# Synthesis and Characterization of Poly(butylene terephthalate-*co*-triethylene terephthalate) Copolyesters

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**ABSTRACT:** Poly(butylene terephthalate-*co*-triethylene terephthalate) random copolymers of various compositions and molecular weights were synthesized in bulk and characterized in terms of their chemical structure and thermal and rheological properties. At room temperature all the copolymers were partially crystalline and showed good thermal stability. The main effect of copolymerization was a decrease in the melting and glass-transition temperatures with respect to the poly(butylene terephthalate) homopolymer. The fusion temperatures were well correlated with the composition by the Baur equation and the equilibrium melting temperature and the heat of fusion extrapolated values for poly(butylene terephthalate) were in good agreement with those reported elsewhere. Triethylene terephthalate units were found to influence the rheological behavior in the melt, the viscosity being significantly higher than that of the poly(butylene terephthalate-*co*-diethylene terephthalate) copolymers investigated previously. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 981–990, 2001

**Key words:** poly(butylene terephthalate); random copolymers; triethylene terephthalate; thermal properties; rheological properties

## INTRODUCTION

In another article[1] we reported the results of a thermal and rheological characterization of statistical poly(butylene terephthalate-*co*-diethylene terephthalate) (PBTDEG) copolyesters of different compositions and molecular weights. We found that the presence of random diethylene terephthalate units in the polymeric chain of poly(butylene terephthalate) (PBT) leads to a lower melting temperature as expected for statistical copolymers. On the contrary, these units did not have a significant effect on the rheological properties in the melt of the polymer. The aim of this study was to show how the modifications in the chemical structure of PBT reflect on its properties, so we extended the investigation to the effect of the presence of triethylene terephthalate units, each of which contained two ether linkages. In addition, the presence of triethylene terephthalate units in polymers of terephthalic acid was recently claimed to improve the properties of polyesters for various applications.[2–4]

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The present article collects the results of an investigation on the thermal and rheological properties of statistical poly(butylene terephthalate-*co*-triethylene terephthalate) (PBTTEG) copolyesters of different compositions and molecular weights that were synthesized in our laboratories.

## EXPERIMENTAL

### Materials

Dimethyl terephthalate (DMT), triethylene glycol (TEG), 1,4-butanediol (BD), and Ti(OBu)$_4$ were reagent grade product and were used as supplied.

### Synthesis of Polymers

Poly(butylene-*co*-triethylene terephthalate) copolymers were synthesized with DMT (about 0.7 g/kg), BD, and TEG with Ti(OBu)$_4$ as the catalyst. Various amounts of BD and TEG (5, 10, and 15 mol % of TEG with respect to BD+TEG) were employed.

The syntheses were carried out in a 1.8-L stainless steel reactor according to the usual two-stage polycondensation procedure. In the second stage, which was carried out at reduced pressure, the temperature was kept at about 250°C. During each run the samples were taken from the bottom of the reactor at different times to obtain samples with the same composition but different molecular weights. The synthesized copolymers were statistical because of the use of Ti(OBu)$_4$ as the catalyst and the high reaction temperature, which favor redistribution reactions.[5] Comonomeric units I and II had the following structures:
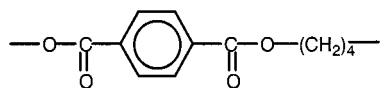
**I**   ($M_\text{I}$ = 220)
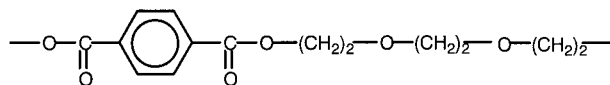
**II**   ($M_\text{II}$ = 280)

### NMR Spectroscopy

The molar composition and the chain structure of the PBTTEG copolymers were determined by means of $^1$H-NMR spectroscopy using a Varian XL-300 spectrometer. Polymer samples were dissolved in a 20/80 (v/v) mixture of trifluoroacetic acid/chloroform-*d* with 0.03% (v/v) tetramethylsilane added as an internal standard.

### End-Group Analysis

#### Carboxyl End Groups

The carboxyl end-group content was determined by direct potentiometric titration. A sample of about 1 g was dissolved in 25 mL of a dichloromethane/*o*-cresol solution (25/75 v/v) under heating. When the sample was completely dissolved and the solution cooled to room temperature, 50 mL of dichloromethane was added and the solution was titrated with a tetrabutylammonium hydroxide solution (0.01$N$). Blank runs were carried out for correction. The titrator was a Mettler DL 25 equipped with a Mettler SC-111 combination electrode.

