

## Poly(ethylene terephthalate), Modified with Bisphenol S Units, with Increased Glass Transition Temperature

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**ABSTRACT:** Novel copolyesters have been prepared by melt mixing poly(ethylene terephthalate) (PET) with an ethoxylated bisphenol S, with the aim to prepare new polyesters with increased  $T_g$ , to be used in a wider range of temperatures with respect to neat PET. No side reactions occur during the synthesis of the samples, as proved by NMR analysis. The insertion of the bisphenol S (sulfonyl-diphenol) groups does not significantly alter the thermal stability of PET. The thermal analysis showed that  $T_m$  and crystallization rate of the copolymers decreased with increasing co-unit content. The  $T_g$  of the copolyesters can be increased by bisphenol S insertion, up to 40°C higher with respect to neat PET, that allows the use of amorphous PET in a wider range of applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** poly(ethylene terephthalate); bisphenol S; high glass transition temperature; melt mixing

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### INTRODUCTION

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer widely used as material for water and soft drinks bottles, for tire cords and for textile fibres<sup>1</sup> and its worldwide production in 2009 was 12.7 million tons.<sup>2</sup> PET is used in the amorphous state in several applications.<sup>3</sup> The discovery of amorphous compositions by incorporation into PET of 1,4-cyclohexanedimethanol (CHDM) was first disclosed in 1959,<sup>4,5</sup> but the commercialization of amorphous copolyesters was only in 1977 by Eastman with the trade name Kodar PETG 6763.<sup>6</sup> Amorphous PET copolymers were first introduced into the market for extrusion blow molding application due to their high clarity and melt strength. The greatest success of these copolymers has been found in extruded sheets, for which its combination of clarity, chemical resistance, and toughness is important.<sup>6</sup> However, the PET copolymers containing CHDM (PETG) have low  $T_g$ <sup>6</sup> in comparison with colorless, transparent commercial polymers such as bisphenol A (BPA) polycarbonate (PC),<sup>7</sup> and poly(methyl methacrylate) (PMMA).<sup>8</sup> In particular, PC and PMMA have a  $T_g$  of 145°C<sup>7</sup> and 100°C,<sup>8</sup> respectively, while amorphous PETGs are characterized by a glass transition temperature of approximately 80°C<sup>9</sup> that limits their industrial application. Considerable research has been done to discover and develop diacids and diols comonomers, that can raise the  $T_g$  without sacrificing the key useful properties of these polyesters.<sup>3</sup> The addition of amide units to the polyester backbone to enhance the crystallization rates and improve the chemical resistance has

been widely studied.<sup>10</sup> Even though some diamines can very effectively raise  $T_g$ ,<sup>11</sup> significant discoloration occurs during the polycondensation process.<sup>6</sup>

BPA PC presents a high  $T_g$  and high impact resistance, even at low temperature,<sup>12</sup> that has been ascribed,<sup>13</sup> to its capability to absorb high impact energy, due to its secondary transitions that involves cooperative motions of BPA at very low temperature ( $T_g = -105^\circ\text{C}$  from dynamic mechanical analysis).<sup>12</sup> However, PC has a poor solvent resistance and for this reason has to be used in blends with terephthalate polyesters for applications where low temperature impact resistance and solvent resistance are both required. A polyester containing BPA and terephthalate esters moieties should be in principle able to show good solvent resistance and good thermomechanical properties in a wide range of temperatures. Indeed, the incorporation of bisphenol units into polyester backbones is known to raise  $T_g$  and can enhance other properties such as thermal stability.<sup>6</sup> However, aromatic diols are not active in esterification reactions with aromatic acids or esters. For this reason, BPA has to be modified in order to be inserted in the polyester backbone during a standard polycondensation process.<sup>1</sup> We have reported<sup>14–17</sup> that the insertion of BPA units inside a terephthalate polyester can be achieved by derivatization of BPA via ethoxylation and the functionalized BPA was used directly in melt mixing with terephthalate polyesters. Bis(hydroxyethyl ether) of bisphenol A (BHEEB), can be prepared by several routes,<sup>18–22</sup> such as for example by reaction between ethylene carbonate (ETC) and

BPA. Ethoxylated BPA units can be inserted in the polyester backbone during the polymerization or by melt mixing. The second method presents the advantage that permits the use of recycled polymers.<sup>14–17</sup> Moreover, can be performed in shorter reaction times compared to the full polymerization procedure.<sup>14–17</sup>

An increase in glass transition temperature and in thermal stability of poly(butylene terephthalate) (PBT), PET, and PPT have been obtained by the insertion of BPA units.<sup>14–17</sup> Koning et al.<sup>18</sup> has obtained similar results on block copolymers prepared by solid state polymerization. However, the  $T_g$  of PET can be increased only of 10°C by the insertion of BPA units.

