

Synthesis and characterization of poly(butylene terephthalate-*co*-diethylene terephthalate) copolyesters

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Abstract

Poly(butylene terephthalate-*co*-diethylene terephthalate) random copolymers of various compositions and molecular weights were synthesized in bulk and characterized in terms of chemical structure and thermal and rheological properties. All copolymers are partially crystalline and thermally stable up to about 300°C. The main effect of copolymerization is a decrease in melting and glass transition temperatures with respect to PBT homopolymer. The fusion temperatures are well correlated to composition by Baur's equation and the T_m° and ΔH_m° extrapolated values for PBT are in good agreement with those reported elsewhere. The presence of diethylene terephthalate units was found to influence slightly the rheological behaviour in the melt. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polybutylene terephthalate; Random copolymers; Diethylene terephthalate

1. Introduction

The wide diffusion of copolymers for an ever-growing number of industrial applications has given a strong impulse to the study of the correlations between the physical properties and the chemical structure of these materials. Indeed, the knowledge of the structural arrangement of the molecular units is the basis for designing synthetic processes leading to materials with properties tailored to fit specific applications. In particular, the investigation of thermal and rheological properties is fundamental to the improvement of manufacturing processes and consequently of the properties of the polymeric materials obtained.

Recently, statistical copolyesters based on terephthalic acid, alkylene and alkylene ether glycols (mainly ethylene, diethylene and triethylene glycols and 1,3- or 1,4-butanediol) have been proposed as compostable materials with good mechanical properties and processability [1,2]. Though the composition of these copolymers is rather complex, a common feature is the presence of ether linkages in the chain, which increase the hydrophilic character of the polymer, favouring its dissolution under environmental conditions.

The effect of the presence of diethylene glycol units on

the properties of poly(ethylene terephthalate) (PET) has been widely investigated [3–5], as low amounts of such units form during the polymerization of PET, depending on the reaction conditions. On the contrary, in the case of poly(butylene terephthalate) (PBT) attention has been mainly focussed on block copolymers containing polyalkylene ether glycol units [6–8], which can give rise to well-known thermoplastic elastomers.

The present paper collects the results of an investigation on the thermal and rheological properties of statistical poly(butylene terephthalate-*co*-diethylene terephthalate) copolyesters of different composition and molecular weight, synthesized in our laboratories.

2. Experimental

2.1. Products

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

2.2. Synthesis of polymers

Poly(butylene-*co*-diethylene terephthalate) copolymers (PBTDEG) were synthesized starting from DMT, BD and DEG with $Ti(OBu)_4$ (about 0.7 g/kg of DMT) as catalyst,

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Table 1
Molecular characterization data for PBTDEG copolymers

| Sample | Composition ^a | | Composition ^b | | b^c | Terminal-group concentration (meq kg ⁻¹) | | | | | M_w |
|-----------|--------------------------|-------------|--------------------------|-------------|-------|--|-------|---------------------|---------------------|----------------|--------|
| | x_{BD}^d | x_{DEG}^d | x_{BD}^d | x_{DEG}^d | | –COOH | –OH | –COOCH ₃ | –CH=CH ₂ | E ^e | |
| PBT10DEG1 | 0.90 | 0.10 | 0.92 | 0.08 | 1.11 | 88.9 | 18.0 | 5.7 | 28.3 | 140.9 | 28,200 |
| PBT10DEG2 | 0.90 | 0.10 | 0.92 | 0.08 | 1.10 | 68.8 | 16.0 | 5.8 | 14.6 | 105.2 | 37,800 |
| PBT10DEG3 | 0.90 | 0.10 | 0.92 | 0.08 | 1.10 | 21.0 | 74.5 | 3.1 | 3.0 | 101.6 | 39,100 |
| PBT10DEG4 | 0.90 | 0.10 | 0.92 | 0.08 | 1.11 | 43.0 | 39.9 | 2.3 | 5.3 | 90.5 | 44,000 |
| PBT20DEG1 | 0.80 | 0.20 | 0.85 | 0.15 | 1.16 | 20.9 | 105.0 | 6.4 | 3.5 | 135.8 | 28,900 |
| PBT20DEG2 | 0.80 | 0.20 | 0.85 | 0.15 | 1.17 | 29.8 | 66.0 | 5.4 | 7.8 | 109.0 | 36,000 |
| PBT20DEG3 | 0.80 | 0.20 | 0.85 | 0.15 | 1.16 | 48.0 | 26.0 | 4.1 | 21.5 | 99.6 | 39,500 |
| PBT30DEG1 | 0.70 | 0.30 | 0.75 | 0.25 | 1.24 | 13.1 | 162.5 | 9.9 | 0 | 185.5 | 21,300 |
| PBT30DEG2 | 0.70 | 0.30 | 0.75 | 0.25 | 1.23 | 22.0 | 107.0 | 7.8 | 8.6 | 145.4 | 27,300 |
| PBT30DEG3 | 0.70 | 0.30 | 0.75 | 0.25 | 1.22 | 25.1 | 79.4 | 3.7 | 5.0 | 113.2 | 35,100 |
| PBT30DEG4 | 0.70 | 0.30 | 0.75 | 0.25 | 1.23 | 45.4 | 46.0 | 3.3 | 12.0 | 106.7 | 37,300 |

