Synthesis and Characterization of a Poly(ether–ester) Copolymer from Poly(2,6 dimethyl-1,4-phenylene oxide) and Poly(ethylene terephthalate)

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ABSTRACT: A series of poly(ether–ester) copolymers were synthesized from poly(2,6 dimethyl-1,4-phenylene oxide) (PPO) and poly(ethylene terephthalate) (PET). The synthesis was carried out by two-step solution polymerization process. PET oligomers were synthesized via glycolysis and subsequently used in the copolymerization reaction. FTIR spectroscopy analysis shows the coexistence of spectral contributions of PPO and PET on the spectra of their ether–ester copolymers. The composition of the poly(ether–ester)s was calculated via ^{1}H NMR spectroscopy. A single glass transition temperature was detected for all synthesized poly-(ether–ester)s. T_g behavior as a function of poly(ether–ester) composition is well represented by the Gordon-Taylor equation. The molar masses of the copolymers synthesized were calculated by viscosimetry. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2124–2131, 2006

Key words: poly(2,6 dimethyl-1,4-phenylene oxide); poly-(ethylene terephthalate); polyethers; polyesters; copolymerization

INTRODUCTION

Thermoplastic elastomers (TPEs) are polymers that act as chemically crosslinked elastomers at ambient temperature, but they flow like conventional thermoplastics at elevated temperatures.[1] Segmented copolymers are characterized for their random structure in which soft and hard segments are intercalated in the chain backbone.[2–5] Soft segments are flexible and they possess a relatively low glass transition temperature (so, it is assumed that it induces a reversible elastic behavior), whereas the hard segments can be glassy amorphous or semicrystalline and acts as "physical crosslinks" (improving mechanical properties).[2,6] In many segmented copolymers, the hard segment is a polyester (TPE-E), polyurethane (TPE-U), or polyamide (TPE-A), while the soft segment is a polyether or also polyester.[7]

Poly(ether–ester)s and poly(ester–ester)s are two types of segmented copolymers with a wide range of applications.[8] Some of these copolymers show a single glass transition temperature (T_g) that is intermediate between the T_gs of the pure components.[3] For these materials, the evolution of the copolymer T_g with respect to hard or soft segment composition has been successfully described by mixing rules used for compatible copolymers[9] (as Gordon-Taylor equation).[10] This is not a rule, and there are some segmented copolymers (i.e., poly(ethylene oxide)–poly(tetramethylene terephthalate)) that show two glass transition temperatures.[11,12]

Segmented copolymers had been synthesized by one- or two-step solution polymerization processes.[8] Synthetic routes to segmented copolyesters take advantage of the reactivity among suitable functional chemical groups present in the parent polymers. In that regard, yields of poly(ether–ester)-segmented copolymers are better if precursors with hydroxyl endgroups modified by highly reactive diisocyanate compounds are used.[13,14]

Poly(2,6 dimethyl-1,4-phenylene oxide) (PPO) is a rigid polyether with high heat resistance and good dimensional stability.[15] PPO's special properties have been advantageously used in the production of many polymer blend formulations.[16,17] The synthesis and properties of segmented copolymers containing PPO in the polymeric backbone have been poorly explored.

TABLE I
Molar Feed Composition of the Prepolymers

Prepolymer type	PPO (mmol)	TDI (mmol)	OCN (mmol) ending groups in TDI
Prepolymer 1	0.1	0.6	1.2
Prepolymer 2	0.1	1.2	2.4

Poly(ethylene terephthalate) (PET) is an important polyester mainly used in the manufacture of soft drink bottles. PET has high strength and stiffness, slip and wear properties, good electrical properties, and high chemical resistance.[18] This engineering thermoplastic has been successfully used in the synthesis of segmented poly(ester–ester) copolymers.[14]

In this work, we report the synthesis of a series of poly(ether–ester) copolymers containing segments of 2,6 dimethyl-1,4-phenylene oxide (PO) and ethylene terephthalate (ET). FTIR spectroscopy was used to chemically characterize the copolymers, and thermal analysis was used to elucidate T_g behavior. Copolymer composition was calculated by ^{1}H NMR. The molar masses of the copolymers, which decrease, as the feed monomer composition is richer in PET oligomers, were evaluated by viscosimetry.

