

Poly(ethylene terephthalate-*co*-isophthalate) Copolyesters Obtained from Ethylene Terephthalate and Isophthalate Oligomers

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ABSTRACT: A series of poly(ethylene terephthalate-*co*-isophthalate) copolyesters containing up to 50%-mole of isophthalic units were prepared by polycondensation from ethylene terephthalate and ethylene isophthalate fractions of linear oligomers containing from 5 to 6 repeating units in average. The polyesters were obtained in good yields and with high-molecular-weights. The microstructure of the copolyesters was studied as a function of reaction time by ¹³C-NMR showing that a random distribution of the comonomers was achieved since the earlier stages of polycondensation. The melting temperature and enthalpy of

the copolyesters decreased with the content of isophthalic units so that copolyesters containing more than 25% of these units were amorphous. Isothermal crystallization studies made on crystalline copolyesters revealed that the crystallization rate of copolyesters decreased with the content in isophthalic units. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1823–1830, 2010

Key words: poly(ethylene terephthalate-*co*-isophthalate); polycondensation; ethylene terephthalate oligomers; NMR; crystallization

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semicrystalline thermoplastic currently obtained from terephthalic acid (TPA) and ethylene glycol (EG). It is widely used in the textile and packaging fields to produce fibers, films, and bottles¹ due to its excellent thermal and mechanical properties, high chemical resistance, and low permeability to gases. Since for some applications, a high transparency is also required, minor amounts of comonomers as diacids^{2–4} or diols^{5–9} are added to repress the tendency of this polymer to crystallize. A review on the thermal properties and crystallization behavior of PET by copolymerization has been published by Kint and Muñoz-Guerra¹⁰ The comonomers mostly used for such purpose in blowing-injection applications are isophthalic acid^{11,12} (IPA) and 1,4-cyclohexanedimethanol¹³ (CHDM) due to the improvement in the

barrier properties and impact resistance they provide to their respective resulting copolyesters, as well as diethyleneglycol (DEG), a comonomer that is also effective in repressing polymer crystallization.¹⁴

Poly(ethylene terephthalate-*co*-isophthalate) copolyesters (PET_{*x*}I_{*y*}) where *x* and *y* denote the molar content of terephthalate and isophthalate units, respectively, are usually obtained by a two-stage melt polycondensation process.^{15,16} In the first step, TPA and IPA react with EG under slight over-pressure (2–5 bar) at around 250–260°C to produce a co-oligomeric mixture containing from 5 to 10 repeating units in average, depending on the excess of glycol added. The molar ratio diacid/glycol frequently used is 1/1.1–1.2 so the final product at the end of the esterification step is a random ethylene terephthalate-*co*-isophthalate oligomer ending mostly in glycolic units. These co-oligomers are then transferred to the polycondensation reactor or reactors, where temperature is increased at 270–285°C and pressure is gradually reduced to 1 mbar to remove the excess of EG produced in the transesterification reaction and to increase therefore the molecular weight. This reaction usually takes around 90 min in the presence of catalyst (Sb₂O₃, GeO₂) to afford a fair molecular weight polyester with a random microstructure. An increase in the polycondensation time gives rise to both yellowing and molecular

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weight decrease due to thermal degradation. Then, the strategy to produce high-molecular-weight copolyesters is to introduce the polymer crystallized as pellets into a solid state polymerization reactor (SSP) where the polycondensation reaction is forced to continue at temperatures near below its melting temperature.¹⁷

Due to the growing production of PET_xI_y copolyesters, new synthesis methodologies and industrial processes are being explored nowadays.^{18,19} However, as far as we know, none of them use linear oligomers as the starting material. This approach would be readily applicable by simple implementation of the common PET line production with an additional esterification reactor where ethylene isophthalate oligomers were produced and then loaded to the reaction vessel just before the polycondensation step. In this work, we have studied the preparation of PET_xI_y copolyesters by polycondensation reaction of mixtures of ethylene terephthalate and ethylene isophthalate linear oligomers which were previously synthesized for this purpose. The evolution of the microstructure with reaction time is assessed by ¹³C-NMR and the thermal properties and crystallizability of the copolyesters are evaluated by DSC and TGA.