^a Feeding.

^b By NMR analysis.

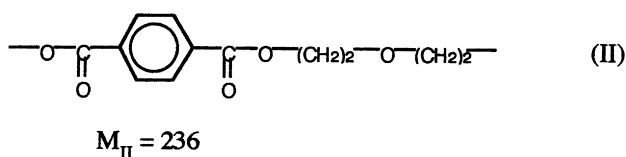
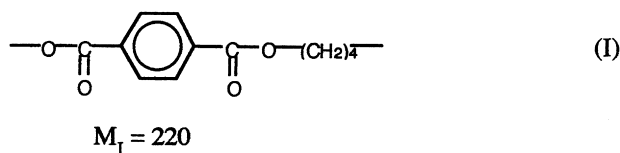
^c Degree of randomness (see text).

^d Mole fraction.

^e Total end-group content.

employing various amounts of BD and DEG (10, 20 and 30 mol% of DEG with respect to BD).

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, carried out at reduced pressure, the temperature was kept at about 250°C. 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 molecular weights. The copolymers obtained are essentially statistical, because of the use of Ti(OBu)₄ as catalyst and the high reaction temperature, which favours the redistribution reactions [9]. The comonomeric units are:



2.3. NMR spectroscopy

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

2.4. End-group analysis

Four different types of end-groups are present in PBTDEG copolymers. In fact, besides the more common hydroxyl and carboxyl terminal groups, the polymeric molecules have also methoxy (deriving from the monomer DMT) and vinyl ester end-groups (these latter arising from the degradation of PBT [10,11]).

Carboxyl end-groups. Carboxyl 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 mod. DL 25 equipped with a Mettler SC-111 combination electrode.

Hydroxyl end-groups. Hydroxyl end-groups were determined using a method derived from that reported by Kosky [12] and based on FT-IR measurements carried out on thin films. The films were prepared by pressing the sample (ca. 0.1–0.2 g) between sheets of PTFE-coated aluminium 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. Finally, these last were dried at 90°C under vacuum for 12 h prior to use. The infrared spectra of the so-obtained films were recorded with a Bruker IFS 48 FTIR spectrophotometer in the range 4000–3000 cm⁻¹ with a resolution of 2 cm⁻¹. The method requires the use of a deuterated PBT reference film to provide both 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 D₂O. After several hours, the film was dried under 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_2O in order to prevent proton exchange with H_2O and dried just before recording the IR background spectrum. The calculation of –OH end-group content was carried out as follows. The spectrum of the deuterated (reference) film was subtracted from the spectrum of each PBTDEG copolymer until the absorbance of the band at 3420 cm^{-1} (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 meq –OH/kg of polymer by the following formula [13]:

$$[\text{OH}]_{\text{meq/kg}} = -3.952 + 249.7(A_{3550}/A_{3420})$$

Vinyl ester and methoxy end-groups. The determination can be conveniently carried out using the $^1\text{H-NMR}$ technique. In fact, in the region of the spectrum from 6.0 to 5.0 ppm, the resonances belonging to the 3-buten-1-oxy ester produced by the β -scission reactions are present and the peak associated with the olefinic resonances of this end-group match the chemical shifts for di(3-buten-1-oxy)-terephthalate reported in the literature [14]. In the present work, the peaks in the region 5.1–5.2 ppm (corresponding to two protons) were used. As to the methoxy end-groups, a characteristic resonance is found as a singlet at about 3.95 ppm, which can be easily integrated to give –OCH₃ end-group content. In order to make the integration of 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 are found at 4.76 and 4.24 ppm.

