

Synthesis and Characterization of Poly(ethylene isophthalate-co-ethylene terephthalate) Copolyesters

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ABSTRACT: Poly(ethylene isophthalate-co-ethylene terephthalate) (PEIPET) copolymers of various compositions and molecular weights were synthesized by melt polycondensation and characterized in terms of chemical structure and thermal and rheological properties. At room temperature, all copolymers were amorphous and thermally stable up to about 400°C. The main effect of copolymerization was a monotonic increase of glass transition temperature (T_g) as the content of ethylene terephthalate units increased. The

Fox equation accurately describes the T_g -composition data. The presence of ethylene terephthalate units was found to influence rheological behavior in the melt, with the Newtonian viscosity increasing as the content of ethylene terephthalate units increased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 186–193, 2004

Key words: copolymerization; thermal properties; rheology; polyesters

INTRODUCTION

It is well known that, in recent decades, copolyesters have been used in an ever-growing number of new applications. The characteristics of these materials can be tailored to fit a wide range of specific needs simply by altering the synthesis process by introducing appropriate comonomeric units into the polymeric chain, varying their relative amounts, arrangement, etc.

Among the copolymeric systems currently employed in industry, poly(ethylene isophthalate-co-terephthalate) copolyesters (PEIPET) are used in several applications, such as blow-molded water and soft drink bottles, thermally shrinkable package films and heat-sealable laminating films for steel cans and metal and ceramic sheets.^{1–6} Recent studies have reported the synthesis and the molecular and thermal characterization of PEIPET copolyesters.^{7–11} In addition, the crystallization kinetics have been investigated both under isothermal and non-isothermal conditions.^{7,12–13}

However, despite their recognized industrial importance, no data have been reported in the literature on the rheological behavior of these copolyesters. Particularly, knowledge of the rheological behavior of polymer melts under different stress field and temperature conditions, and of its dependence on copolymer structure and composition, is fundamental in the im-

provement of manufacturing processes and consequently of the properties of the polymeric materials obtained.

This article reports the results of a detailed investigation of the thermal and rheological properties of random PEIPET copolyesters of different compositions and molecular weights, synthesized in our laboratories and studied in order to obtain structure-property relationships.

EXPERIMENTAL

Materials

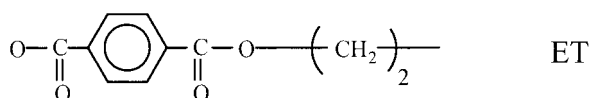
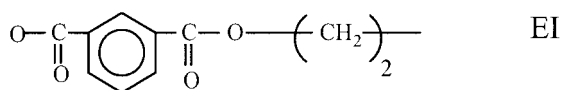
Dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), ethylene glycol (EG) and $\text{Ti}(\text{OBU})_4$ were reagent grade products (Aldrich, Milan, Italy) and were used as supplied.

Synthesis of polymers

Poly(ethylene isophthalate) (PEI) and PEIPET samples were synthesized starting from DMI, DMT and EG, in the presence of $\text{Ti}(\text{OBU})_4$ [about 0.7 g/kg of (DMT + DMI)] as a catalyst, employing various amounts of DMT and DMI in order to obtain copolymers with different compositions (from 20 to 80 mol % of terephthalate units). The syntheses were carried out in a 1.8 L stainless steel reactor according to the usual two-stage polycondensation procedure. The first stage was carried out at atmospheric pressure, adding the catalyst to the mixture of monomers preheated to 170°C.

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The temperature was gradually increased to 230°C with continuous removal of the methanol formed; when the volume of distillate reached 95% of the theoretical amount of volatiles, the second stage was started by gradually reducing the pressure to 0.5 mbar and increasing the temperature to 270°C. These conditions were reached in 20 min and maintained throughout the second stage. During each run, samples were taken from the bottom of the reactor at different times, in order to obtain polymers with the same composition but different molecular weights. The copolymers synthesized are statistical, because of the use of $\text{Ti}(\text{O}i\text{Bu})_4$ as a catalyst and the high reaction temperature, which favor the redistribution reactions.¹⁴ The comonomeric units were:



NMR spectroscopy

The molar compositions and the chain structures of PEIPET 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 an internal standard.

