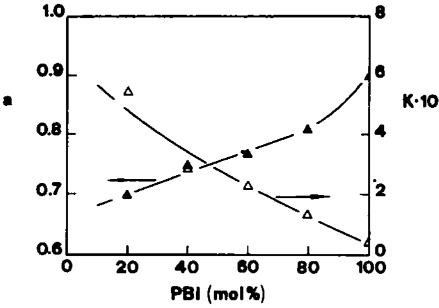

Fig. 2. Dependence of the parameters a (▲) and K (△) of the MHS equation on the content of isophthalate units.

The two-parameter theory has been successfully extended to copolymers [16, 17] and equation (9) has been found to hold also for such systems. In the present work, the Stockmayer–Fixman equation has been applied to PBI/PBT copolymers viscosity data, using $\bar{M}_w$ as molecular weight and substituting the modified intrinsic viscosity $[\eta]/q_w$ to $[\eta]$, to take into account the effect of polydispersity. The corresponding plots are reported in Fig. 3 and the results obtained are collected in Table 2 in terms of K_Θ and $\overline{R_0^2}/\bar{M}_w$. Though few and rather scattered data are available for each composition, a clear increase of K_Θ with increasing terephthalate units is apparent. The K_Θ values are consistent with that of PBI previously obtained [7] and that of PBT reported in the literature [18] derived from measurements in a different kind of solvent.

THERMAL PROPERTIES

Melting and crystallization

It is well established that the melting behaviour of a polymer is affected by its previous thermal history. In order to provide the same heat treatment to all samples investigated, specimens were compression moulded at 230°, slowly cooled to room temperature and then annealed at 90° for 8 days in an oven under

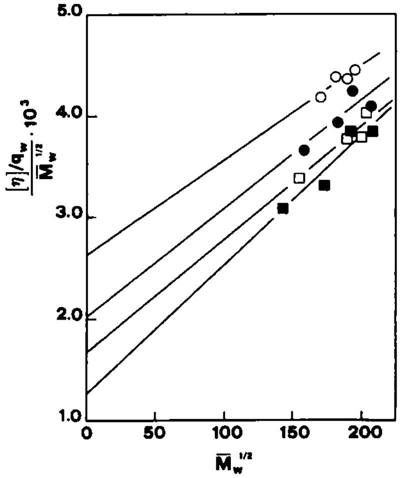

Fig. 3. Stockmayer–Fixman plots for: ○, 20PBIPBT; ●, 40PBIPBT; □, 60PBIPBT; and ■, 80PBIPBT copolymers.

Table 2. K_θ and unperturbed chain dimensions

Polymer	$K_\theta \times 10^3$	$(\bar{R}_0^2/\bar{M}_w) \times 10^{17}$
PBT*	3.50	11.41
20PBIPBT	2.62	9.41
40PBIPBT	2.01	7.89
60PBIPBT	1.66	6.94
80PBIPBT	1.25	5.75
PBI†	0.38	2.58

*Data from Ref. [18].
†Data from Ref. [7].

vacuum. Typical calorimetric curves of such samples are collected in Fig. 4 and show a glass transition in the range 30–60°, followed by melting endotherms whose main peak location depends on composition. The lower melting phenomenon, which appears as a separate peak or as a shoulder at 120–130°, is clearly due to the melting of crystals produced upon annealing, either by crystallization from the amorphous phase or by reorganization of pre-existing crystals formed during cooling.

The DSC curves indicate that an increase in the amount of comonomer added to PBI or to PBT leads to a marked reduction of the heat of fusion, and therefore to a reduced level of crystallinity in the copolymers with respect to the homopolymers.

The calorimetric results regarding the melting of annealed samples are collected in Table 3 and plotted in Fig. 5 as a function of PBI content. Both the minimum in the heat of fusion and the melting point-composition dependence, constituted of two independent curves, are typical of random copolymers, where both comonomers are able to crystallize but at each composition only the unit present in major proportion takes part in the crystallization process [19, 20]. According to Flory's theory [21], the temperature T_m at which crystallinity disappears in these copolymers is related to the molar fraction x_A of the crystallizing A units by the equation:

$$(1/T_m - 1/T_m^\circ) = -(R/\Delta H_u)\ln x_A \qquad (10)$$

where T_m° and ΔH_u are the melting temperature and the heat of fusion of the completely crystalline A homopolymer respectively. According to this relationship the plot of $1/T_m$ vs $-\ln x_A$ should be a straight line with a slope $R/\Delta H_u$.