We have reported<sup>23</sup> that the insertion of sulfonyldiphenol units (bisphenol S, BPS) into poly(butylene terephthalate) improves its  $T_g$  more than BPA derivatives. This behavior has been attributed to the higher rigidity of the BPS unit. Moreover, a significant improvement in thermal stability by the insertion of BPS units was observed. However, PBT polymers are mainly crystalline and the higher  $T_g$  does not widen the range of PBT industrial applications while in the case of PET, that is often used in the amorphous state, an increased  $T_g$  permits a wider range of applications as it can be used at higher temperatures compared to neat PET.

Turner and Sublett from Eastman Kodak<sup>24</sup> have patented the synthesis of copolyesters based on terephthalic acid, ethylene glycol, CHDM, and ethoxylated bisphenol S (BHEBS) obtaining PETG copolymers with increased  $T_g$  and higher environmental stress cracking resistance after lipid exposure.<sup>24</sup> However, they did not present any data regarding a PET with only BHEBS units.

Therefore, in our opinion, it is of interest for the industrial and scientific community a complete and detailed study of the effect of BHEBS units on PET thermal properties and the development of a new class of poly(ethylene terephthalate) with high glass transition temperature, good optical properties, and solvent resistance.

In this article, we report for the first time the synthesis by melt mixing, together with the molecular and thermal characterization of this new class of poly(ethylene terephthalate) copolymers.

## EXPERIMENTAL

### Materials

Poly(ethylene terephthalate) (PET,  $M_w = 61240$ ) was a gift from SABIC-IP. PET was dried overnight at 120°C under vacuum before use. Titanium butoxide (TBT) (from Aldrich Chemicals) was a high purity product and was not purified before use. BHEBS was produced from ETC and BPA according to the procedure previously reported.<sup>23</sup>

### Synthesis of Copolyesters by Melt Mixing of PET with BHEBS

The melt mixing of PET and BHEBS was performed in a Brabender Plasticorder PL2000/W50. 50.0 g of PET were charged in the Brabender mixer heated at 275°C. After the complete melting of the polymer, BHEBS (in different amounts depending on the percentage of BHEBS to be inserted in the polymer chain) and 100 ppm of TBT used as catalyst (as titanium with respect to the final terephthalate polyester) were added and the mixing chamber closed with a cover to seal the mixer.

The reactions were performed in two stages; the first stage was carried out at atmospheric pressure for 15 minutes. In the second stage, the pressure was carefully reduced down to 2 mbar in 30 minutes and butanediol was distilled off from the mixing chamber and recovered in a condenser. The reaction was stopped when no further increase in the torque signal was observed. The second stage time varied from 30 minutes to 2 h depending on the BHEBS amount added. The copolyesters obtained and analyzed in this work will be indicated as PET-co-BHEBSTX, where X is the amount of BHEBST co-units expressed as mol % and T is the terephthalate group.

### Gel Permeation Chromatography

Molecular weight data were obtained by gel permeation chromatography at 30°C using a 1100 Agilent Series system with an UV spectrophotometer (at 254 nm wavelength) as detector, equipped with Agilent PLgel 5 $\mu$  MiniMIX-C column. A mixture of chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (CHCl<sub>3</sub>/HFIP) (95/5 v/v) was used as eluent with a 0.3 mL/min flow, and sample concentrations of about 2 mg/mL were applied. A molecular weight calibration curve was obtained with monodisperse polystyrene standards.

### NMR Spectroscopy

<sup>1</sup>H NMR spectra were recorded with a Varian XL-400 spectrometer (chemical shifts are downfield from tetramethylsilane) while <sup>13</sup>C NMR spectra were recorded with a Inova-600 MHz (delay 3 s, acquisition time 1.3 sec, 12,000 acquisitions) using in both cases a mixture of CF<sub>3</sub>COOD/CDCl<sub>3</sub> (20/80 v/v) as solvent.