End-group analysis

Carboxyl End-groups

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 (0.01N, determined using a standard solution of benzoic acid). Blank runs were carried out for correction. The titrator was a Mettler DL 25 equipped with a SC-111 combination electrode.

Hydroxyl End-groups

Hydroxyl end-groups were determined using a method derived from that reported by Kosky¹⁵ and based on absorbance measurements by FTIR carried out on thin films. The films were prepared by pressing

samples (about 0.1-0.2 g) between sheets of poly(tetrafluoro ethylene (PTFE)-coated aluminium in a Carver press at 260°C for 1 min. The samples were then rapidly quenched in an acetone-ice bath, in order to obtain transparent films, which were dried at 80°C under vacuum for 12 h prior to use. The infrared spectra of the 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} . This method requires the use of a deuterated poly (ethylene terephthalate (PET) 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 PET film was prepared by heating a PET film in D_2O . After several hours, the film was dried under vacuum and then the infrared 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 reference 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 PEIPET 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 drawing a baseline from 3600 to 3475 cm^{-1} . The absorbance values were converted into milliequivalents of -OH per kilogram of polymer using the following formula:¹⁶

$$[\text{OH}]_{\text{meq/kg}} = -3.952 + 249.7 (A_{3550}/A_{3420}) \quad (1)$$

where A_{3420} was taken as a normalization factor to account for film thickness.

Vinyl ester and methoxy End-groups

In addition to -COOH and -OH end groups, vinyl ester and methoxy end groups must be considered. The latter arise from unreacted methyl ester groups of DMI and DMT, whereas the vinyl ester groups are produced from the thermal degradation reactions of PET sequences^{17,18} that may take place, especially during the last stage of polymerization where high temperatures are required. Both types of end groups can be conveniently detected by a ^1H -NMR technique. In particular, methoxy end groups give rise to a singlet at 4.00 ppm, whereas the presence of vinyl ester end groups has been associated with the appearance of the olefinic peaks around 5.10 ppm. As reported in the literature,¹⁹ the assignment of the latter has been confirmed by using di(3-buten-1-oxy)terephthalate as a model compound. Usually, because the peaks of vinyl ester and methoxy end groups have very low inten-

TABLE I
Molecular Characterization Data for PEIPET Copolymers

Sample	EI (mol %) ^a	DEG (mol %) ^a	Terminal-Group Content (mEq/kg)			E ^b	M _w
			-COOH	-OH	-COOCH ₃		
PEI1	100	1.4	17.9	127.0	16.1	161.0	24700
PEI2	100	1.6	23.0	69.6	12.6	105.2	37800
PEI3	100	1.9	25.2	33.3	23.3	81.8	48700
PEI4	100	1.9	27.5	32.9	9.3	69.7	57200
80PEI20PET1	80	1.8	33.3	116.8	11.3	161.4	24600
80PEI20PET2	80	1.6	22.9	77.5	11.8	112.2	35500
80PEI20PET3	80	2.0	32.5	49.1	6.1	87.7	45400
80PEI20PET4	80	2.2	43.4	27.3	14.6	85.3	46700
60PEI40PET1	60	2.8	26.4	185.7	7.9	220.0	18000
60PEI40PET2	60	1.9	26.6	116.0	12.1	154.7	25700
60PEI40PET3	60	2.5	23.9	48.1	21.4	93.4	42600
60PEI40PET4	60	2.6	29.9	40.7	10.1	80.7	49400
40PEI60PET1	40	2.0	20.1	124.0	7.2	151.3	26200
40PEI60PET2	40	1.7	25.8	76.3	11.9	114.0	34900
40PEI60PET3	40	1.8	29.8	57.1	6.0	92.9	42900
40PEI60PET4	40	1.8	35.6	34.0	11.1	80.7	49400
20PEI80PET1	20	1.7	13.0	155.5	21.4	189.9	20900
20PEI80PET2	20	2.0	20.3	84.1	20.7	125.1	31800
20PEI80PET3	20	1.6	29.7	53.0	10.3	93.0	42800
20PEI80PET4	20	1.4	31.7	45.6	7.4	84.7	47000

^a Measured by ¹H-NMR

^b Total end-group content

sity, in order to increase the accuracy of the test, the ¹³C-satellite peaks at 5.04 and 4.54 ppm of aliphatic protons are used as a reference for integration and the subsequent calculations.