#### Hydroxyl End Groups

The hydroxyl end groups were determined using a method derived from that reported by Kosky et al.[6] and based on FTIR measurements carried out on thin films. The films were prepared by pressing the samples (ca. 0.1–0.2 g) between sheets of poly-(tetrafluoroethylene) coated aluminum in a Carver press at 235°C for 2 min. Then the samples were rapidly quenched in an acetone ice bath in order to obtain transparent films. These films were dried at 90°C under a vacuum for 12 h prior to use. The IR spectra of the obtained films were recorded with a Bruker IFS 48 FTIR spectrophotometer in the range of 4000–3000 cm$^{-1}$ with a resolution of 2 cm$^{-1}$. The method requires the use of a deuterated PBT reference film to provide the background for zero —OH content and to take into account the different thicknesses of the pressed films. The fully deuterated PBT film was prepared by heating a PBT film in D$_2$O. After several hours the film was dried under a vacuum and then the IR spectrum was recorded. The deuteration procedure was repeated until the absorbance of the free —OH band at 3550 cm$^{-1}$ had almost completely vanished. This reference film was kept in contact with D$_2$O in order to prevent the proton exchange with H$_2$O and dried just before recording the IR background spectrum. The calculation of the —OH end-group content was carried out as follows. The spectrum of the deuterated (reference) film was subtracted from the

**Table I  Molecular Characterization Data for PBTTEG Copolymers**

| Sample | Composition[a] | | | Terminal-Group Concentration (meq kg$^{-1}$) | | | | |
| | $x_{\text{TEG}}$ | $x_{\text{BD}}$ | $b$ | —COOH | —OH | CH=CH$_2$ | $E$ | $M_w$ |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| PBT5TEG1 | 0.95 | 0.05 | 1.16 | 25.1 | 157.0 | 0.7 | 182.8 | 21,700 |
| PBT5TEG2 | 0.95 | 0.05 | 1.15 | 100.4 | 21.5 | 9.6 | 131.5 | 30,200 |
| PBT5TEG3 | 0.95 | 0.05 | 1.16 | 55.9 | 61.7 | 2.4 | 120.0 | 33,100 |
| PBT5TEG4 | 0.95 | 0.05 | 1.16 | 83.2 | 27.4 | 5.7 | 116.3 | 34,200 |
| PBT10TEG1 | 0.90 | 0.10 | 1.08 | 17.0 | 178.5 | 3.1 | 198.6 | 19,900 |
| PBT10TEG2 | 0.90 | 0.10 | 1.08 | 33.4 | 99.9 | 3.8 | 137.1 | 29,000 |
| PBT10TEG3 | 0.90 | 0.10 | 1.08 | 73.6 | 27.5 | 10.7 | 111.8 | 35,600 |
| PBT10TEG4 | 0.90 | 0.10 | 1.12 | 52.9 | 40.8 | 5.5 | 99.2 | 40,100 |
| PBT15TEG1 | 0.85 | 0.15 | 1.16 | 20.4 | 117.0 | 3.7 | 141.1 | 28,100 |
| PBT15TEG2 | 0.85 | 0.15 | 1.15 | 86.7 | 22.0 | 7.1 | 115.8 | 34,300 |
| PBT15TEG3 | 0.85 | 0.15 | 1.16 | 42.9 | 69.0 | 3.4 | 115.3 | 34,500 |
| PBT15TEG4 | 0.85 | 0.15 | 1.16 | 55.8 | 27.9 | 9.8 | 93.5 | 42,600 |

$x$, mole fraction; $b$, degree of randomness (see text); $E$, total end-group content.
[a] By NMR analysis.

spectrum of each PBTTEG copolymer until the absorbance of the band at 3420 cm$^{-1}$ ($A_{3420}$, carbonyl stretching overtone) was equal to zero. Then the net absorbance of the free —OH band in the difference spectrum was measured by taking into account a baseline from 3600 to 3475 cm$^{-1}$. The absorbance values were converted into milliequivalents of —OH/kg of polymer by the following formula[7]:

$$[OH] = -3.952 + 249.7(A_{3550}/A_{3420})$$

### Vinyl Ester End Groups

The determination of the vinyl ester end groups, which arise from the degradation of PBT sequences,[8,9] can be conveniently carried out using the $^1$H-NMR technique. In fact, in the region of the spectrum from 6.0 to 5.0 ppm, the resonances belonging to the 3-buten-1-oxyester produced by the $\beta$-scission reactions were present and the peak associated with the olefinic resonances of this end group matched the chemical shifts for di(3-buten-1-oxy)terephthalate reported in the literature.[10] In the present work the peaks in the region of 5.1–5.2 ppm (corresponding to two protons) were used. In order to make the integration of the small peaks more accurate, the $^{13}$C-satellite peaks of aromatic protons were used as a reference for the integration. The $^{13}$C-satellite peaks were found at 4.76 and 4.24 ppm.

The values of the end-group contents reported in Table I are the averages of replicates.

### Thermal Analysis

Calorimetric measurements were carried out by means of a differential scanning calorimeter (Perkin–Elmer DSC7). The external block temperature control was set at $-140$°C. The instrument temperature and energy were calibrated with high-purity standards (indium and cyclohexane). Weighted samples (ca. 10 mg) were encapsulated in aluminum pans, heated to 240°C at a rate of 20°C/min (first scan), kept at this temperature for 1 min, and then rapidly quenched to $-80$°C. They were finally reheated from $-80$ to 240°C at a heating rate of 20°C/min (second scan).

The glass-transition temperature ($T_g$) was taken as the fictive temperature, which is the temperature defined by the intersection of the extrapolated pretransition and posttransition enthalpy data.[11] The melting temperature ($T_m$) was taken as the peak value of the endothermal phenomenon in the differential scanning calorimetry (DSC) curve. Repeated measurements on each sample showed excellent reproducibility.