Considering PBT as homopolymer A, experimental T_m data of the copolymers under investigation fit very well onto a straight line down to $x_A = 0.4$ but the value of ΔH_u (60 J/g) that is deduced from the slope is significantly lower than that determined by other methods [22]. This is however a widespread observation that has been reported in the literature [19, 20] for several different statistical copolymers and has been ascribed to the inability of a real random copolymer system to achieve the conditions postulated by the equilibrium theory. Theory requires a melting temperature relative to the disappearance of very long sequences of A units; however, in real conditions, the concentration of such sequences in random copolymers is relatively low and decreases as the co-unit content increases. As a consequence, observed T_m values are lower than predicted and will result in an apparent low enthalpy of fusion.

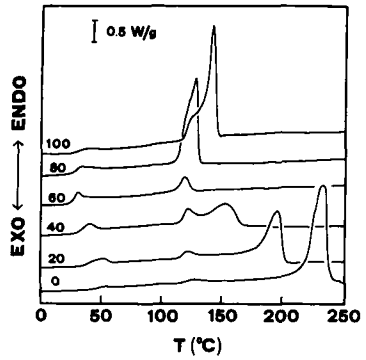

Fig. 4. Calorimetric curves of PBI/PBT random copolymers annealed at 90°. PBI mol% is indicated on curves.

Glass transition

A partially crystalline material is expected to exhibit different glass transition behaviour than when it is completely amorphous. Although some conflicting results are reported in the literature [23], crystallinity usually acts like crosslinking and raises T_g through its restrictive effect on segmental motion of amorphous polymer chains. In order to study the influence of chemical structure on the glass transition of random copolymers, the phenomenon should be examined in the absence of crystallinity. Rapid cooling (quenching) from the melt is the method commonly used to prevent crystallization and to obtain polymers in an amorphous condition. Following this procedure, the samples were melted at 250° and rapidly cooled to −50°. The subsequent DSC scans, shown in Fig. 6, indicate a quite different thermal behaviour of PBI and PBT homopolymers. The former is completely amorphous as revealed by the sharp and intense endothermal baseline deviation associated with the glass transition, while the latter is partially crystalline and exhibits a considerable melting endotherm. As a matter of fact, PBT cannot be easily frozen in an amorphous glassy state due to its high rate of crystallization [24].

Table 3. Calorimetric data of PBI/PBT random copolymers

Polymer	T_m* (°C)	ΔH_m* (J/g)	T_g† (°C)	Δc_p† (J/g deg)	T_m† (°C)	ΔH_m† (J/g)
PBT	233.0	55.5	43.0	0.08	229.0	43.0
20PBIPBT	194.5	50.0	38.0	0.20	194.0	32.0
40PBIPBT	152.0	28.0	32.0	0.35	152.0	23.0
60PBIPBT	117.5	6.0	29.5	0.35	—	—
80PBIPBT	126.0	36.0	29.0	0.34	—	—
PBI	140.0	47.0	27.0	0.35	—	—

*First DSC scan on samples annealed at 90°.
†Second DSC scan on samples rapidly cooled from the melt.

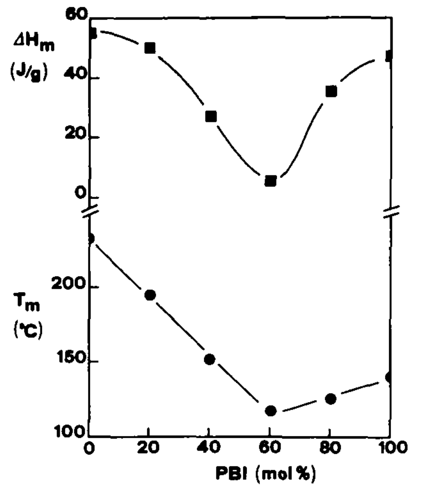

Fig. 5. Composition dependence of T_m (●) and ΔH_m (■) in PBI/PBT random copolymers.