The values of end-group contents, reported in Table 1, are the averages of replicates.

2.5. 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 was calibrated in temperature and energy 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 $20^\circ\text{C}/\text{min}$ (first scan), kept at this temperature for 1 min and then rapidly quenched to -80°C . Finally they were reheated from -80 to 240°C at a heating rate of $20^\circ\text{C}/\text{min}$ (second scan).

The glass transition temperature (T_g) was taken as the fictive temperature, that is the temperature defined by the intersection of the extrapolated pre-transition and post-transition enthalpy data [15]. The melting temperature T_m was taken as the peak value of the endothermic phenomenon in the DSC curve.

Repeated measurements on each sample showed excellent reproducibility.

Thermogravimetric curves were obtained in air and under nitrogen atmospheres using a Perkin–Elmer TGA7 apparatus (gas flow $50\text{ ml}/\text{min}$) at $10^\circ\text{C}/\text{min}$ heating rate up to 900°C .

2.6. Rheological measurements

The viscosities of copolymer samples in the molten state were measured at various shear rates (in the range 10 – 2500 s^{-1}) using a Rheoscope 1000 (CEAST) capillary rheometer. The instrument is basically an electrically thermostated stainless-steel barrel, in the bottom of which one of a number of interchangeable capillaries can be inserted. The polymer melt is forced through the capillary at preselected constant rates by a plunger; the force necessary to drive it at a fixed speed is measured by a compression load cell. The capillary used had a nominal inner diameter of 1.00 mm, a length-to-diameter ratio L/D of 40 and an entrance angle of 90° . Before each test, carried out in the temperature range 230 – 260° for a period of time of 15 – 20 min, the polymer samples were dried under vacuum at 90°C overnight; under these conditions the samples proved to be thermally stable. In the procedure employed to evaluate viscosity the assumptions are that there is no slip at the wall of the capillary and that the entrance effects can be neglected.

The apparent Newtonian shear rate 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 [16] to take into account the non-Newtonian behaviour of the fluid and to obtain the true shear rate at the wall:

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

(n' being defined as the slope of a log–log plot of the wall shear stress $\tau = PR/2L$ vs. $\dot{\gamma}_a$ where P is the pressure).

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

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

3. Results and discussion

At room temperature PBTDEG copolyesters appear as semicrystalline solids. They are not soluble in the most common organic solvents, showing a behaviour similar to PBT. The homopolymer and the copolymers synthesized are listed in Table 1, where some molecular characterization data are also reported. The chemical structure of all polyesters was determined by $^1\text{H-NMR}$ spectroscopy: a typical $^1\text{H-NMR}$ spectrum is shown in Fig. 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