Thermogravimetic curves were obtained in air and under a nitrogen atmosphere using a Perkin–Elmer TGA 7 apparatus (50 mL/min gas flow) at a 10°C/min heating rate up to 900°C.

### Rheological Measurements

The viscosities of the copolymer samples in the molten state were measured at various shear rates (10–2500 s$^{-1}$) using a Rheoscope 1000
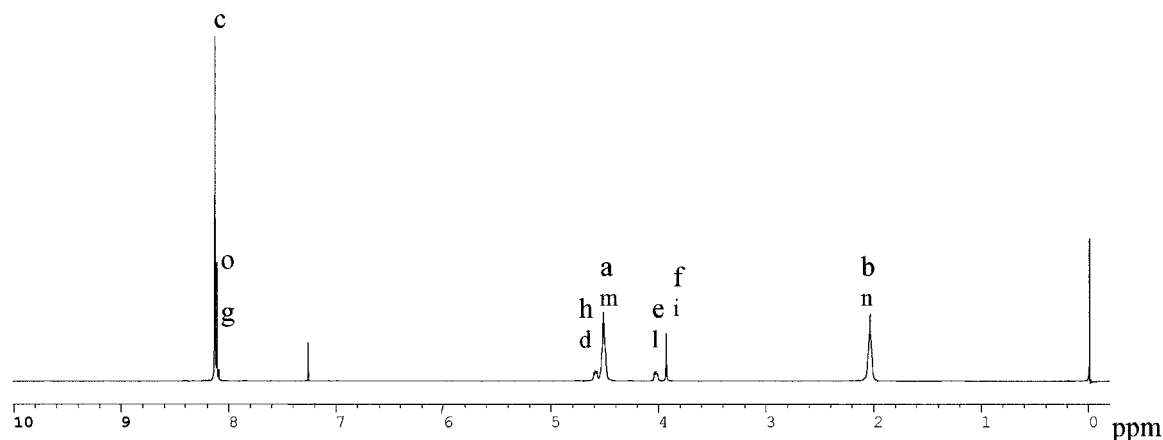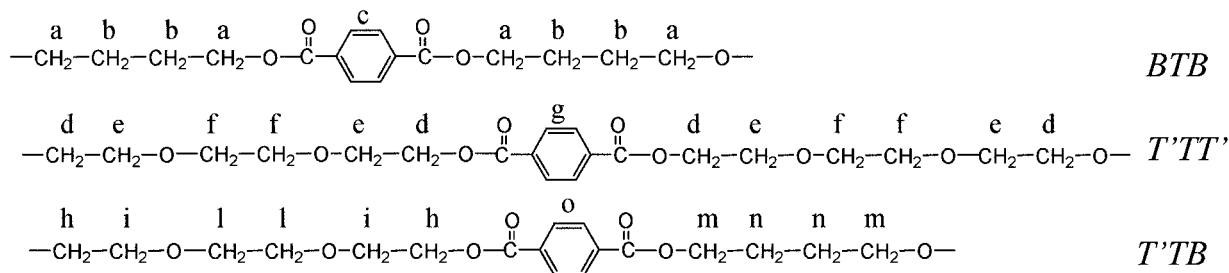
**Figure 1** The $^1$H-NMR spectrum of the PBT15TEG copolymer.

(Ceast) capillary rheometer. The instrument was basically an electrically thermostatted stainless-steel barrel, in the bottom of which one of a number of interchangeable capillaries can be inserted. The polymer melt was forced through the capillary at preselected constant rates by a plunger; the force necessary to drive it at a fixed speed was measured by a compression load cell. The capillary used had a nominal inner diameter of 1.00 mm, a length to diameter ($L/D$) ratio of 40, and an entrance angle of 90°. Before each test, which was carried out at 240°C for 10–15 min, the polymer samples were dried under a vacuum at 90°C overnight; under these conditions the samples were thermally stable. In the procedure employed to evaluate the viscosity the assumptions were that there was no slip at the wall of the capillary and the entrance effects could be neglected.

The apparent shear rate $\dot{\gamma}_a$ at the wall,

$$\dot{\gamma}_a = 4Q/\pi R^3$$

(where $Q$ is the volumetric flow rate and $R$ is the capillary radius) was calculated and corrected by means of the well-known Rabinowitsch procedure[12] to take the non-Newtonian behavior of the fluid into account and to obtain the true shear rate at the wall,

$$\dot{\gamma} = \dot{\gamma}_a(3n' + 1)/4n'$$

where $n'$ is the slope of a log–log plot of the wall shear stress ($\tau$), which is $\tau = PR/2L$, versus $\dot{\gamma}$ (where $P$ is the pressure).