The values of end-group contents, reported in Table I, are the averages of several repetitions.

Thermal analysis

Calorimetric measurements were carried out with a differential scanning calorimeter Perkin–Elmer DSC7. The external block temperature control was set at –60°C. The instrument was calibrated in temperature and energy with high-purity standards (indium and cyclohexane). Weighed samples (approx. 10 mg) were encapsulated in aluminium pans, heated from –30°C to 270°C at a rate of 20°C/min (first scan) and then rapidly quenched to –30°C. Then they were reheated from –30°C to 270°C at a heating rate of 20°C/min (second scan).

The *T_g* values were measured as the midpoint of the heat capacity increment Δc_p associated with the glass-to-rubber transition. Repeated measurements on each sample showed excellent reproducibility. No significant influence of molecular weight on calorimetric results was found in the range of molecular weights investigated.

Thermogravimetric curves were obtained in air and under nitrogen atmospheres using a Perkin–Elmer TGA7 apparatus (gas flow: 50 mL/min) at a 10°C/min heating rate up to 900°C.

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, into 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 in this study 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 at 230°C, 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 were that there was no slip at the wall of the capillary and that the entrance effects could be neglected.

The apparent shear rate at the wall:

$$\dot{\gamma} = 4Q / \pi R^3 \quad (2)$$

(where *Q* is the volumetric flow rate and *R* is the capillary radius) was calculated.

The viscosity was obtained as the ratio between the shear stress ($\tau = PR/2L$, where *P* is the pressure) and the shear rate at the wall:

$$\eta = \tau / \dot{\gamma} \quad (3)$$

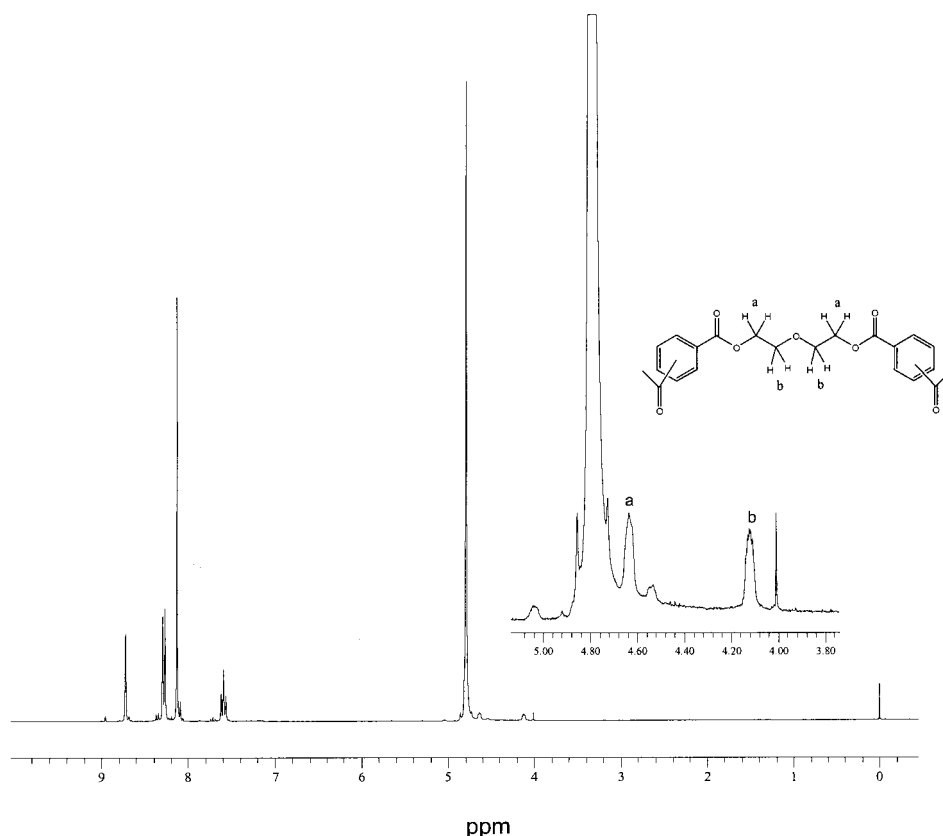


Figure 1 $^1\text{H-NMR}$ spectrum of 60PEI40PET4 copolymer. Inset shows the assignment of signals used to determine DEG unit content.