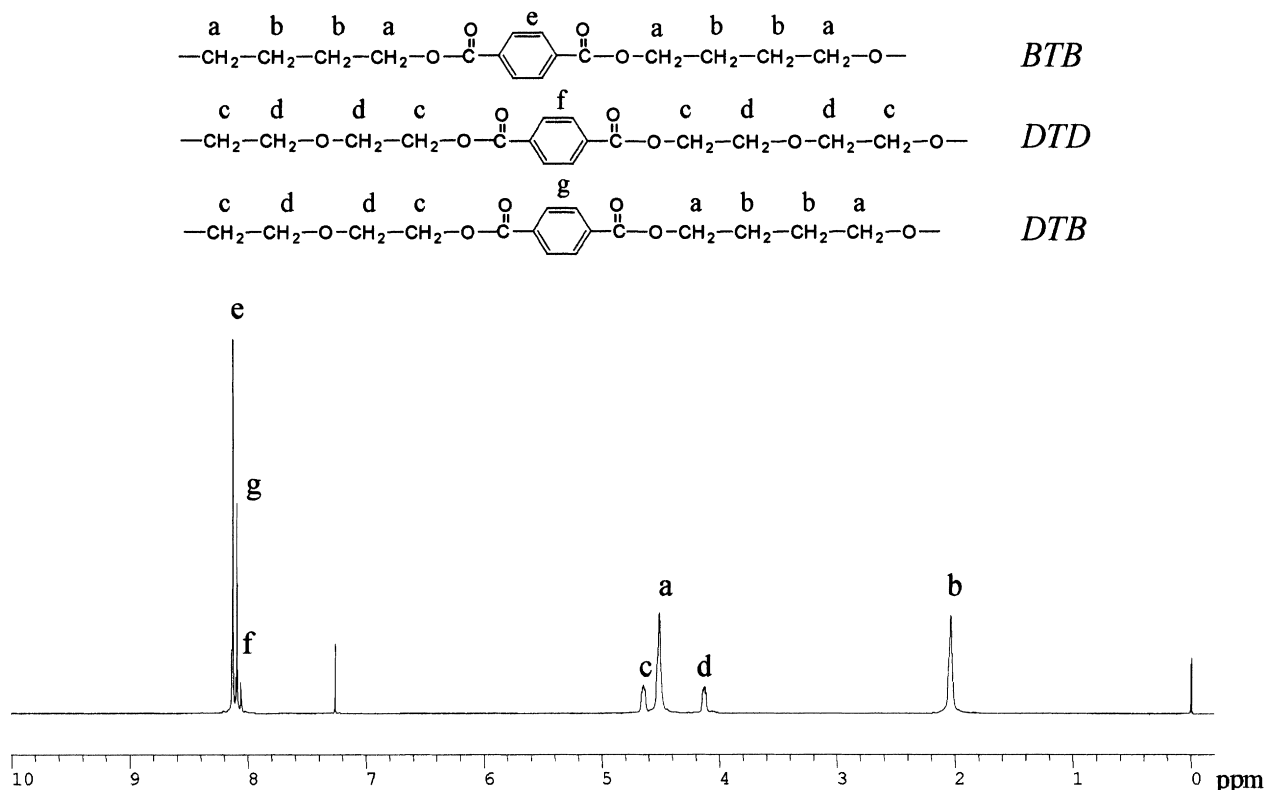


Fig. 1. ^1H NMR spectrum of PBT30DEG copolymer.

areas of the ^1H -NMR resonance peaks of the α -methylene group next to ether-oxygen at 4.14 ppm and of the β -methylene group next to carbonyl at 2.03 ppm. The data, summarized in Table 1, show that the final polymer composition is slightly different from the feeding one. This result could be ascribed to differences in reactivity of the glycols as well as in their vapour pressures [10].

It is well known that the random or alternate or block nature of copolymers is an important factor which can influence strongly their final properties. Information on the arrangement of the comonomeric units in the chain can be deduced by the degree of randomness b , which can be determined by ^1H NMR spectroscopy [17–20]. As can be seen in Fig. 1, the resonance peak of the aromatic proton of the terephthalate unit is really a triplet corresponding to *DTD*, *DTB* and *BTB* sequences resonated at 8.06, 8.09 and 8.13 ppm, respectively, where *T* is terephthalate unit, *B* is butylene unit and *D* is diethylene unit. Really, the chemical environments of aromatic protons of *T*-units in *DTB* sequence are not identical. Nevertheless, the effect on the chemical shift of these protons is certainly very slight, so that we can assume that the resonance peak occurs as a singlet. It has to be emphasized that b is equal to 1 for random copolymers, equal to 2 for alternate copolymers and is close to zero for block copolymers.

The degree of randomness is defined as [20]

$$b = P_{DB} + P_{BD}, \quad (1)$$

being:

$$P_{DB} = \frac{I_{DTB}}{I_{DTB} + I_{DTD}}, \quad P_{BD} = \frac{I_{BTD}}{I_{BTD} + I_{BTB}}$$

where P_{DB} and P_{BD} are the probability of finding a *B* unit next to a *D* unit and the probability of finding *D* unit next to a *B* unit, respectively, and I_{BTB} , I_{DTB} , I_{BTD} and I_{DTD} represent the integrated intensities of the resonance signals of *BTB*, *DTB*, *BTD* and *DTD* sequences, respectively (and of course $I_{DTB} = I_{BTD}$).

Table 1 lists the value of b obtained for all samples investigated. In all cases the degree of randomness is closed to 1, indicating the random nature of the copolyesters synthesized. These results confirm that the reaction conditions adopted (high temperature and $\text{Ti}(\text{O}i\text{Bu})_4$ as catalyst) favour a random distribution of the various sequences [9].