EXPERIMENTAL

Materials

PPO (M_v = 44,350 g/mol derived from viscosimetry measurements in chloroform at 25°C using the corresponding Mark-Houwink equation) and 2,4-toluene diisocyanate (TDI) (80 : 20 w/w mixture of 2,4-and 2,6-isomers) were obtained from Aldrich and PET bottle waste flakes (Glezco Plastic; bottle grade material) were used as received. The molar mass of PET (M_v = 37,000 g/mol) was also determined by viscosimetry, with dichloroacetic acid as solvent at 45°C. Dichloroacetic acid (Alfa Aesar 99%), diethylene glycol (DEG) (Lancaster 99%), acetic anhydride 99%, pyridine 99.9%, benzene 99.9%, toluene 99%, and ethanol 99.9% were purchased from Fermont and used as received. Reactive grade phenolphthalein indicator (SeaLab) and 0.5N KOH (SeaLab) standards were used in all volumetric determinations.

Synthesis

PET depolymerization process

Low-molecular weight PET was obtained by glycolysis. Glycolysis reaction was carried out at 220°C for 4 h. Five hundred grams equivalent to 2.60 mol repeating unit (molar mass 192 g/mol) of PET waste flakes were added to 300 g DEG (molar mass 106 g/mol) such that the molar ratio of PET repeating unit

to DEG was 1 : 1.08. This mixture was charged into a steel reactor with nitrogen atmosphere, reflux condenser, stirrer, and thermometer. After the depolymerization process, the product was washed with cold water to eliminate DEG excess. PET oligomers were then titrated to determine the hydroxyl number (n_{OH}) that indicates the extent of depolymerization, according to ASTM D2849 Method A.[19]

Preparation of PO-ET segmented copolymers

The copolymers were prepared by solution polymerization. In the first step, a "prepolymer" was prepared from the end-capping reaction between PPO and TDI for 2 h. In the second step, the prepolymer reacts with PET oligomers also for 2 h. An excess of TDI was used in the first step to achieve a complete end-capping reaction. PPO : TDI ratios of 1 : 6 and 1 : 12 were used. The products were named here as prepolymer 1 and prepolymer 2, respectively. Four different molar ratios of terminal OCN groups from prepolymers to OH groups from PET oligomers were used to obtain the copolymers. Table I lists the molar formulation of each prepolymer, while the PO-ETs molar feed compositions are shown in Table II.

An example of a typical synthesis of a PO-ET copolymer is now described. In the first reaction, 4.65 g (0.1 mmol) of PPO is dissolved in 40 mL of chloroform. This solution is charged into a reactor cooled at ~4°C under nitrogen atmosphere. A solution of 0.1044 g (0.6 mmol) of TDI in 20 mL of chloroform was added dropwise to the reactor. As prepolymers are unstable, reaction product (the prepolymer 1) was added to the depolymerized PET immediately without further purification. In the second reaction, 4.7544 g of prepolymer 1 (~0.6 mmol of isocyanate ending groups) was added to 0.526 g of depolymerized PET (n_{OH} = 128, corresponding to ~1.2 mmol of —OH ending groups) that was previously dissolved in 40 mL of chloroform. The resultant solution is charged into a glass reactor provided with a water bath, and the reaction was carried out at 60°C. Once the reaction has been completed, solvent was evaporated. Final polymer was

TABLE II
Molar Formulations Used to Obtain a Series of PO-ET Copolymers

Precursor precopolymer	PO-ET copolymer	OCN (mmol) ending groups in prepolymer	OH (mmol) ending groups in PET oligomers
Prepolymer 1	PO-ET 1	0.6	1.2
Prepolymer 2	PO-ET 2	1.2	2.4
	PO-ET 3	1.2	3.6
Prepolymer 1	PO-ET 4	0.6	3.6

recrystallized from chloroform/methanol and dried in an oven with air reflux for 24 h at 60°C. Yield was calculated from the final weight of the dried polymer. A similar procedure was followed to synthesize the other copolymers using different initial feed molar ratios. Prepolymer yields were calculated after recrystallization with chloroform–methanol.

Measurements

Fourier transform infrared (FTIR) spectroscopy

Prepolymers and PO-ET samples were analyzed by FTIR spectroscopy in a Spectrum One Perkin–Elmer spectrophotometer. IR spectra were recorded from films obtained from chloroform solutions (whose concentration was 0.02 g/mL) over NaCl pellets. Reported IR spectra were the average of a minimum of 60 scans and with a resolution of 4 cm^{-1}.

Nuclear magnetic resonance (NMR) spectroscopy

Compositions of PO-ET copolymers were determined using a Varian Unity *Plus* 300 NMR spectrometer at room temperature. ^{1}H and ^{13}C spectra were obtained from samples dissolved in CDCl$_3$. PET/PPO molar ratios were calculated from the total area for the aromatic region of PET (7.94–8.12 ppm) and the area for the aromatic protons of PPO at 6.45 ppm.