### Thermal Analysis

**TGA Measurements.** Thermogravimetric (TGA) 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.

### Differential scanning calorimetry (DSC) 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). With the aim of measuring the glass transition and the melting temperatures of the polymers under investigation, the external block temperature control was set at -60°C and weighed samples of about 10 mg were encapsulated in aluminum pans and heated to about 40°C above fusion temperature at a rate of 20°C/min (first scan), held there for 3 min, and then rapidly quenched to -10°C. Finally, they were reheated from -10°C to a temperature well above the fusion temperature of the sample 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  $\Delta c_p$  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 the exothermal phenomena in the DSC curve, respectively. The specific heat increment  $\Delta c_p$  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 ( $\Delta H_m$ ) and the heat of crystallization ( $\Delta H_c$ ) of the crystal phase were calculated from the areas of the DSC endotherm and exotherm, respectively.

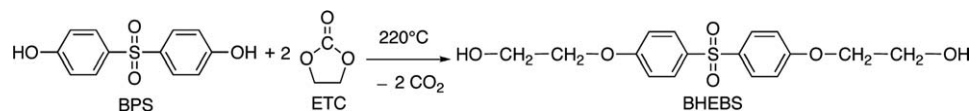


Figure 1. Ethoxylated bisphenol S (BHEBS) synthesis.

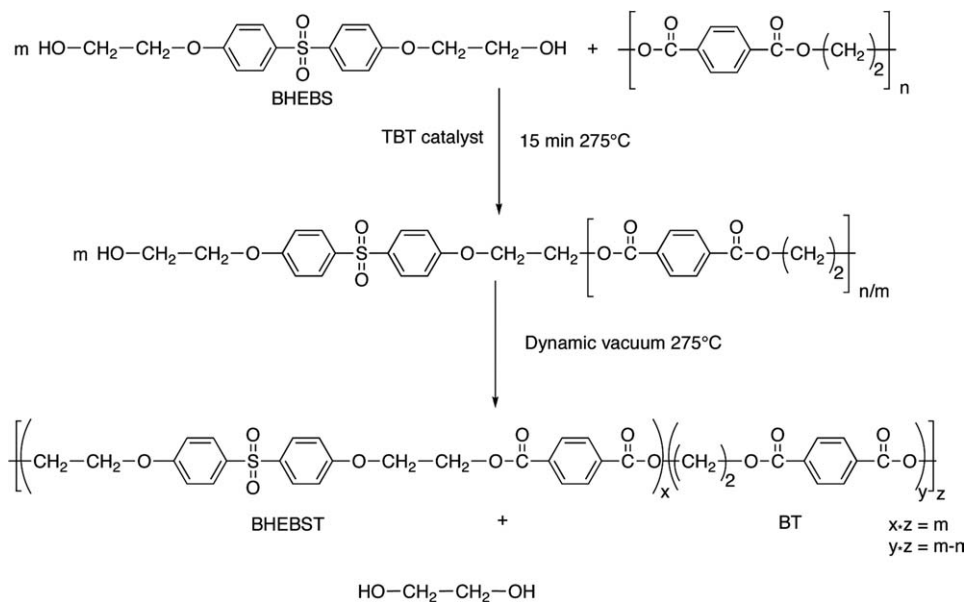


Figure 2. Insertion of ethoxylated BPS units inside the polyester chain by reactive blending with PET.

## RESULTS AND DISCUSSION

BPS have been ethoxylated in high yields by reaction with ethylene carbonate (Figure 1) according to the procedure previously reported in the literature.<sup>23</sup>

The insertion of ethoxylated BPS inside the polyester has been performed by melt mixing with the polyester and subsequent polycondensation to reach high molecular weight (Figure 2). We have chosen this method respect to the standard polycon-

denation starting from monomers as it allows the use of recycled terephthalate polyesters and can be performed in shorter reaction times compared with the full polymerization procedure.<sup>14,22,24</sup>

The <sup>1</sup>H NMR spectrum in Figure 3 show the presence of aliphatic-aliphatic ether linkage at  $\delta = 4.65$  and 4.15 ppm. Part of the ether linkages (2.0 mol %) is already present in the starting PET, while part is formed (1.8 mol %) during the reactive