Finally, the viscosity was obtained as the ratio between the shear stress and the shear rate at the wall,

$$\eta = \tau/\dot{\gamma}$$

## RESULTS AND DISCUSSION

All the PBTTEG copolyesters at room temperature were colorless, semicrystalline solids and insoluble in the most common organic solvents, which is similar to PBT. The homopolymer and the synthesized copolymers are listed in Table I, and some molecular characterization data are also reported. The chemical structure of all polyesters was determined by $^1$H-NMR spectroscopy;

a typical ^{1}H-NMR spectrum is shown in Figure 1, together with the chemical shift assignments. In all cases the spectra were found to be consistent with the expected structure. The copolymer composition was calculated from the relative areas of the ^{1}H-NMR resonance peaks of the methylene group next to ether-oxygen at 3.94 ppm and the β-methylene group next to carbonyl at 2.03 ppm. The feed composition and the composition determined by ^{1}H-NMR were in good agreement and are reported in Table I.

Information on the arrangement of the comonomeric units in the chain, which affected some of the polymer properties, was deduced by employing the degree of randomness ($b$). This parameter can be determined by ^{1}H-NMR spectroscopy.[1,13–16] As shown in Figure 1, the resonance peak of the aromatic protons of the terephthalate unit was a triplet corresponding to $T'TT'$, $T'TB$, and $BTB$ sequences resonated at 8.08, 8.10, and 8.13 ppm, respectively, where $T$ is the terephthalate unit, $B$ is the butylene unit, and $T'$ is the triethylene unit. The chemical environments of the aromatic protons of the $T$ units in the $T'TB$ sequence were not identical. Nevertheless, the effect on the chemical shift of these protons was certainly very slight, so we assumed that the resonance peak occurred as a singlet.

The degree of randomness is defined as[16]

$$b = P_{T'B} + P_{BT'} \tag{1}$$

with

$$P_{T'B} = I_{T'TB}/(I_{T'TB} + I_{T'TT'})$$

$$P_{BT'} = I_{BTT'}/(I_{BTT'} + I_{BTB})$$

where $P_{T'B}$ and $P_{BT'}$ are the probability of finding a $B$ unit next to a $T'$ unit and the probability of finding a $T'$ unit next to a $B$ unit, respectively; and $I_{BTB}$, $I_{T'TB}$, $I_{BTT'}$, and $I_{T'TT'}$ represent the integrated intensities of the resonance signals of $BTB$, $T'TB$, $BTT'$, and $T'TT$ sequences, respectively (and, of course, $I_{T'TB} = I_{BTT'}$). Note that $b$ = 1 for random copolymers, $b$ = 2 for alternate copolymers, and $b$ is close to zero for block copolymers.

Table I lists the value of $b$ obtained for all samples investigated. In all cases, as previously found[1] for poly(butylene terephthalate-co-diethylene terephthalate) copolymers, the degree of randomness was close to 1, indicating the random nature of the synthesized copolyesters. These results confirmed that the reaction conditions adopted [high temperature and Ti(OBu)$_4$ as the catalyst] favored a random distribution of the sequences.[5]

The end-group content was determined in order to calculate the weight-average molecular weight ($M_w$). Assuming that the most probable molecular weight distribution was established and neglecting the presence of cyclic molecules, the following expression was employed[17]:

$$M_w = M_{w,0} + 2pM_{n,0}/(1 - p)$$

where $M_{n,0} = x_I M_I + x_{II} M_{II}$ and $M_{w,0} = w_I M_I + w_{II} M_{II}$ are the number-average and weight-average molecular weights of the repeating unit, respectively; and $x_I$, $x_{II}$, $w_I$, and $w_{II}$ are the respective molar and weight fractions of the two kinds of monomeric units.

The conversion $p$ was calculated from the end-group content $E$ by

$$p = 1 - EM_{n,0}/2 \tag{2}$$

Table I presents the terminal group content and the $M_w$ for the samples under investigation, which are listed for each composition in the order of increasing $M_w$. It must be noted that the —OCH$_3$ end-group content, which was derived from the starting material (DMT), is not reported. In fact, its determination by ^{1}H-NMR spectroscopy was not possible for the PBTTEG copolymers: the characteristic resonance of these protons (a singlet at about 3.95 ppm) was completely masked by a strong resonance peak due to the central ethylene moiety of TEG. In another study[1] we succeeded in determining —OCH$_3$ end-group content on PBTDEG copolymers, which were prepared under the same experimental conditions used for the PBTTEG samples. Because it was reasonable to assume that the methylester content was of the same order of magnitude in the two copolymer series, we concluded that the error introduced in calculating the $M_w$ by neglecting the —OCH$_3$ groups was up to 5%.