Differential scanning calorimetry (DSC)

Analysis by DSC was performed on a Mettler Toledo 822e calorimeter. A previous calibration was run with indium. Samples of PO-ETs were heated at a rate of 20°C/min from 30 to 250°C and the second scan was reported. The temperature at the midpoint of the heat capacity change is defined as the glass transition temperature (T_g). All the experiments were run under argon atmosphere, using a flow rate of 50 mL/ min.

Viscosimetry

The molar masses of the PO-ETs copolymers were calculated from viscometric measurements. Molar masses of copolymers were derived using the Mark-Houwink parameters for PPO ($K = 48.3 \times 10^{-3}$ mL/g, $a = 0.64$) at 25°C with chloroform as solvent.[20]

Gel permeation chromatography (GPC)

GPC was used to calculate the molar mass of the PET oligomers with a Waters 1525 Chromatographer at 40°C previously calibrated with polystyrene standards. A dilute solution (10 mg/10 mL) was prepared in tetrahydrofuran (THF) and stirred for 1 h. Solutions were filtered through a 0.45 mm filter (GHP, Acrodis Gelman).

RESULTS AND DISCUSSION

The thermal behavior of PPO is well known. This amorphous polymer has its glass temperature at high temperature. We detected the T_g of PPO at 212°C. PET is a semicrystalline polymer that shows the classical thermal behavior of this type of polymers. In the calorimetric curve of PET (not shown here), three events were observed: (i) the glass transition temperature of the PET (74°C) detected by a jump in the line base, (ii) the exothermic peak of PET crystallization ($T_c = 152$°C and $\Delta H_c = 15.8$ J/g), and (iii) at higher temperature an endothermic melting peak ($T_m = 244$°C and $\Delta H_m = -40.9$ J/g). After the glycolysis process, strong changes are produced in the chemical structure of PET. Now, only one jump detected at lower temperatures indicates the range of temperature where PET oligomers have their glass transition. For PET oligomers prepared after glycolisis process, the T_g is -24°C. The strong decrease in the glass transition temperature is due to the low molar mass of PET oligomers ($M_w = 1143$ g/mol and P. I. = 1.20 measured by GPC).

Figure 1(A) depicts the FTIR spectrum of the prepolymer 2. To facilitate the comparison of the spectral contributions in this spectrum, the maximum intensity of the more intense peak was normalized to unity. Similar treatment was realized for all spectra shown in this work. In Figure 1(A), it is evident that the spectral contributions originated by vibrations of the characteristic chemical groups of PPO dominate the appearance of the spectrum. So, the asymmetric stretching vibration of the ether (C—O) group appears at 1189 cm^{-1}, while the symmetric stretching (a less intense peak) produces the peak at 1021 cm^{-1}.[21] Other band caused by stretching of C—O group appears at 1306 cm^{-1}, although vibrations of bending type of O—H group (included in the structure) also could contribute to originate this band, because vibrations of both groups have been reported in the same range of wavenumber.[21] At 1472 cm^{-1}, a peak appears due to bending vibrations of the C—H bond included in methyl groups of the PPO.[22] A band appears at 1604 cm^{-1} induced from C=C bond stretching of the PPO aromatic groups. C—H bond vibrations produce several peaks that appear at higher frequencies. At 2954, 2921, and 2860 cm^{-1}, three peaks due to asymmetric and symmetric stretching vibrations of the C—H methyl groups are well resolved. There are few peaks attributed to isocyanate functionality in the spectrum. At 2264 cm^{-1}, a peak due to asymmetric stretching vibrations of isocyanate (N=C=O) groups is detected. This peak indicates the presence of N=C=O "free" groups in prepolymer 2. As each molecule of TDI has two

(A)

(B)

(C)