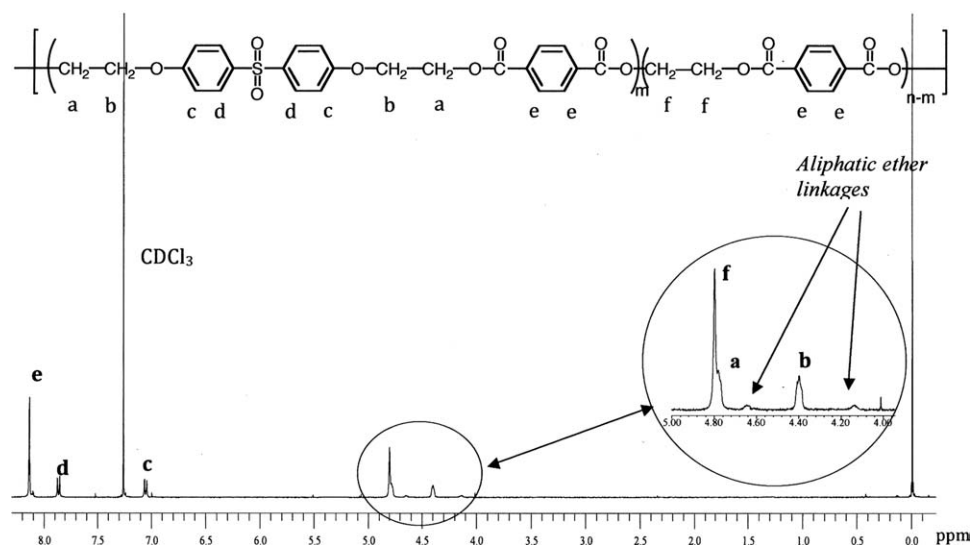
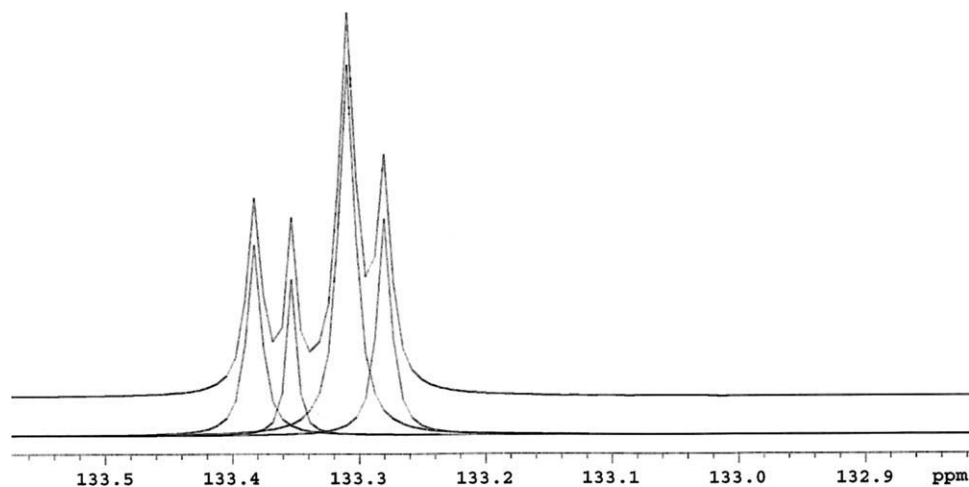


Figure 3. <sup>1</sup>H NMR of PET-co-BHEBST with 30% of BHEBS units.



**Figure 4.**  $^{13}\text{C}$  NMR of PET-*co*-BHEBST with 30% of BHEBS units, enlargement of aromatic quaternary carbons of terephthalic acid group and peak deconvolution.