## Thermal Properties

The copolyesters were examined by thermogravimetric analysis (TGA) and DSC. The investigation on the thermal stability of the PBTTEG copolymers was carried out in air and under a ni-
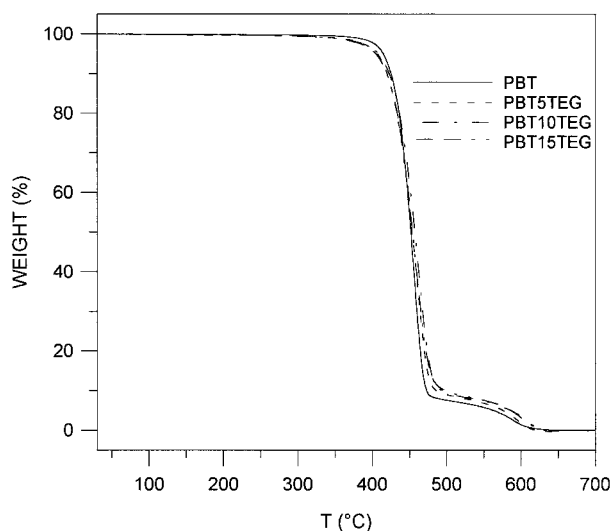
**Figure 2** TGA curves of PBT and PBTTEG copolymers in air at 10°/min.

trogen atmosphere. Figure 2 shows the TG curves in air, from which the temperature of the initial decomposition ($T_{id}$), the temperature corresponding to the maximum weight loss rate ($T_{max}$), and the weight loss percent at $T_{id}$, collected in Table II, were determined. In all cases the weight loss took place practically in one step, and the thermal stabilities of all the polymers were quite comparable, all being practically stable up to 300°C. For all PBTTEG copolymers the temperature at which the weight loss rate was the highest turned

out to be in the range of 429–432°C, and there were only slight differences with respect to PBT. Similar results were obtained when the TGA measurements were carried out under a nitrogen atmosphere. It needs to be emphasized that the PBTDEG copolymers previously investigated by us showed analogous behavior. Therefore, we concluded that the presence of TEG units or diethylene terephthalate units did not significantly alter the thermal stability of PBT.

As far as the calorimetric results were concerned, a preliminary investigation was performed to evaluate the possible influence of the molecular weight on the glass transition and melting of the synthesized copolymers. The calorimetric measurements, which were carried out on samples with the same composition but different $M_w$ values, gave practically identical results. Therefore, the data reported here refer to the sample with the highest molecular weight available for each composition.

Typical calorimetric curves of PBT and PBT-TEG copolymers obtained after rapid cooling from the melt are reported in Figures 3 and 4 and the corresponding data are collected in Table II. An endothermal baseline shift associated with the glass transition was observed in the temperature range between 15 and 50°C; after a broad prefusion beginning at approximately 120°C and a small exothermic drop, the DSC curves showed a melting peak whose location depended on the copolymer composition.

**Table II   Thermogravimetric, Calorimetric, and Melt Viscosity Data of PBTTEG Random Copolymers**

| Sample | $T_{id}$ (°C) | $T_{max}$ (°C) | Weight Loss at $T_{id}$ (%) | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $\eta_o$[a] (Pa s) |
|---|---|---|---|---|---|---|---|
| PBT | 432 | 456 | 0.3 | 40 | 222 | 49 | — |
| PBT5TEG1 | | | | | | | 70 |
| PBT5TEG2 | | | | | | | 210 |
| PBT5TEG3 | | | | | | | 310 |
| PBT5TEG4 | 429 | 461 | 0.7 | 37 | 216 | 44 | 360 |
| PBT10TEG1 | | | | | | | 55 |
| PBT10TEG2 | | | | | | | 230 |
| PBT10TEG3 | | | | | | | 430 |
| PBT10TEG4 | 432 | 463 | 0.2 | 30 | 209 | 41 | 600 |
| PBT15TEG1 | | | | | | | 160 |
| PBT15TEG2 | | | | | | | 360 |
| PBT15TEG3 | | | | | | | 360 |
| PBT15TEG4 | 429 | 457 | 0.2 | 27 | 200 | 38 | 550 |

The thermogravimetric and calorimetric analyses were in air at 10°/min and with a second DSC scan after rapid quenching from the melt, respectively.
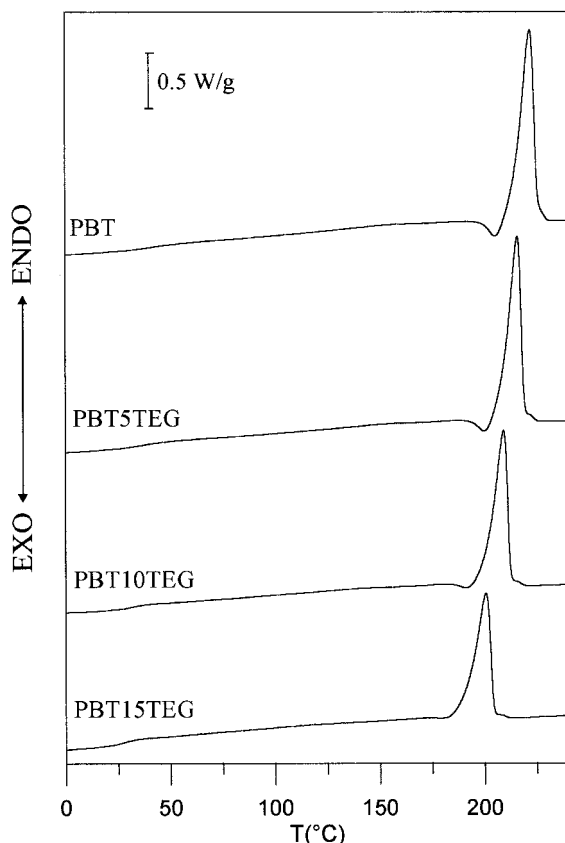
[a] At 240°C.