Figure 1 FTIR spectrum of (A) prepolymer 2, (B) PO-ET 1, and (C) PO-ET 3.
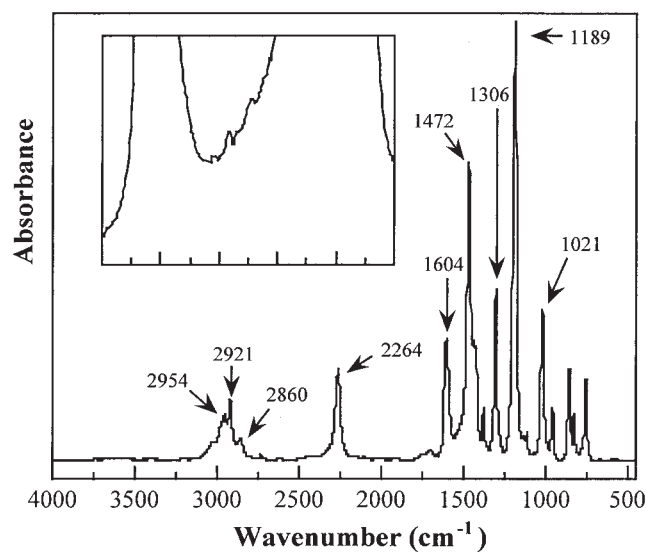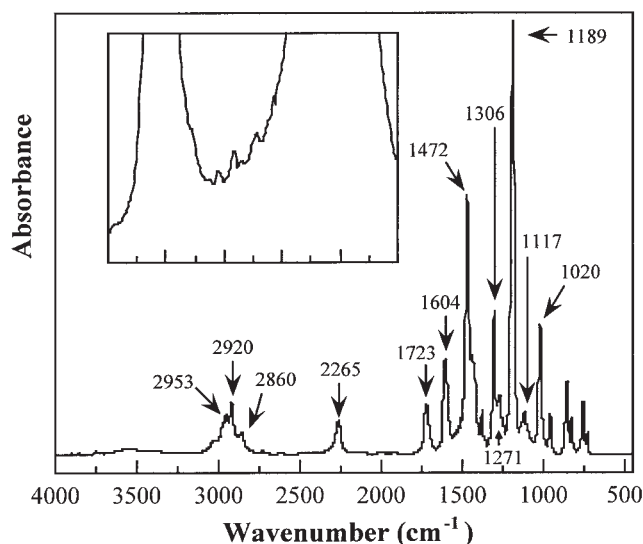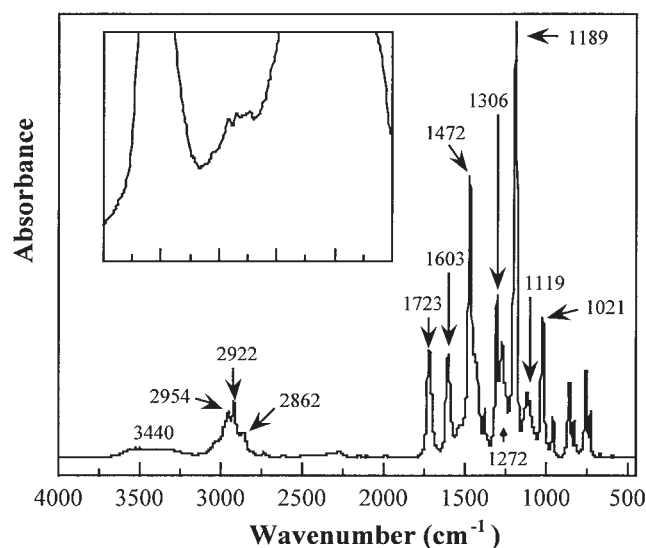
isocyanate groups, based on the stoichiometric ratio used, it is expected that contributions to this peak comes from the groups that has not coupled with terminal OH groups of PPO, as the isocyanate groups reacts with OH groups from PPO forming urethane groups (RO—CO—NHR'). Bands due to bending vibrations of the N—H bond in urethane groups have been reported in the range of 1560–1535 cm^{-1}.[14,21] However, the peak pattern observed in this region is dominated by the contribution of the bending vibrations of the methyl groups of PPO at 1472 cm^{-1}. Nevertheless, expansion of region comprised between 1400 and 1650 cm^{-1} [see inset in the Fig. 1(A)] shows small peaks that can be attributed to the formed urethane chemical groups.

The IR spectrum of the prepolymer 1 (not shown here) shows a peak pattern similar to that observed for prepolymer 2.

Figure 1(B) shows the IR spectrum of PO-ET 1. The main peaks associated with PPO are yet the most intense of the spectrum; it is also evident that the presence of three new spectral contributions are not present in the spectrum of the prepolymer 1 (precursor of PO-ET 1): (i) at 1723 cm^{-1}, a weak peak appears due to stretching vibrations of carbonyl group; this group is a part of PET repeating unit and also is present in the urethane groups, (ii) at 1271 cm^{-1}, other weak peak is detected, which is resolved as a shoulder of the band at 1306 cm^{-1} (characteristic of PPO); this peak is due to asymmetric stretching vibrations of the C—O—C group included in the ester (R—CO—OR') functionality, and (iii) at 1117 cm^{-1}, a low intensity peak originated from symmetric stretching vibrations in ester group.[21] Coexistence of spectral contributions of PPO and PET evidence the formation of copolymer through a chemical reaction between both PET oligomers and the prepolymer 1 end-groups. Observation of signals at 2265 cm^{-1} in the final product indicates the existence of "free" isocyanate groups, which remain unreacted probably due to steric reasons. In the inset of Figure 1(B), peaks for urethane groups formed through coupling reactions are seen. So, at 1541 cm^{-1}, a weak band due to bending vibrations of the N—H bond of urethane groups is present. This band is more intense than the urethane band detected in the spectrum of the precursor (prepolymer 1), and confirms the formation of new urethane groups in the second step of the synthesis. In the final polymer, hydroxyl end-groups from PET and "free" isocyanate groups from prepolymer 1 are present.