RESULTS AND DISCUSSION

All PEIPET copolyesters at room temperature appear as colorless solids and were found to be soluble (except for 20PEI80PET) in the most common organic solvents. The homopolymer PEI and the copolymers synthesized are listed in Table I, where some molecular characterization data are also reported. The copolymer composition was determined by $^1\text{H-NMR}$ spectroscopy to determine whether it was consistent with the feed composition (e.g. Fig. 1). The isophthalate/terephthalate unit ratio was calculated by comparing the area of the peak at 8.70 ppm (corresponding to one aromatic proton from an isophthalate unit) to the area of the peak at 8.13 ppm (corresponding to four aromatic protons from a terephthalate unit). In all cases the spectra were found to be consistent with the expected structure, and the copolymer composition was found to correspond to the feed composition.

As is well known, during the polymerization of PET, under certain conditions, the ethylene glycol can undergo a hydration reaction to produce diethylene glycol, which may polymerize with the terephthalate moiety. The incorporation of the ether linkage into the polymer chain by this method gives rise to a number of undesirable polymer properties, including a de-

pressed melting point. Consequently, the diethylene glycol content needed to be investigated in the PEIPET copolymers. Its amount was determined by $^1\text{H-NMR}$ analysis (e.g. Fig.1), and the results obtained are reported in Table I. For the calculation of DEG unit content, the areas of the peaks at 4.10 and 4.60 ppm (assigned to the aliphatic protons of the methylene groups in DEG) were measured and compared to the area of the main peak at 4.76 ppm due to the protons of the methylene units of ethylene glycol. As shown in Table I, PEI and PEIPET samples are characterized by comparable DEG contents; this result is not surprising when taking into account that PEI homopolymer and PEIPET copolymers were prepared under the same polycondensation conditions (temperature–time profile). As a matter of fact, it is well known that DEG formation is strongly dependent on the adopted polymerization procedure.

End-group content was determined in order to calculate the weight-average molecular weight (M_w). Assuming the most probable molecular weight distribution and neglecting the presence of cyclic molecules, the following expression was employed:²⁰

$$M_w = M_{w,0} + 2pM_{n,0}/(1 - p) \quad (4)$$

where $M_{n,0} = x_I M_I + x_{II} M_{II}$ and $M_{w,0} = w_I M_I + w_{II} M_{II}$ represent the number-average and the weight-average molecular weights of the repeating unit. The values of x_I , x_{II} , w_I and w_{II} are the molar and the weight fractions of the monomeric units I and II.

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

$$p = 1 - EM_{n,0}/2 \quad (5)$$

In Table I, the terminal group contents and the weight-average molecular weights are reported for the samples under investigation, which are listed for each composition in order of increasing M_w .

The different kinds of terminal-groups in the polymer molecules 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.¹⁸ Moreover, if the polymerization is carried out beginning with glycols and methylesters of a carboxylic acid, as in this study, $-\text{OH}$ and small amounts of $-\text{OCH}_3$ groups are also present in the polymer molecules. Nevertheless, vinyl ester end-groups were not detectable in our PEIPET copolymer samples. This finding can be accounted for by the fact that, in PET, the end-groups are predominantly of the $-\text{OH}$ type (a large excess of ethylene glycol is used in polymerization), and vinyl ester end-groups, once formed, undergo a transesterification reaction with hydroxyl end-groups, with the consequent elimination of vinyl alcohol, which can undergo a further oxidation to yield acetaldehyde.²¹

Thermal properties

The copolyesters were preliminarily examined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Investigation of the thermal stability was carried out both in air and under a