**Figure 3** Calorimetric curves of PBT and PBTTEG copolymers after cooling from the melt (20°/min heating rate).

It is well known that the thermal behavior of a polymer is affected by its previous thermal history and that the amorphous and crystallinity contents depend on the cooling rate to which the sample is subjected. As can be seen in Figure 3, neither PBT nor PBTTEG copolymers, because of their high crystallization rate, could be frozen in a totally amorphous state[18] by using the procedure described in the Experimental section.

The calorimetric results indicated that an increase in the amount of the comonomer led to a reduction of the melting temperature in the samples subjected to the same thermal history. The melting depression in a random copolymer system can be expressed as a function of the copolymer composition as predicted by Flory,[19] Baur,[20] Sanchez and Eby,[21] Helfand and Lauritizen,[22] Allegra et al.,[23] and Goldbeck-Wood.[24] In particular, when only one co-unit can crystallize, the second one being completely excluded from the crystals, the melting point reduction is commonly examined using the Flory equation,

$$1/T_m - 1/T_m^o = -(R/\Delta H_m^o)\ln x_C \quad (3)$$

where $T_m$ is the melting temperature of a random copolymer with a mole fraction $x_C$ of crystallizable comonomer $C$; $T_m^o$ and $\Delta H_m^o$ are the equilibrium melting temperature and the heat of fusion, respectively, of the completely crystalline homopolymer $C$; and $R$ is the gas constant.

Taking into account the effect of the sequence length of crystallizable units that can crystallize only when their length corresponds to the crystal thickness, a modified exclusion theory as proposed by Baur is expressed by the equation

$$1/T_m = 1/T_m^o - (R/\Delta H_m^o)[\ln x_C - 2x_C(1 - x_C)] \quad (4)$$

As far as PBTTEG copolymers were concerned, according to the results of X-ray measurements,[25] the triethylene terephthalate units were completely excluded from the PBT crystals, so the above models could be applied. As commonly
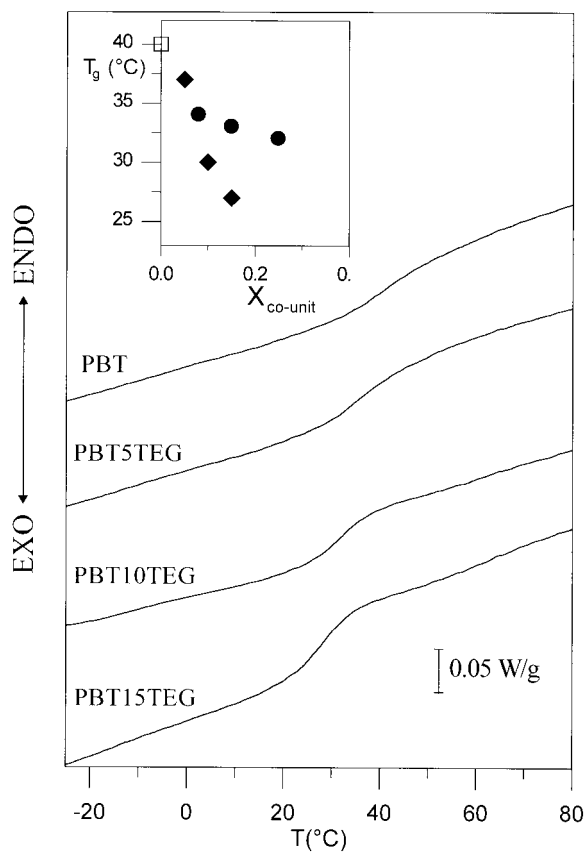


**Figure 4** Calorimetric curves of PBT and PBTTEG copolymers (20°/min heating rate) in the glass-transition ($T_g$) range of (□) PBT, (◆) PBTTEG, and (●) PBT-DEG copolymers as a function of the composition.
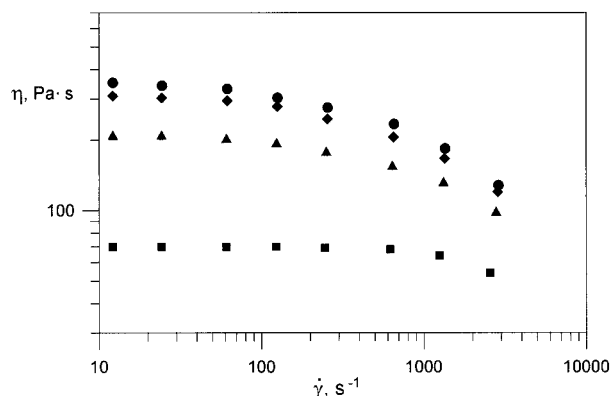
**Figure 5** The melt viscosity versus the shear rate for PBT5TEG at 240°C: $M_w =$ (■) 21,700, (▲) 30,200, (◆) 33,100, and (●) 34,200.

found for the random copolymers, the Flory equation underestimates the melting point depression; on the contrary, the Baur equation fits well with our experimental data and the $T_m^o$ and $\Delta H_m^o$ derived values (227°C and 151 J/g, respectively) were in good agreement with those previously reported.[1,26,27]

In regard to the enthalpy of fusion, note that an exact determination could not be carried out because of the broad premelting peak connected to the fusion of defective crystallites formed during the cooling step. However, an estimate after normalization for the butylene terephthalate units content led to values ranging from 47 to 49 J/g, corresponding to 32–34% of the crystallinity, assuming 145 J/g as the heat of fusion of perfectly crystalline PBT.[27] Therefore, the random incorporation of small quantities of noncrystallizable triethylene terephthalate units into the PBT backbone, even if it led to a depression of the melting temperature, slightly influenced the total crystallinity degree of PBT.