Figure 1(C) shows the FTIR spectrum of PO-ET 3. This spectrum confirms, as expected, that an increase

in the quantity of PET oligomers on feed composition lead to a lower amount of unreacted isocyanate groups. In contrast to Figure 1(B), Figure 1(C) shows that the band originated by isocyanate "free" groups practically disappears. This result indicates that the majority of "free" isocyanate groups react and therefore more PET oligomers add to precursor (prepolymer 2). In fact, the inset of Figure 1(C) shows that the band at 1534 cm^{-1} due to the urethane groups, resolved as a shoulder of the band at 1472 cm^{-1}, is more intense than the urethane band observed in the spectrum of the prepolymer 2 depicted in the Figure 1(A). Although the spectral contributions of PPO are the most important, it is evident that the three peaks from PET (at 1723, 1272, and 1119 cm^{-1}) described before for the spectrum of PO-ET 1 [see Fig. 1(B)] increase in intensity. This behavior suggests that more chemical groups from PET have been incorporated in PO-ET 3. Also, a broad weak band centered at 3440 cm^{-1} [that appears very weak in the Fig. 1(B)] is present. This band is produced by (i) stretching vibration of the N—H bond of the urethane groups[23] and (ii) stretching vibration of PET hydroxyl end-groups.[21] Hydroxyl groups can also be involved in hydrogen-bonding interactions.[24]

The yield of the first and the second steps of the PO-ETs synthesis was calculated following the procedure described in Experimental Section. So, for the prepolymer 1, the yield was 99%, while for prepolymer 2, it was close to 100%. These results indicate that the "end capping" reactions (first step of the synthesis) were complete. Therefore the structure of the prepolymers is NCO—PPO—NCO. On the other hand, yields for the copolymers were 89% for PO-ET1, 82% for PO-ET2, 74% for PO-ET3, and 73% for PO-ET4. This behavior indicates that an augment in the feed composition of PET oligomers decrease the yielding of the second step. This result suggests that stereochemical hindrance limits the addition of PET oligomers to isocyanate groups during the final stages of copolymerization.