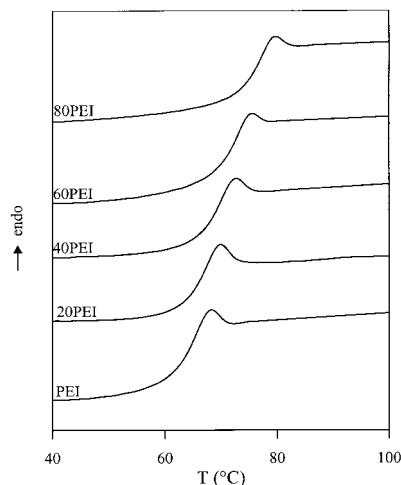


Figure 2 Calorimetric curves of PEI and PEIPET copolymers after cooling from the melt (heating rate = 20°C/min).

nitrogen atmosphere. From the thermogravimetric curves in air, the temperature of initial decomposition (T_{id}), the temperature corresponding to the maximum weight loss rate (T_{max}) and the percent weight loss at T_{id} were determined and collected in Table II. In all cases the weight loss takes place practically in one step, and the samples under investigation were found to be characterized by analogous thermal stabilities, up to 400°C. Similar results were obtained when the TGA measurements were carried out under a nitrogen atmosphere.

It has been well documented that the thermal behavior of a polymer is affected by its previous thermal history. Therefore, to erase the thermal history and provide the same heat treatment to all samples, the specimens were subjected to the thermal cycle described in the Experimental section. Calorimetric curves of PEIPET copolymers obtained after rapid cooling from the melt are shown in Figure 2, and the corresponding data are reported in Table II. In all cases, an endothermal baseline shift associated with the glass transition is observed in the temperature range between 60 and 80°C. As can be seen from Figure 2 and from the data collected in Table II, the glass transition temperature is influenced by the amount of comonomeric units in the chain. In fact, T_g values were found to increase with increasing ethylene terephthalate unit content, in agreement with the theory of group contribution additivity, which ascribes a higher contribution to the T_g of the *para*-group compared to the *meta*-substituted phenylene group.²²

The values of T_g and of the specific heat increment Δc_p associated with the glass transition are plotted in Figure 3 as a function of ethylene terephthalate unit content.

In amorphous random copolymers, T_g is usually a monotonic function of composition²³ and the most

TABLE II
Thermogravimetric and Calorimetric Data for PEIPET Random Copolymers

Copolymer	T_{id} (°C)	T_{max} (°C)	Weight Loss at T_{id} (%)	T_g (°C)	Δc_p (J/g·°C)
PEI	417	445	0.3	63.4	0.348
80PEI20PET	418	439	0.7	67.1	0.338
60PEI40PET	419	438	0.5	69.3	0.340
40PEI60PET	421	448	0.2	73.5	0.341
20PEI80PET	417	445	0.4	76.5	0.337

TGA measurements made in air at 10°/min. DSC measurements taken from second scan after rapid quenching from melt.

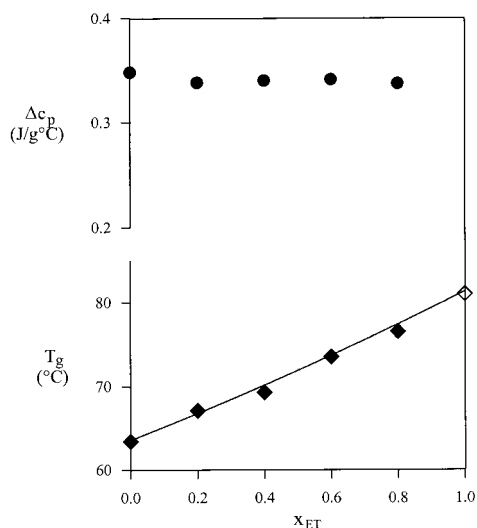


Figure 3 Composition dependence of (◆) T_g and (●) Δc_p for PEIPET random copolymers. Solid line: theoretical curve of T_g versus composition drawn based on Fox equation.

common relationship used to predict the T_g as a function of comonomer concentration is the Fox equation:²⁴

$$1/T_g = w_I/T_{gI} + w_{II}/T_{gII} \quad (6)$$

where T_{gI} and T_{gII} are the glass transition temperatures of the pure homopolymers and w_I and w_{II} are the respective weight fractions. The equation was found to accurately fit the experimental data, using the experimentally determined glass transition temperature for PEI and the value of 82°C for PET, taken from the literature.⁹ It must be emphasized that the applicability of the Fox equation is evidence of the random nature of the copolymers under investigation.