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 [21]:

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

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 the weight-average molecular weights of the repeating unit, x_I , x_{II} , w_I and w_{II} being the

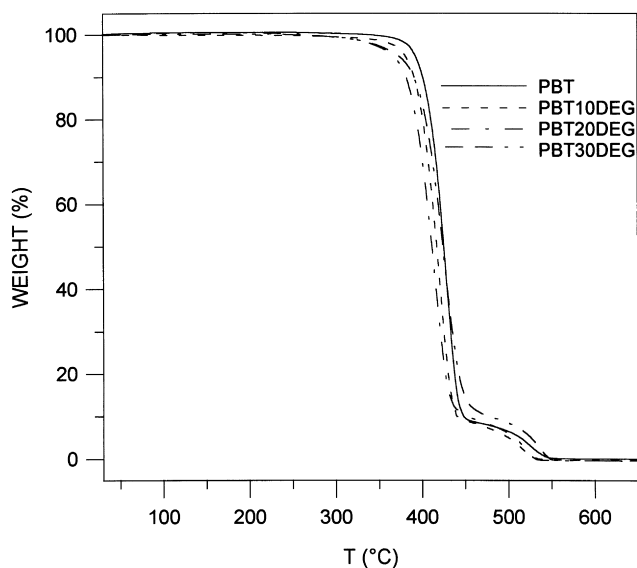


Fig. 2. TGA curves of PBT and PBTDEG copolymers in air at 10 °/min.

molar and the weight fractions of the monomeric units of the two kinds.

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

$$p = 1 - \frac{EM_{n,0}}{2} \quad (2)$$

In Table 1, the terminal-group content as well as the weight-average molecular weight are also reported for the samples under investigation, listed for each composition in order of increasing M_w .

As for the different kinds of terminal-groups in polymer molecules, they are influenced by the type of thermal degradation reaction taking place during polycondensation. The main reaction involved in the degradation process of most common polyesters of terephthalic acid is the well-known β -scission leading to the formation of $-\text{COOH}$ and $\text{CH}_2=\text{CH}-$ end-groups [11]. The fragments containing the vinyl ester end-group can undergo a further degradation reaction, forming other $-\text{COOH}$ end-groups. Moreover, if the polymerization is carried out, as we did, starting from glycols and methylesters of a carboxylic acid, $-\text{OH}$ and low amounts of $-\text{OCH}_3$ groups are also present in polymer molecules. Usually, for progressively longer reaction times, the $-\text{OH}$ and $-\text{OCH}_3$ groups content is going to decrease while that of $-\text{COOH}$ and $\text{CH}_2=\text{CH}-$ end-groups

increases. Such a trend was observed for the polymeric samples obtained in each synthesis.

3.1. Thermal properties

The copolyesters were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The investigation of the thermal stability of PBTDEG copolymers was carried out both in air and under nitrogen atmosphere. Fig. 2 shows the thermogravimetric curves in air, from which the temperature of initial decomposition (T_{id}), the temperature corresponding to the maximum weight loss rate (T_{max}) and the weight loss percentage at T_{id} , collected in Table 2, were determined. It can be seen that in all cases the weight loss takes place practically in one step. The thermal stabilities of all the polymers are quite comparable and they are practically stable up to 300 °C. For all PBTDEG copolymers the temperature at which the weight loss rate is the highest turned out to be in the range 413–420 °C, with only slight differences with respect to PBT. Similar results were obtained when the TGA measurements were carried out under nitrogen atmosphere.

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

Typical calorimetric curves of PBT and PBTDEG copolymers obtained after cooling from the melt are reported in Figs. 3 and 4, and the corresponding data collected in Table 2. An endothermic baseline shift associated with the glass transition is observed in the temperature range between 20 and 50 °C; after a broad pre-fusion, beginning at approximately 120 °C, and a small exothermic drop, the DSC curves show a melting peak whose location depends on copolymer composition.

It is well known that the thermal behaviour of a polymer is affected by its previous thermal history and that the amorphous and crystalline contents depend on the rate at which the sample has been cooled. Owing to its high crystallization rate [22] PBT cannot be frozen in a totally amorphous state with the usual cooling procedures [23]. From Fig. 3 it is apparent that the thermal treatment described in the