blending and during the polycondensation step. No peak due to other side reactions (e.g., vinyl end-groups) has been found in the NMR spectrum. The effective incorporation of the BHEBS groups was confirmed by  $^1\text{H}$  NMR after dissolution in a  $\text{CHCl}_3$ /hexafluoroisopropanol 95/5 (v/v) solution and precipitation in methanol, as the amount of BHEBS in the purified polymer was the same of the BHEBS content in the unpurified polymer. The degree of randomness of the comonomeric units has been analyzed by  $^{13}\text{C}$  NMR. The series of signals at 133 ppm (ascribed to the aromatic carbons linked to the carbonyl group) have been used to determine the degree of randomness (Figure 4). In particular, using the  $^{13}\text{C}$  analysis of the two homopolymers, the peak at 133.30 has been ascribed to the PET homopolymer sequence, the peak at 133.35 to the PBHEBST homopolymer sequence, while the two peaks at 133.38 and 133.27 to the mixed sequences. The degree of randomness has been calculated using a method previously reported in the literature<sup>25</sup> using peak deconvolution before integration, as the signals were very close. The degree of randomness obtained for the polymer with 30% of BHEBS units was 0.92 and therefore, analogously to what observed for PBT-*co*-BHEBST copolymers,<sup>23</sup> the structure of the copolymers can be considered random. This was also expected as the reaction was conducted for a reaction time comprised between 75 and 165 minutes at high temperature (275°C) with a catalyst (TBT) that is well known<sup>26</sup> to promote the exchange reactions that give rise to copolymer randomization.

The BHEBS insertion by reactive blending is quantitative. The amount of BHEBS inserted, the number average molecular weight ( $M_n$ ) and the weight average molecular weight ( $M_w$ ) of the polymers obtained are reported in Table I. The amount of BHEBS inserted has been calculated by  $^1\text{H}$  NMR analysis comparing the peak of the bisphenol S units at  $\delta = 7.0$  ppm (4H) with that of the terephthalate group at  $\delta = 8.1$  ppm (4H) after dissolution of the polymer in a mixture of  $\text{CHCl}_3/\text{CF}_3\text{COOH}$  80/20 (v/v) and precipitation in methanol (that is a solvent for BHEBS).

The homopolymer of dimethyl terephthalate (DMT) and BHEBS (PBHEBST) was obtained according to the procedure previously reported.<sup>23</sup>

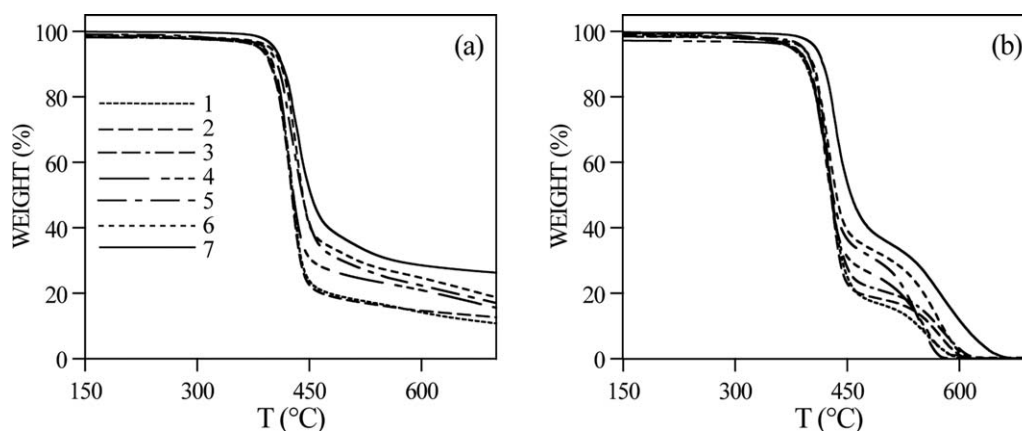
#### THERMAL CHARACTERIZATION OF PET/BHEBST

The copolyesters were examined by thermogravimetric analysis. The investigation on the thermal stability was carried out both in air and under nitrogen atmosphere. Figure 5(a) shows the thermogravimetric curves of some samples under nitrogen atmosphere.