Figure 2(A) shows the ^{1}H NMR spectra for a PET/PPO blend (50 : 50 (w/w)) and the PO-ET 3 (whose final composition is 14.8% of PET and 85.2% of PPO). Spectral peak patterns for both samples are alike. Assignments were made by comparison to the spectra of the homopolymers. As expected, spectra for blend and copolymer appear mostly as a composite of the two polymeric components.[2,25] Small bands in the region 6.7–7.35 ppm due to aromatic protons of TDI are
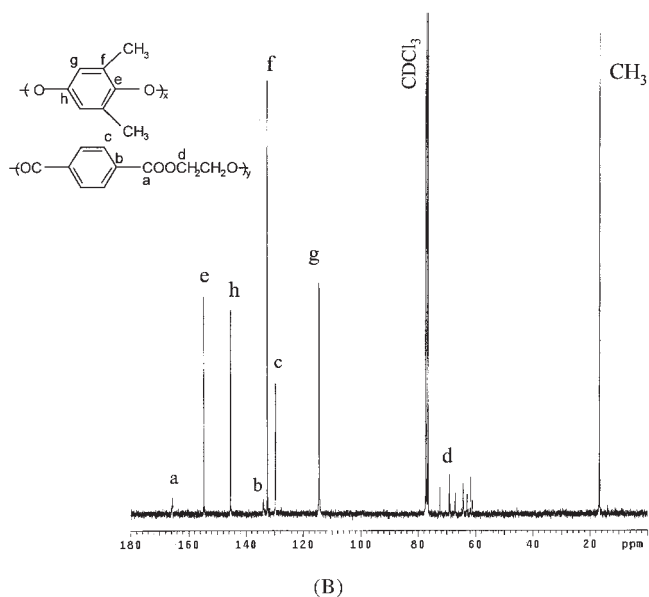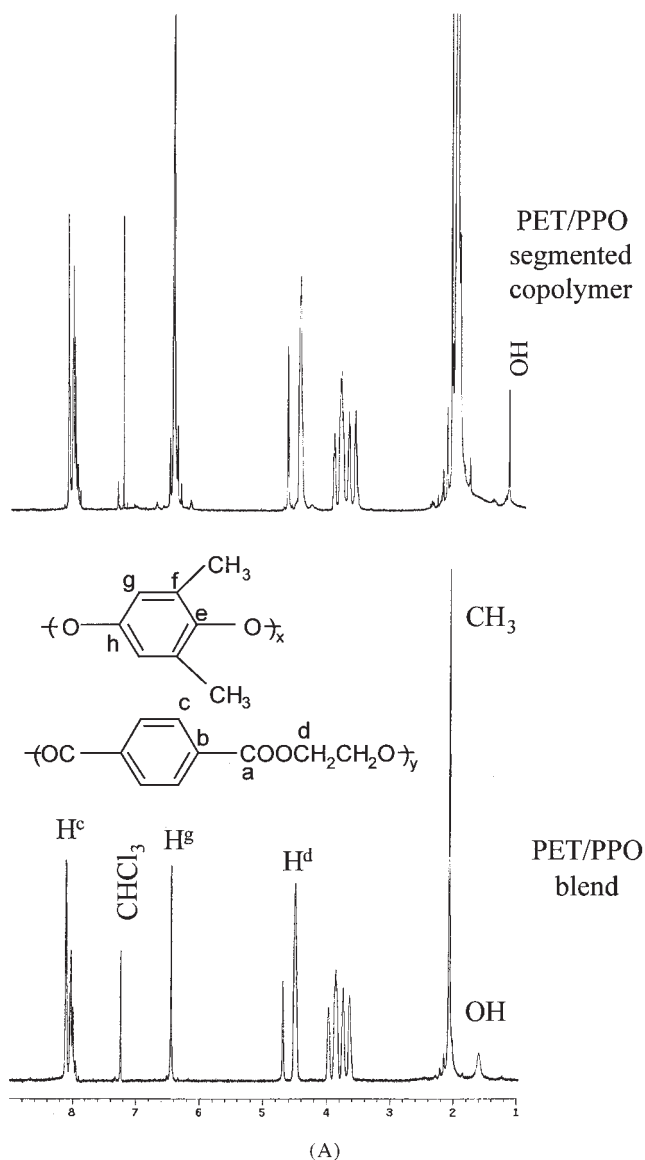

Figure 2 (A) ^{1}H NMR spectra of a PET/PEG blend (50:50, bottom) and the PO-ET 3 (14.8 : 85.2, top) in CDCl$_3$. Spectrum for copolymer has been expanded to show the signals due to PET component. (B) ^{13}C NMR spectrum of the PO-ET 3 copolymer in CDCl$_3$.

TABLE III
Compositions Obtained by ¹NMR of the PO-ET Segmented Copolymers Obtained

Sample	Composition (mol %)	
	2,6 Dimethyl-1,4-phenylene oxide	Ethylene terephthalate
PO-ET 1	95.0	5.0
PO-ET 2	90.0	10.0
PO-ET 3	85.2	14.8
PO-ET 4	84.0	16.0

present in the copolymer spectrum. These bands undergone a significant shift toward lower fields in comparison to those observed for TDI, as a consequence of the conversion of isocyanate groups into urethane groups. As in the case of poly(ethylene terephthalate)–poly(ethylene glycol) copolymer studied before by our group, transesterification reactions are not important during the preparation of the PO-ET copolymers, as aromatic and aliphatic signals do not show important modifications.[26]

Spectral peak pattern observed in the ^{13}C NMR spectra of segmented copolymers is also a composite of the two polymeric components spectra. To establish carbon multiplicities, one-dimensional spectrum was compared with attached proton test (APT) spectrum (not shown here). Partial assignments of the ^{13}C NMR for PO-ET 3 are shown in Figure 2(B). Brandolini and Hills have reported spectrum for PPO in a recent compilation of polymer spectra.[27] Note that assignments for carbons f and g are reversed in this reference.

The Table III lists the composition for all PO-ET synthesized. As the PET oligomers concentration in feed composition increases, more PET is incorporated into copolymer. Obtained PE-ETs copolymers contain a higher amount of PPO, and so these units must have a stronger influence in the final properties (such as molecular masses) of these polymers.