Table 2
Thermogravimetric (in air at 10 °/min) and calorimetric (second DSC scan, after rapid quenching from the melt) data of PBTDEG random copolymers

| Copolymer | T_{id} (°C) | T_{max} (°C) | Weight loss at T_{id} (%) | T_g (°C) | T_m (°C) | ΔH_m (J/g) |
|-----------|---------------|----------------|-----------------------------|------------|------------|--------------------|
| PBT | 392 | 418 | 1.0 | 40 | 222 | 49 |
| PBT10DEG | 395 | 417 | 1.1 | 34 | 214 | 44 |
| PBT20DEG | 388 | 413 | 0.8 | 33 | 204 | 41 |
| PBT30DEG | 398 | 420 | 0.7 | 32 | 190 | 36 |

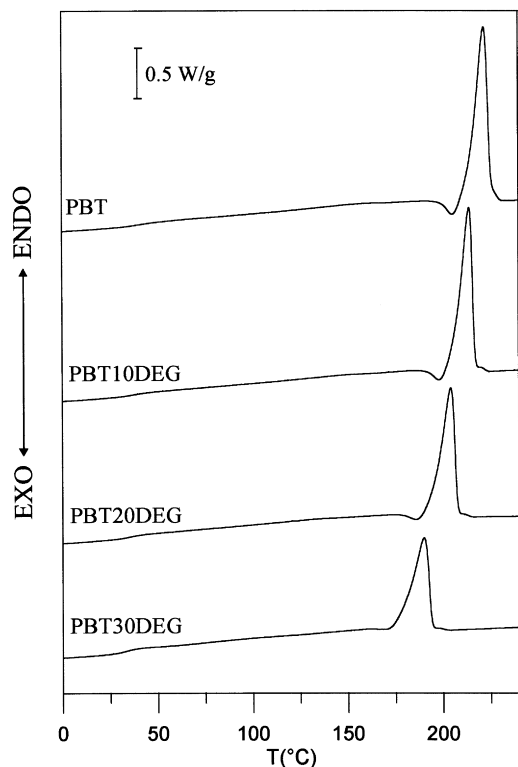


Fig. 3. Calorimetric curves of PBT and PBTDEG copolymers after cooling from the melt (heating rate = 20 °/min).

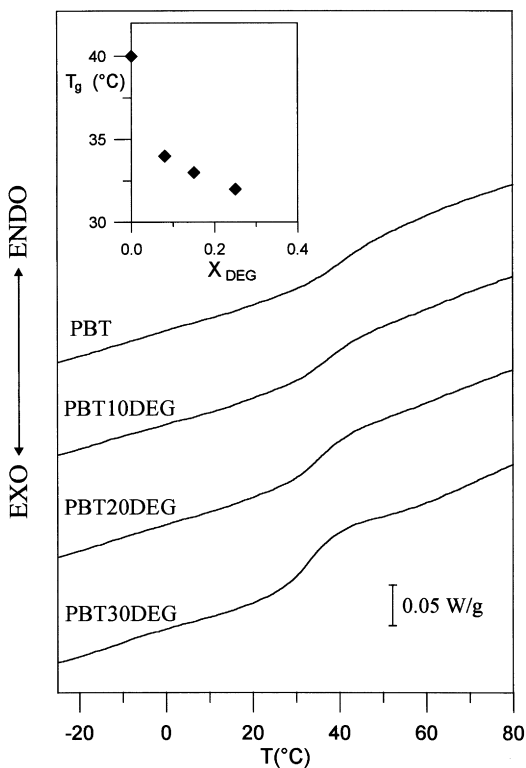


Fig. 4. Calorimetric curves of PBT and PBTDEG copolymers (heating rate = 20 °/min) in the glass transition range. In the inset: glass transition temperature as a function of diethylene terephthalate unit content.

experimental section is insufficient to prevent crystallization in PBT as well as in PBTDEG copolymers.

The calorimetric results indicate that an increase in the amount of the comonomer leads to a reduction of the melting temperature in samples subjected to the same thermal history. This behaviour is typical of random copolymers in which only one co-unit takes part in the crystallization process. As a matter of fact, X-ray measurements carried out on PBT and PBTDEG copolymers have shown that the crystal phase which develops in the copolymers is related to the lattice characteristic of butylene terephthalate units [24].

The melting point reduction can be examined in order to estimate the equilibrium melting temperature T_m° and the equilibrium heat of fusion ΔH_m° of the crystallizable unit. The Flory treatment [25], commonly used in the past and derived assuming that the fusion concerns the disappearance of long sequences of crystallizable units, underestimates the melting point depression of random copolymers. As a matter of fact, the concentration of long sequences decreases with increasing co-unit content, and the experimental T_m values are consequently lower than postulated by the theory.