It can be noted that the weight loss takes place almost completely in one-step. Thermal stability was similar for all the copolymers under investigation and practically identical to that of PET. On the contrary, the char residues of copolymers are intermediate between those of parent homopolymers, increasing regularly as the amount of BHEBST co-units is increased. An analogous dependence on composition of the thermal stability was observed in air [Figure 5(b)], even though all the samples are characterized by a weight-loss of 100% and the thermal degradation process takes place always in two separate steps, the latter one being more evident as higher is the amount of BHEBST unit in the polymeric chain. Therefore, the introduction of BHEBST co-units along PET polymer chain does not alter sensibly its thermal stability, differently from PBT-*co*-BHEBST copolymers previously investigated.<sup>23</sup>

**Table I.** Molecular Characterization Data of PET/BHEBS Samples

Sample	BHEBS feed (mol %)	BHEBS inserted (mol %)	$M_w$	$M_n$
PET	0	0	61,240	25,500
PET/BHEBST5	5	4.3	57,650	20,480
PET/BHEBST10	10	10.5	45,350	17,060
PET/BHEBST15	15	14.9	53,570	17,600
PET/BHEBST30	30	32.1	66,540	23,200
PET/BHEBST60	60	57.9	29,380	12,600
PBHEBST	100	100	29,860	13,480



**Figure 5.** TGA curves of (1) PET, (2) PET-*co*-BHEBST5, (3) PET-*co*-BHEBST10, (4) PET-*co*-BHEBST15, (5) PET-*co*-BHEBST30, (6) PET-*co*-BHEBST60, (7) PBHEBST at 10°C/min in (a) nitrogen; (b) air.

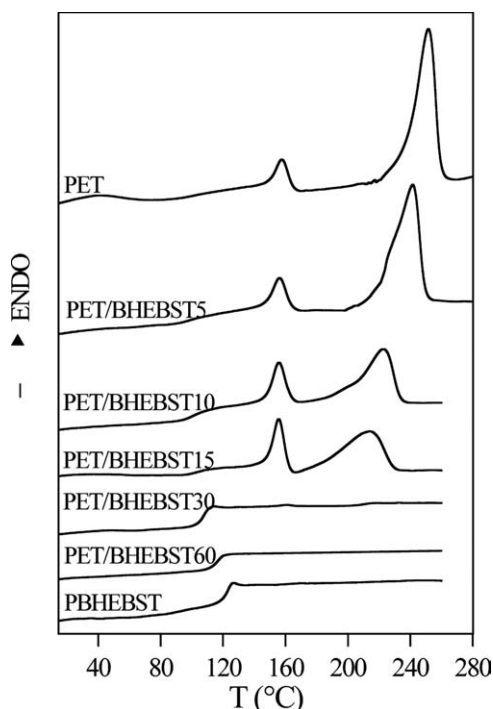
The melting behavior of polymers is affected by its previous thermal history. Therefore, each sample was kept at room temperature for about 4 weeks before the analysis, in order to provide the same heat treatment to all the samples investigated. The DSC traces of the copolyesters are reported in Figure 5 and the results obtained in Table II. Being the samples characterized by high molecular weights, an influence of molecular weight on the glass transition and melting of the polymers synthesized can be excluded. The results in Table II show that PET copolymers containing 30% of BPS units present a  $T_g$  of 106°C that is significantly higher compared to the highest  $T_g$  reported in the Eastman patent by Turner et al.<sup>24</sup> (100.3°C). The glass transition temperature can be further increased up to 122°C by increasing the BHEBS content. The  $T_g$  obtained in this work are also higher compared to those obtained in our previous works on PBT-*co*-BHEBST (94°C with 50% of BPS units)<sup>23</sup> and PET-*co*-BHEEB (84°C with 100% of BPA units).<sup>17</sup> For this reason PET-*co*-BHEBST copolymers can be used in applications where a higher  $T_g$  with respect to that of the polymers patented by Eastman<sup>24</sup> or prepared in our previous works<sup>14–17,23</sup> is required. Moreover, the copolymers reported in Eastman patent contains other comonomeric units (1,4-cyclohexanedimethanol and neopentyl glycol) so in that case it is difficult to clarify the effect of BPS units on the thermal properties of the copolymers. On the contrary, in our work we have only used BHEBS units and

therefore, we can perform a detailed studies on the thermal properties of this class of high  $T_g$  copolyesters.