The phase behaviour of PBI/PBT copolymers depends on composition: amorphous or semicrystalline samples are obtained at high PBI or high PBT content respectively (see Table 3). The copolymer whose composition is closed to equimolar ratio (40% PBI) shares characteristics of both comonomer units; the DSC curve in Fig. 6 shows an intense glass transition followed by an exothermal "cold crystallization" peak at 94° and by a melting endotherm at higher temperature. The enthalpy associated with the crystallization exotherm (20 J/g) very well compares with the heat of fusion, indicating that the polymer is vitrified into the amorphous state by quenching and that, once T_g is exceeded, the amorphous chains acquire enough mobility to rearrange and crystallize.

The values of T_g and of the specific heat increment Δc_p associated with the glass transition are plotted in Fig. 7 as a function of PBI content. It is clear that the experimental results pertaining to partially crystalline samples (PBT and 20PBIPBT copolymer) do not follow the same composition dependence as that of the amorphous polymers (PBI content from 40 to 100 mol%). Amorphous samples show a constant Δc_p value (equal to 0.35 J/g deg), while the magnitude of the heat capacity change is considerably lower for pure PBT and the copolymer containing 20% PBI. This is an obvious consequence of the crystallinity present in these two samples, which reduces the amorphous phase undergoing the transition. Analogous considerations deserve the corresponding T_gs: crystallites hinder the motion of the amorphous chains leading to T_g values higher than expected.

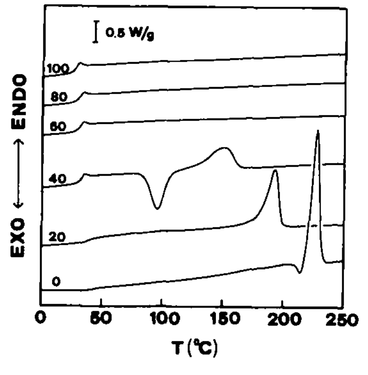

Fig. 6. Calorimetric curves of PBI/PBT random copolymers after melt quenching. PBI mol% is indicated on curves.

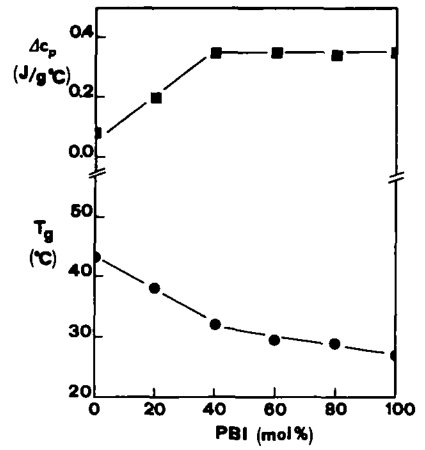

Fig. 7. Composition dependence of T_g (●) and Δc_p (■) in PBI/PBT random copolymers.

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

$$1/T_g = w_I/T_{gI} + w_{II}/T_{gII} \qquad (11)$$

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 data of PBI/PBT polymers in the amorphous state (PBI 40–100 mol%) can be fitted to equation (11) to calculate the glass transition temperature of wholly amorphous PBT, which cannot be determined experimentally, due to the high crystallization rate of this polymer. The calculated T_g turns out to be 35°, a temperature slightly higher than that of PBI, in line with the value obtained by group contribution additivity which ascribes a higher contribution to T_g of the para- with respect to the meta-substituted phenylene group [27]. The calculated T_g is also consistent with the results of a recent paper by Cheng *et al.* [24], where a value of 37° has been reported for a 100% rigid amorphous PBT phase. Using solid and liquid heat capacity data, the same authors calculate an increase in specific heat equal to 0.35 J/g deg at $T_g = 37°$. Quite interestingly, this Δc_p value is the same as that presently found for amorphous PBI homopolymer and amorphous PBI/PBT copolymers (see Table 3), thus explaining the absence of dependence on composition of Δc_p in the copolymer system investigated.

CONCLUSIONS

The results of the present work show that the PBI/PBT copolymers investigated have solution and bulk properties intermediate between those of PBI and PBT homopolymers, in agreement with a random distribution of butylene-terephthalate and isophthalate units. Unperturbed dimensions derived from viscometric data increase with increasing terephthalate content and compare well with literature data for homopolymers, suggesting that calculations in good solvents are not influenced by specific solvent effects. The same trend is followed by the glass transition temperature which changes monotonically from 27 (PBI) to 35° (PBT), in line with the higher rigidity contributed by the terephthaloyl residue.

Finally, a marked reduction of crystallinity is brought about by increasing amount of counits in the copolymers and the morphology can be varied from semicrystalline to amorphous under specific heat treatment.

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