On the contrary, the following equation proposed by Baur [26] takes into account the effect of sequences length:

$$\frac{1}{T_m} = \frac{1}{T_m^\circ} - \frac{R}{\Delta H_m^\circ} (\ln x_C - 2x_C(1 - x_C)) \quad (3)$$

where T_m is the melting temperature of a random copolymer with mole fraction x_C of crystallizable comonomer C, T_m° is the equilibrium melting temperature of the corresponding homopolymer and R is the gas constant.

Eq. (3) fits well the few experimental data and the T_m° and ΔH_m° derived values (230°C and 151 J/g, respectively) are in good agreement with those previously reported [22,27].

As far as the enthalpy of fusion is concerned, it has to be pointed out that an exact determination cannot be carried out due to the broad pre-melting peak, connected to the fusion of defective crystallites formed during the cooling step. However, an estimate after normalization for the butylene terephthalate units content, leads in all cases to a value of 49 J/g, which corresponds to 34% crystallinity, assuming 145 J/g as the heat of fusion of perfectly crystalline PBT [27]. Therefore, the random incorporation of small quantities of non-crystallizable diethylene terephthalate units into the PBT backbone, even if it leads to a depression of the melting temperature, does not influence the total crystallinity degree of PBT, which crystallizes in the copolymer in the same percentage as in the pure state.

In Fig. 4 the portion of the calorimetric curves concerning the glass transition of PBT and PBTDEG copolymers is reported. As also shown in the inset, the glass transition temperature decreases with increasing diethylene terephthalate unit content. It is well known that the influence of chemical structure on the glass transition should be examined in the complete absence of crystallinity, since this latter, acting as physical crosslinking, raises the T_g through its restrictive effect on the segmental motions of the amorphous

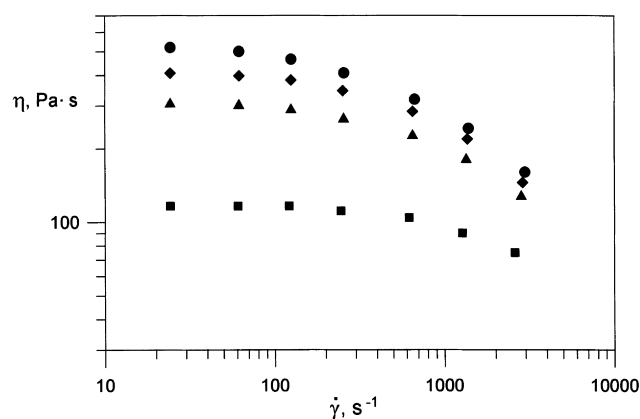


Fig. 5. Melt viscosity vs. shear rate for PBT10DEG at 240°C: (■) M_w is 28,200, (▲) M_w is 37,800, (◆) M_w is 39,100 and (●) M_w is 44,000.

polymer chains. Since the samples under investigation cannot be quenched in a totally amorphous phase, only qualitative considerations can be discussed. The glass transition phenomenon associated with the onset of long-range segmental motion, is generally considered as a measure of the polymer chain flexibility: the more flexible the chain is, the lower is the T_g . It is well known that the incorporation of flexible groups, as for example the ether-oxygen, produces a decrease in the T_g of the polymer [28]. In this connection, the reduction of the glass transition temperature for the copolymers under investigation can be explained considering the plasticization effect played by the very flexible oxygen-containing segments.

3.2. Rheological properties

In Figs. 5 and 6 typical flow curves for samples of different composition and molecular weight are reported in terms of η vs. $\dot{\gamma}$. From the extrapolation of these curves at $\dot{\gamma} = 0$, the Newtonian (or zero-shear) viscosity η_0 was determined. The values of η_0 at 240°C are collected in Table 3, along with the activation energy data, which will be discussed later.