The curves in Figure 6 show that PET and copolymers having up to 15 mol % of BHEBST units show a glass transition phenomenon followed by a double melting peak. The endotherm at lower temperature is at constant temperature, whereas the location of the high temperature melting peak appears to depend on composition. The reduction in both the melting temperature and the heat of fusion of the high temperature melting peak, indicates a reduced level of crystallinity in the copolymers with respect to the homopolymer PET. Moreover, the endotherm region is broader for the copolymers with respect to the standard PET, suggesting the presence of a larger distribution of crystallites with different degree of perfection. The low temperature melting peak can be attributed to the fusion of poor crystals, characterized by a very low degree of perfection. The DSC curves of samples containing from 30 mol % up to 100 mol % of BHEBST units are instead characterized only by an intense endothermal baseline deviation associated with the glass transition phenomenon, indicating the completely amorphous nature of such samples. As it is well known, the crystallization capacity of a polymer is correlated with several factors, such as the symmetry and the flexibility of the polymeric chain. As concerns copolymers, the presence of 30 mol % of very rigid bisphenol S group causes a drastic reduction

**Table II.** Thermal Characterization Data of PET/BHEBST Random Copolymers.

Sample	1st scan				2nd scan			
	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_g$ (°C)	$\Delta c_p$ (J/g°C)	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)
PET	252	59	78	0.400	140	44	252	45
PET/BHEBST5	242	51	82	0.392	166	28	238	28
PET/BHEBST10	223	39	91	0.380	–	–	–	–
PET/BHEBST15	214	27	93	0.378	–	–	–	–
PET/BHEBST30	–	–	106	0.355	–	–	–	–
PET/BHEBST60	–	–	114	0.340	–	–	–	–
PBHEBST	–	–	122	0.325	–	–	–	–



**Figure 6.** Calorimetric curves of PET, PBHEBST, and their random copolymers (1st scan).

of flexibility, hindering completely the ability of crystallizing of Ethylene terephthalate (ET) polymer chains.

Therefore, the phase behavior of the two parent homopolymers is opposite: as a matter of fact, PET is semicrystalline, whereas PBHEBST is completely amorphous. Moreover, the phase behavior of PET-*co*-BHEBST copolymers depends on composition: semicrystalline samples are exclusively obtained at high ET content. Semicrystalline materials usually exhibit a different glass transition behavior with respect to the completely amorphous analogous. In fact, even if some conflicting results are reported in the literature,<sup>27</sup> crystallinity usually acts as crosslink, raising the  $T_g$  through its restrictive effect on the segmental motion of amorphous polymer chains. For this reason, the influence of the chemical structure on the  $T_g$  of random copolymers should be examined in the total absence of crystallinity. In this view, all the samples under investigation were subjected to rapid cooling (quenching) from the melt (see the Experimental section for the details). The DSC curves after melt quenching are shown in Figure 7 and the corresponding data collected in Table II.

PET and PET-*co*-BHEBST5 copolymer show a glass transition followed by an exothermic “cold crystallization” peak and a melting endotherm at higher temperature. In both cases, the enthalpy of crystallization very well compares with the corresponding heat of fusion, indicating that the samples are completely amorphous.

The calorimetric curves of pure PBHEBST and copolymers containing more than 10 mol % of BHEBST units, only an intense endothermal baseline deviation associated with the glass transition is observed. Therefore, the DSC scans indicate a quite dif-

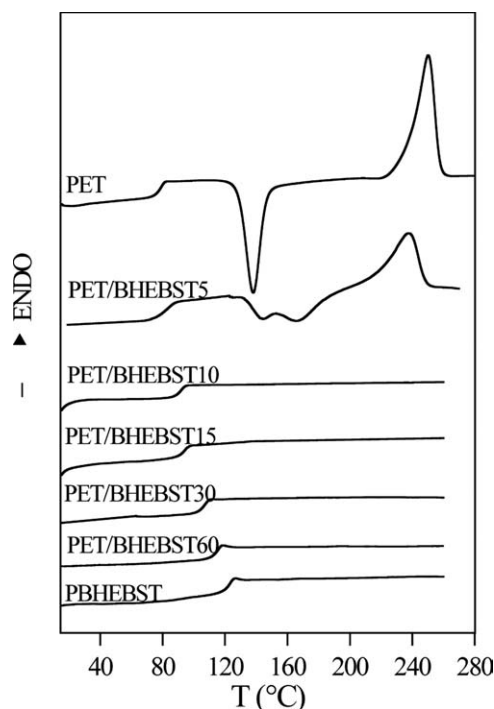
ferent thermal behavior of PET and PBHEBST homopolymers: in fact, both are completely amorphous after melt quenching, but in the case of PET a portion of amorphous material, once  $T_g$  is exceeded, acquires enough mobility to rearrange and crystallize. This result can be explained on the basis of the higher flexibility of PET polymer chains respect to PBHEBST ones.