In Figure 4 the portion of the calorimetric curves concerning the glass transition of PBT and PBTTEG copolymers is reported. As shown in the inset, the $T_g$ decreased with increasing triethylene terephthalate unit content. It is well known that the influence of the chemical structure on the glass transition should be examined in the complete absence of the crystallinity, because the crystallinity, acting as physical crosslinking, raises the $T_g$ through its restrictive affect on the segmental motions of the amorphous polymer chains. Because the samples under investigation could not be quenched in a totally amorphous phase, only qualitative considerations can be dis-

cussed. Chain flexibility, chain regularity, and molecular weight are the main factors determining the $T_g$ values in a polymer. The flexibility of the chain constituents (due to the presence of $CH_2$ groups and ether oxygens) appeared to be the factor in the PBTTEG copolymers that produced the observed decrease in the $T_g$ as the content of terephthalate units was increased. As can be seen in the inset of Figure 4, the $T_g$ values of the PBTTEG copolymers were lower than those of the PBTDEG ones.[1] This behavior can be explained as being attributable to the higher content of the $CH_2$ and ether oxygen groups per TEG unit, which gave rise to more flexible polymeric chains.

## Rheological Properties

In Figures 5 and 6 typical flow curves at 240°C for samples of different compositions and molecular weights are reported in terms of $\eta$ versus $\dot{\gamma}$. From the extrapolation at $\dot{\gamma} = 0$, the Newtonian (or zero shear) viscosities $\eta_o$ were determined and the values are collected in Table II.

From these figures it appears that all copolymers were pseudo-plastic, but with a rather wide range of shear rates in which the melts were Newtonian. No effect of the copolymer composition on the pseudo-plastic behavior was evident for samples with the same $\eta_o$; in fact, the flow curves of samples of different compositions and characterized by the same Newtonian viscosity were practically identical. Similar behavior was previously found[1,28] for other copolymers of PBT.

In order to evaluate the effect of the composition on the melt viscosity, the $\eta_o$ was plotted as a function of the $M_w$ (Fig. 7). Although the data
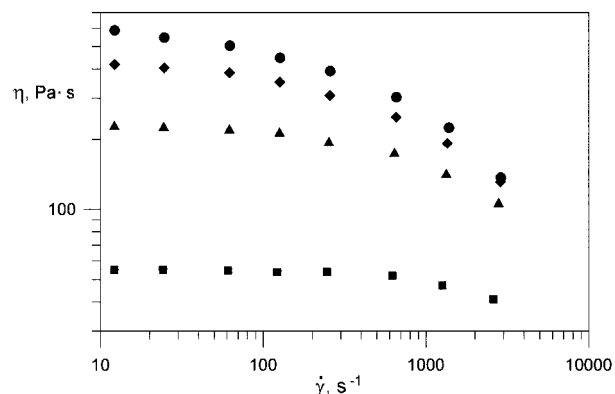


**Figure 6** The melt viscosity versus the shear rate for PBT10TEG at 240°C: $M_w$ (■) 19,900, (▲) 29,000, (◆) 35,600, and (●) 40,100.
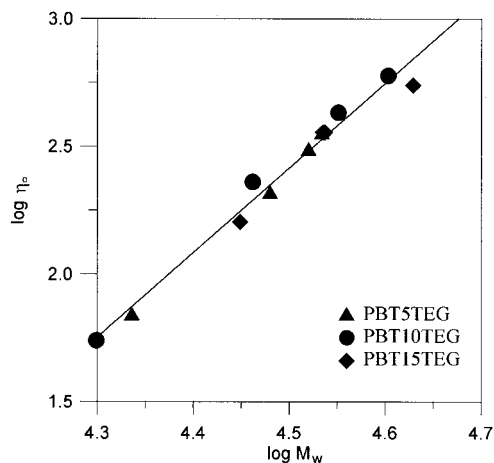
**Figure 7** The Newtonian melt viscosity ($\eta_o$) at 240°C versus the $M_w$ for (▲) PBT5TEG, (●) PBT10TEG, and (◆) PBT15TEG copolymers.

were rather scattered, the Newtonian viscosity appeared to not be significantly affected by the content of triethylene terephthalate units; the differences observed could be mainly attributed to the uncertainies in the $M_w$ values.