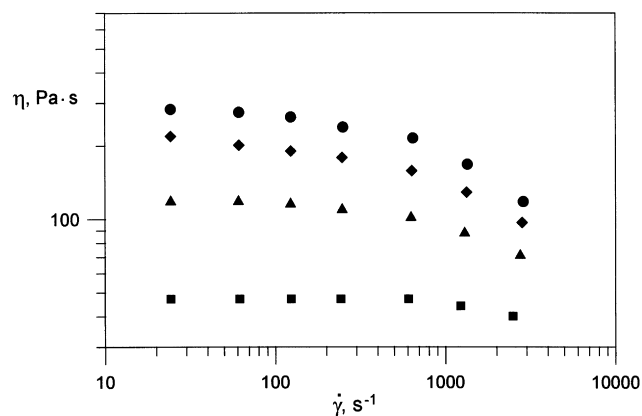


Fig. 6. Melt viscosity vs. shear rate for PBT30DEG at 240°C: (■) M_w is 21,300, (▲) M_w is 27,300, (◆) M_w is 35,100 and (●) M_w is 37,300.

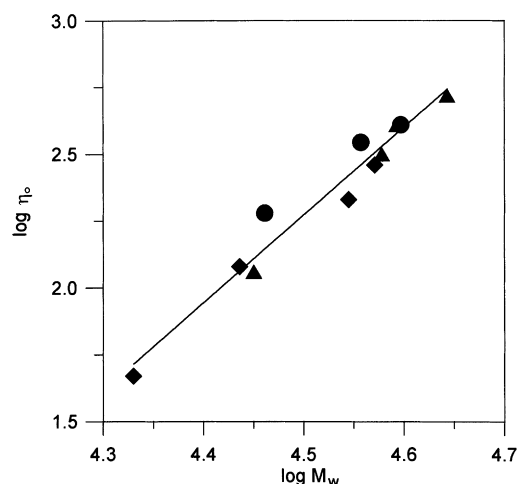


Fig. 7. Newtonian melt viscosity η_0 vs. weight-average molecular weight M_w for PBT10DEG (▲), PBT20DEG (●), PBT30DEG (◆) copolymers.

From Figs. 5 and 6 it appears that all copolymers are pseudo-plastic, but with a rather wide range of shear rates in which the melts are Newtonian, their viscosity being independent of $\dot{\gamma}$. No effect of the copolymer composition on the pseudo-plastic behaviour is evident for samples with the same η_0 , the flow curves of samples of different composition and characterized by the same Newtonian viscosity being practically identical. A similar behaviour was previously found [29] for other copolymers of PBT.

In order to evaluate the effect of composition on melt viscosity, η_0 was plotted as a function of the weight-average molecular weight M_w (see Fig. 7). Although the data are rather scattered, it appears that for a fixed value of M_w , η_0 practically is not affected by the content of diethylene terephthalate units; the differences observed can be mainly attributed to the uncertainties in M_w values.

As well known, for polydisperse polymers the correlation between Newtonian viscosity and M_w is [30]:

$$\eta_0 = KM_w^n \quad (4)$$

with the exponent n assuming the “universal” value of 3.4

Table 3
Rheological data of PBTDEG copolymers

| Sample | η_0^a (Pa s) | E_a (kcal/mol) |
|-----------|-------------------|------------------|
| PBT10DEG1 | 115 | 14 |
| PBT10DEG2 | 316 | |
| PBT10DEG3 | 404 | |
| PBT10DEG4 | 525 | |
| PBT20DEG1 | 190 | |
| PBT20DEG2 | 350 | 16 |
| PBT20DEG3 | 407 | |
| PBT30DEG1 | 47 | |
| PBT30DEG2 | 120 | |
| PBT30DEG3 | 214 | |
| PBT30DEG4 | 288 | 16 |

^a At 240°C.

[30], provided that molecular weights are sufficiently high (i.e. greater than the critical molecular weight, M_c). Due to the low number of samples for each composition and the uncertainties in M_w , it is not possible to fit by this equation the data concerning each copolymer. Nevertheless, if a least-square analysis of all data is performed on the basis of Eq. (3) one obtains a value of n of about 3.3, very close to the universal one of 3.4.

As far as the temperature dependence of viscosity is concerned, the values of η_0 were found to be well correlated to temperature by the Arrhenius-type equation:

$$\eta_0 = Ae^{E_a/RT} \quad (5)$$

where E_a is the activation energy for melt flow. From the linear plots of $\ln \eta_0$ vs. $1/T$, E_a was calculated for each copolymer and the results are collected in Table 3. It appears that the activation energy is only slightly affected by composition, increasing as the content of diethylene terephthalate units is increased. In conclusion, the presence of diethylene terephthalate units does not affect significantly the rheological behaviour of PBT in the melt state, influencing only slightly the temperature dependence of Newtonian viscosity.

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