Moreover, the phase behavior of PET-*co*-PBHEBST copolymers depends on composition: as a matter of fact, only at high ethylene terephthalate unit content, the samples are able to crystallize during heating. This fact can be considered the result of two effects, which become more significant with increasing of BHEBST unit content:

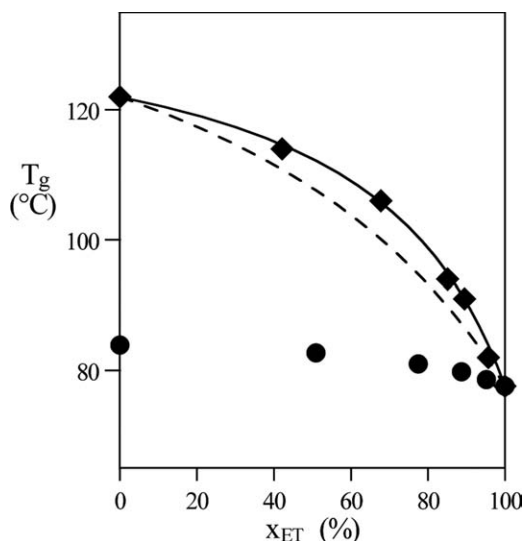
The former is an increment of the copolymer  $T_g$  together with a decrease of the copolymer  $T_m$  which reduce the  $T_g/T_m$  window, hindering the PET crystallization process (the mobilization and the consequent rearrangement of the macromolecules into 3-dimensional order can occur in a narrower temperature range); the latter is a marked decrement of flexibility of crystallizable chains, due to the stiffening effect of the moieties deriving from bisphenol S.

The data reported in Figure 7 and in Table II show that  $T_g$  is influenced by the amount of BHEBST units. Figure 8 reports  $T_g$  as a function of ET unit content. PET-*co*-BHEBST copolymers (copolymers with ethoxylated BPA) previously investigated are also reported in Figure 8 for comparison.<sup>15</sup>

The results obtained shows that  $T_g$  values consistently increase with BHEBST unit content. The results can be explained on the basis of the stiffening effect of BPS moieties.



**Figure 7.** Calorimetric curves of PET, PBHEBST, and their random copolymers after melt quenching (2nd scan).



**Figure 8.** Composition dependence of  $T_g$  for (◆) PET-co-BHEBST and (●) PET-co-BHEEBT (from Ref. 23.) random copolymers; theoretical curve of  $T_g$  vs. composition calculated on the basis of Wood equation (solid line) or Fox equation (dotted line).

Comparing the  $T_g$  the two copolymeric systems it can be observed that the  $T_g$  increment is more consistent for PET-co-BHEBST copolymers, due to the higher rigidity of BPS compared to BPA.

Glass transition temperature is usually a monotonic function of composition for amorphous random copolymers.<sup>28</sup> The Fox equation is the most commonly used relation to predict  $T_g$  as a function of comonomer content<sup>29</sup>:

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

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 PET-co-BHEBST copolymers appears to be higher than the predicted values, even though they follow the same trend, i.e.,  $T_g$  increases with increasing the amount of BHEBST units: this is not surprising, being well known that the Fox equation has some limitations, as 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<sup>30</sup>:

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

where  $k$  is a constant parameter.

As shown in Figure 7, the equation fits well the experimental data (with the parameter  $k = \frac{\Delta C_{p,PET}}{\Delta C_{p,PBHEBST}}$ ), using for PET and PBHEBST the glass transition temperatures experimentally measured by us.

## CONCLUSIONS

We have prepared for the first time a series of PET copolymers containing rigid bisphenol S (BPS) units. The incorporation has been performed by melt mixing of ethoxylated BPS (BHEBS) units and subsequent polycondensation under reduced pressure. The insertion of BPS units is quantitative and no side reactions have been observed. A consistent increase in  $T_g$  has been observed by addition of BHEBS units. This increase in  $T_g$  allows the use of PET copolymers in a wide range of applications that were not possible before due to the lower  $T_g$  of amorphous PET copolymers. Lastly, phase behavior can be properly modified by changing copolymer composition: semicrystalline polymers can be obtained at high ET co-unit content.

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