In conclusion, the thermal results appear to be in agreement with the data reported in the literature.^{7,10-11}

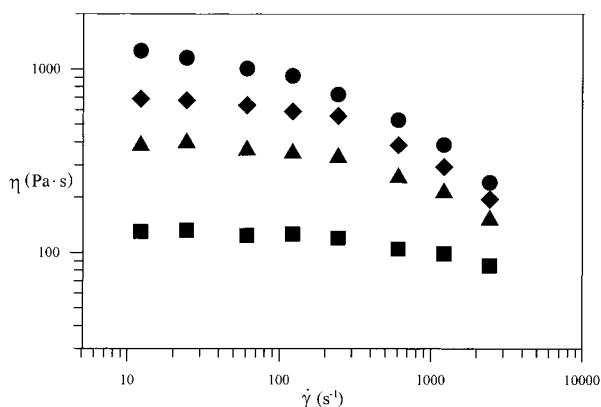


Figure 4 Melt viscosity versus shear rate for different molecular weights of 40PEI60PET at 230°C: (■) $M_w = 26200$, (▲) $M_w = 34900$, (◆) $M_w = 42900$, (●) $M_w = 49400$.

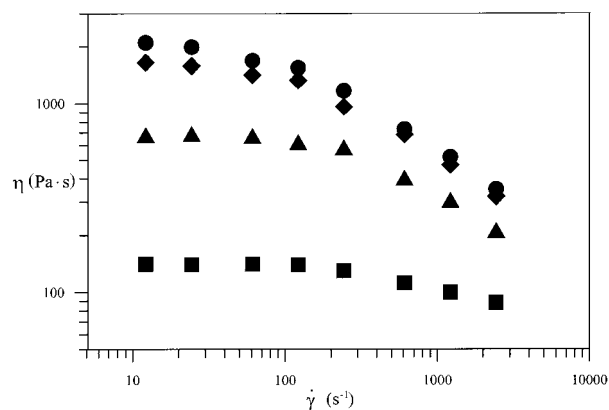


Figure 5 Melt viscosity versus shear rate for different molecular weights of 20PEI80PET at 230°C: (■) $M_w = 20900$, (▲) $M_w = 31800$, (◆) $M_w = 42800$, (●) $M_w = 47000$.

Rheological properties

In Figures 4 and 5, typical flow curves at 230°C for samples of different compositions and molecular weights are reported in terms of η versus $\dot{\gamma}$. From the extrapolation at $\dot{\gamma} = 0$, the Newtonian (or zero-shear) viscosities, η_0 , were determined, and the values are collected in Table III.

From these figures, it appears that all copolymers are pseudo-plastic, with a range of shear rates in which the melts are Newtonian. No effect of the copolymer composition on the pseudo-plastic behavior is evident; in fact, the flow curves of samples of different composition and characterized by the same Newtonian viscosity are practically identical. A simi-

TABLE III
Rheological Data for PEIPET Copolymers

Sample	η_0^a (Pa · s)
PEI1	31
PEI2	140
PEI3	350
PEI4	430
80PEI20PET1	42
80PEI20PET2	170
80PEI20PET3	370
80PEI20PET4	350
60PEI40PET1	24
60PEI40PET2	70
60PEI40PET3	390
60PEI40PET4	870
40PEI60PET1	130
40PEI60PET2	400
40PEI60PET3	680
40PEI60PET4	1200
20PEI80PET1	140
20PEI80PET2	700
20PEI80PET3	1700
20PEI80PET4	2200