The molar mass of PO-ETs copolymers was calculated by viscosimetry. Viscosity molar mass (M_v) of copolymers were as follows: M_v = 53,750 g/mol for PO-ET1, M_v = 58,050 g/mol for PO-ET2, M_v = 54,900 g/mol for PO-ET3, and M_v = 51,250 g/mol for PO-ET4. As the main component of the copolymers is the PPO, we use the Mark-Houwink constants for the PPO to make the viscosimetric determination. So, the molar mass reported for the copolymers are closer to the real molar mass. As it was mentioned earlier, incorporation of PET units into PPO is more inefficient when higher amounts of PET are used in the initial feed mixture. This is also reflected in the obtained molar mass, as they are slightly higher than that for pure PPO (M_v = 44,350 g/mol). It is evident that the average amount of PPO units in the copolymers is close to one.

The results obtained strongly suggest that the block copolymers obtained in this work consist of a central segment of PPO surrounded by several units of PET. Based on this and the previous discussion, the following mechanism is proposed for the obtainment of PO-ETs (Scheme 1), where the final structure involves two arms of PET units irradiating from PO units.

Figure 3 depicts a calorimetric curve of PO-ET 1. This and the other copolymers obtained are amorphous. In this thermogram, only one jump in the line base characteristic of the glass transition temperature is resolved at high temperatures. The T_g of PO-ET 1 is 197°C. This T_g is lower than T_g of pure PPO (212°C). In fact, all PO-ETs showed lower T_gs than that of PPO. This means that the incorporation of segments from PET oligomers to PPO backbone decreases the glass transition temperature of the final copolymer. This fact is in agreement with the low T_g value recorded for PET oligomers (−24°C).

Figure 4 shows the best fit curve based on the Gordon-Taylor equation (where k = 2.06 was taken as adjustable parameter). Gordon-Taylor equation has been successfully used to represent the evolution of experimental T_g as a function of the composition for several segmented copolymers, such as ethylene terephthalate-ε-caprolactone[2] and tetramethylene oxide–tetramethylene terephthalate.[9] The Gordon-Taylor equation was originally derived for random copolymers. Recently, this equation has been used to describe, with reasonable accuracy, the T_g behavior for miscible polymer blends, with positive or negative deviations of the simple linear mixing rule.[24] The reasonable prediction of the Gordon-Taylor equation for T_g-composition curve of PO-ETs can be due to the morphological features of the copolymers, and indicates a high degree of mixing between PPO and PET units. In fact, the PPO units (the medium molar mass), but whose molar mass is higher than that for PET units, inhibit the appearance of phase separation between the two structural units present in the PE-ETs copolymers.
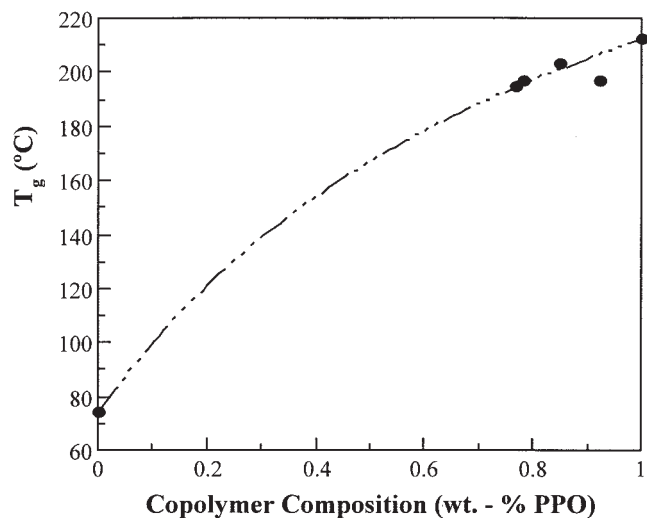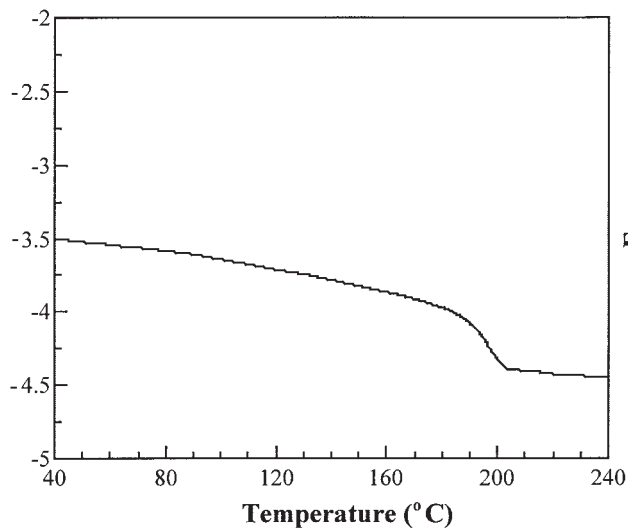
CONCLUSIONS