As is well known, for polydisperse polymers the following correlation holds[29]:

$$\eta_o = KM_w^n \tag{5}$$

with the exponent $n$ assuming the "universal" value of 3.4,[29] provided that the molecular weights are sufficiently high (i.e., greater than the critical molecular weight). Because of the low number of samples for each composition and the uncertainties in the $M_w$, it was not possible to use this equation to fit the data concerning each copolymer. Nevertheless, if a least-squares analysis of all data is performed on the basis of eq. (5), one obtains a value of $n$ of about 3.3, which is very close to the universal value of 3.4. The comparison with the data concerning the poly(butylene-co-diethylene terephthalate) statistical copolymers previously investigated[1] showed a higher melt viscosity for the PBTTEG samples. This behavior might be ascribed to stronger interchain interactions, which were originated by the two ether-oxygen atoms in each triethylene terephthalate unit.

## CONCLUSIONS

The random PBTTEG copolymers at room temperature appeared as semicrystalline materials with good thermal stability, similar to that of PBT. In the results of the calorimetric characterization the glass-transition phenomenon was detected for all samples. The $T_g$ values decreased as the content of triethylene terephthalate units increased. A comparison with the data concerning PBTDEG random copolymers showed lower $T_g$ values for PBTTEG copolyesters, which were due to the well-known flexibilization effect on the polymeric chain of the methylene and ether-oxygen groups.

Baur's equation, whose applicability was evidence of the random nature of the copolymers, proved a good correlation of the fusion temperatures to composition and permitted the calculation of the equilibrium melting temperature and the heat of fusion for the repeating unit of the completely crystalline PBT homopolymer. The results obtained were in good agreement with data reported in the literature.

The presence of triethylene terephthalate units was found to increase the Newtonian melt viscosity with respect to the PBTDEG copolymers investigated previously.

## REFERENCES

1. Lotti, N.; Finelli, L.; Fiorini, M.; Righetti, M. C.; Munari, A. Polymer, to appear.
2. Gallagher, F. G.; Hamilton, C. J.; Hansen, S. M.; Shin, H.; Tietz, R. F. WO Pat. 93/07197A1, 1993.
3. Saiki, N.; Yokomizo, H. Eur. Pat. 894618 A3, 1999.
4. Otonari, S.; Sato, Y.; Masuda, N.; Kotani, T. Eur. Pat. 300372 B1, 1994.
5. Pilati, F. In Comprehensive Polymer Science; Allen, G., Bevington, J. C., Eds.; Pergamon: Oxford, UK, 1989; Vol. 5.
6. Kosky, P. G.; McDonald, R. S.; Guggenheim, E. A. Polym Eng Sci 1985, 25, 389.
7. Banach, T. E. personal communication, 1995.
8. Siggia, S.; Hanna, J. G.; Stengle, T. R. In The Chemistry of the Hydroxyl Group; Patai, S., Ed.; Interscience Press: New York, 1971; Vol. 1.
9. Zimmermann, H. In Developments in Polymer Degradation; Grassie, N., Ed.; Applied Science: London, 1984; Vol 5.
10. Passalacqua, V.; Pilati, F.; Zamboni, V.; Manaresi, P. Polymer 1976, 17, 1044.
11. Richardson, M. J. In Comprehensive Polymer Science; Allen, G., Bevington, J. C., Eds.; Pergamon: Oxford, UK, 1989; Vol. 1.
12. Rabinowitsch, B. Z Phys Chem A 1929, 1, 145.
13. Sandhu, M. A.; Fields, R. D. J Polym Sci Polym Chem Ed 1980, 18, 1189.

14. Yamadera, R.; Murano, M. J Polym Sci A1 1967, 5, 2259.

15. Devaux, J.; Godard, P.; Mercier, J. P. J Polym Sci Polym Phys Ed 1982, 20, 1875.

16. Chen, M. S.; Chang, S. J.; Chang, R. S.; Kuo, W. F.; Tsai, H. B. J Appl Polym Sci 1990, 40, 1053.

17. Munari, A.; Manaresi, P. Chim Ind (Milan) 1984, 66, 755.

18. Cheng, S. Z. D.; Pan, R.; Wunderlich, B. Makromol Chem 1988, 189, 2443.

19. Flory, P. J. Trans Faraday Soc 1955, 51, 848.

20. Baur, H. Makromol Chem 1966, 98, 297.

21. Sanchez, I. C.; Eby, R. K. Macromolecules 1975, 8, 638.

22. Helfand, E.; Lauritzen, J. I. Macromolecules 1973, 6, 631.

23. Allegra, G.; Marchessault, R. H.; Bloembergen, S. J Polym Sci Part B 1992, 30, 809.

24. Goldbeck-Wood, G. Polymer 1992, 33, 778.

25. Finelli, L.; Lotti, N.; Righetti, M. C.; Munari, A. manuscript in preparation.

26. Righetti, M. C; Munari, A. Macromol Chem Phys 1997, 198, 363.

27. Wunderlich, B.; Cheng, S. Z. D.; Loufakis, K. In Encyclopedia of Polymer Science and Engineering; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley Interscience: New York, 1989; Vol. 16.

28. Bandiera, M.; Munari, A.; Pezzin, G. Eur Polym J 1997, 33, 497.

29. Ferry, J. D. Viscoelastic Properties of Polymers, 2nd ed.; Wiley: New York, 1970.