^a at 230°C

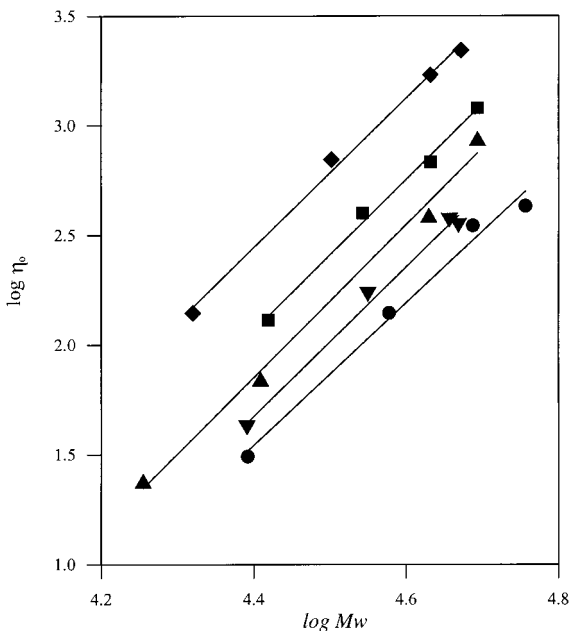


Figure 6 Newtonian melt viscosity, η_0 , versus M_w for (●) PEI, (▼) 80PEI20PET, (▲) 60PEI40PET, (■) 40PEI60PET, (◆) 20PEI80PET copolymers.

lar behavior was previously found for some copolymers of PBT.^{25–27}

In order to evaluate the effect of composition on melt viscosity, η_0 was plotted as a function of M_w (see Fig. 6). As is well known, for polydisperse polymers the following correlation holds:

$$\eta_0 = KM_w^n \quad (7)$$

with the exponent n assuming the universal value of 3.4,²⁸ provided that molecular weights are sufficiently high (i.e. greater than the critical molecular weight, M_c). If for each sample a least-square analysis of data is performed on the basis of eq. (7), a value of n ranging from 3.3 to 3.5, very close to the universal 3.4, can be obtained.

From Figure 6, it is clear that, for a fixed value of M_w , the Newtonian viscosity is significantly affected by the content of ethylene terephthalate units, increasing regularly as the content of the units increases. A similar effect was found in investigating the rheological behavior in the melt of poly(butylene isophthalate-co-butylene terephthalate) copolymers.²⁵

In order to explain the observed trend, it must be noted that the difference between the test temperature and the glass transition temperature is a factor affecting the rheological behavior of a polymer.

Even though it is well known that an increase of the glass-transition temperature usually gives rise to an increase in the Newtonian melt-viscosity of a polymer,²⁹ until now the problem has not been completely clarified from a theoretical point of view. This fact

derives from the difficulty of describing the temperature dependence of η_0 using simple equations in the entire temperature range starting from T_g . The well-known William-Landel-Ferry (WLF) equation, expressed in terms of T_g is as follows:²⁸

$$\ln \frac{\eta_0}{\eta_{0,g}} = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \quad (8)$$

C_1 and C_2 are universal constants, which can be applied in the range from T_g to $T_g + 100^\circ\text{C}$. On the other hand, for T values greater than $T_g + 200^\circ\text{C}$, the linearity of the plot of $\ln \eta_0$ versus $1/T$ suggests the presence of an activated phenomenon, and therefore the validity of an Arrhenius-type equation.³⁰

When the temperature lies between these two regions, as is the case of PEIPET copolymers tested at 230°C (under these conditions the temperature ranges from about $T_g + 154$ to $T_g + 167^\circ\text{C}$), the situation is more complex; Berry and Fox suggested the use of the following relationship, obtained on the basis of the Doolittle theory:^{30–31}

$$\ln \eta_0 = A + \frac{B}{f_g + \alpha_g(T - T_g)} \quad (9)$$

where A and B are constants dependent on molecular weight, f_g is the fractional free volume at T_g , and α_g is the expansion coefficient of the fractional free volume. This equation has been reported to hold from T_g to $T_g + 200^\circ\text{C}$.

Because the values of all of the parameters appearing in eqs. (8) and (9) can hardly be obtained or calculated precisely for all PEIPET copolymers, and because the two homopolymers are very similar in chemical structure, as a first approximation the parameters could be considered to be independent of composition. Under these assumptions, on the basis of eq. (8) or (9), it appears to be clear that, for a fixed value of T , the higher the T_g of the copolymer, the higher the η_0 , as was experimentally observed for the PEIPET copolymers investigated.

CONCLUSIONS

Thermal and rheological characterization data of PEI-PET random copolyesters led to the conclusion that these materials have good thermal stability and that their glass-transition temperatures are influenced by their composition, increasing as the content of ET units increases. This result agrees with the calculations carried out using the group contribution method. The higher T_g of the copolymers rich in ET units is reflected in higher Newtonian viscosity, as predicted by theory.

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