The synthesis of a series of PO-ET was achieved by a two-step process. In the first step, an end-capping reaction between PPO and TDI was carried out with high yields. In the second step, PO-ET copolymers were obtained by adding PET oligomers (previously obtained through glycolysis) to adduct obtained in the first step. FTIR spectroscopy indicates the quantitative formation of urethane groups in the final copolymer. PO-ET copolymers contain a higher percent of PPO units, as determined by ¹H NMR. The Gordon-Taylor equation fit well the T_g behavior of the PO-ETs obtained. Evaluation of the molar masses by viscometry, based on the Mark-Houwink equation for PPO, rep-

Scheme 1
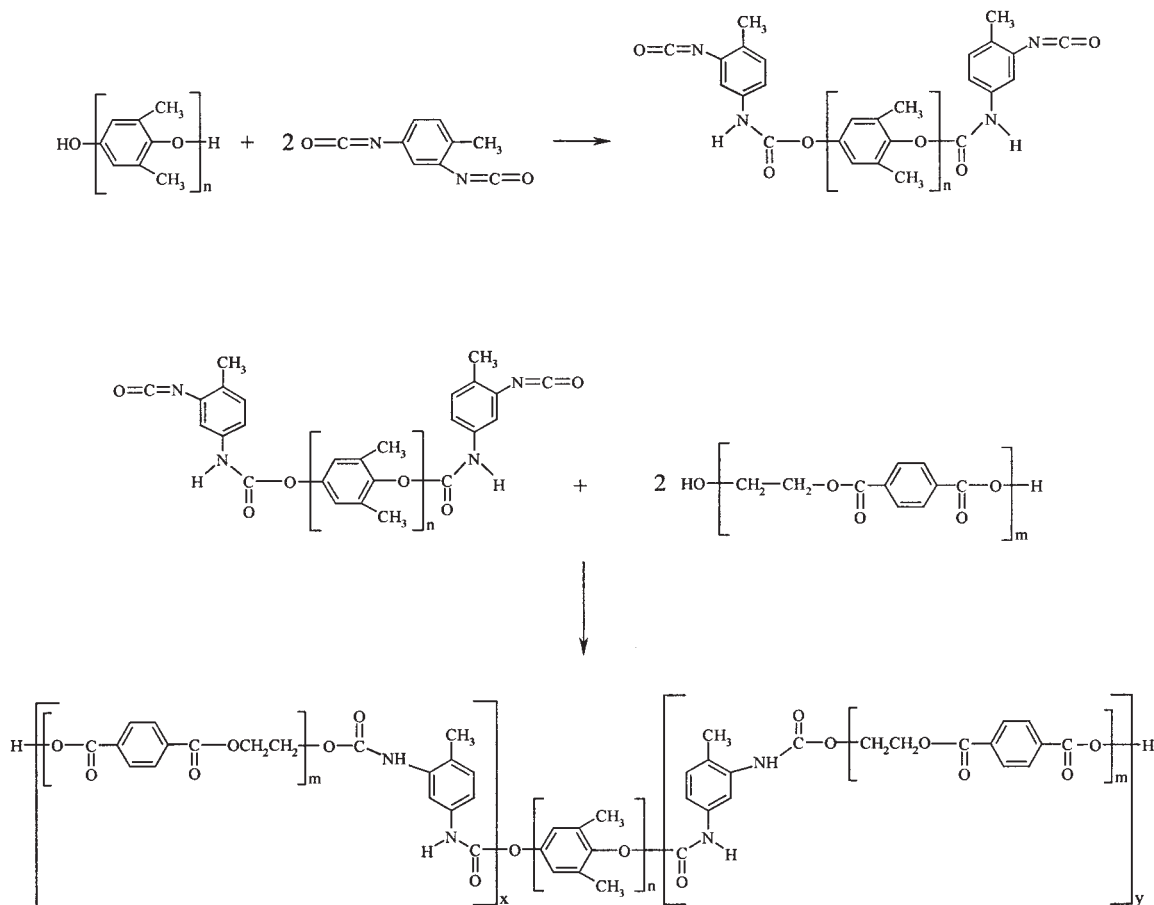
resent a reasonable estimation of the real molar mass of the copolymers as mainly PPO repeating units forms these. The final structure of the all PO-ET copolymers consists in average of a central chain of PPO and two arms containing several units of PET.

Figure 3   DSC thermogram for PO-ET 1.

Figure 4   The glass transition temperatures of PO-ETs copolymers as a function of PPO composition. The broken line represents the best fit to the Gordon-Taylor equation.

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