EXPERIMENTAL SECTION

Materials

Terephthalic acid (TPA) (99%), isophthalic acid (IPA) (99%), ethylene glycol (EG) (99%), and germanium dioxide (99%) were kindly supplied by Artenius Prat (La Seda de Barcelona S.A.) and used without further purification. Dichloro acetic acid and diethyl ether used for purification and other analytical purposes were analytical grade (Aldrich) and used as received.

Synthesis

The procedure applied for the synthesis of PET and PEI oligomers (OET and OEI, respectively) was as follows: 350 g of TPA or IPA (2.11 mol), 157.2 g of EG (2.53 mol), and 0.1 g of GeO₂ catalyst (0.95 mmol) were added to a Karl Kurt Juchheim stainless steel reactor of 1.5 L equipped with a distillation column, a condenser, a nitrogen inlet, a drain valve, and a mechanical anchor stirrer. First, the pressure of the reactor was set at 3 bar and the temperature was gradually increased to 255°C and maintained at this temperature for 70 min under vigorous agitation. Then, atmospheric pressure was recovered and the reaction temperature was increased to 260°C and maintained for 5 min. Finally the linear oligomers were collected from the reactor through the drain

valve and characterized by NMR and end-group titration with a base.

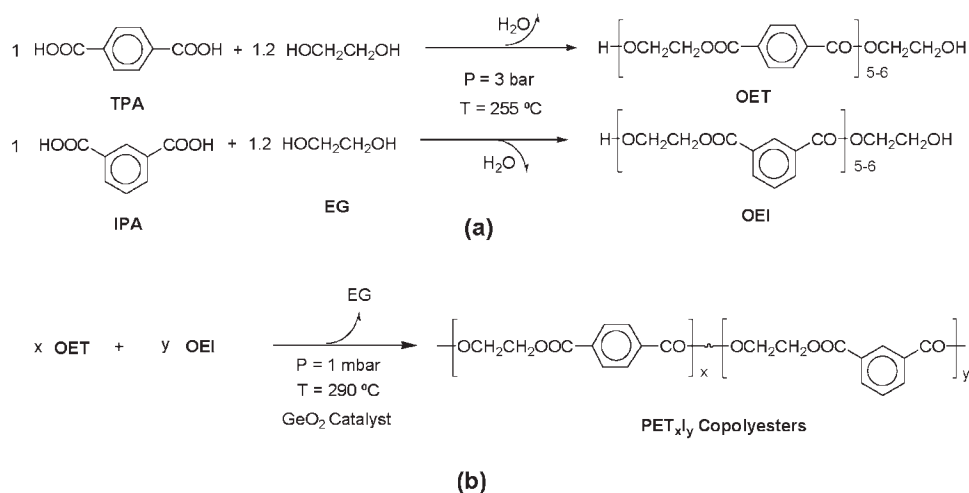
For the synthesis of PET_xI_y copolymers, the following procedure was applied: About 30 g of mixtures of PET and PEI linear oligomers obtained as described earlier were placed in a three-necked 100-mL round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. Molar ratios *x/y* ranging from 96/4 to 50/50 were assayed. The flask was introduced into a nitrate salt bath and the temperature was increased to 260°C and maintained at this temperature for 30 min. The pressure was gradually reduced to 1 mbar for a period of 30 min and the temperature was gradually increased upto 290°C, and the polycondensation left to proceed under such conditions for 90 min. After this period of time, the release of EG ceased and a viscous liquid was finally obtained. The reaction mixture was then cooled to room temperature and the atmospheric pressure was recovered with a nitrogen flow to prevent degradation. The solid mass was dried at 60°C under reduced pressure for 48 h previous to characterization.

Measurements

Intrinsic viscosities of the polymers dissolved in dichloroacetic acid were measured using an Ubbelohde viscosimeter thermostated at 25°C ± 0.1°C. Gel permeation chromatography (GPC) was carried out using an *o*-chlorophenol/chloroform mixture (1/9 v/v) as the mobile phase at 35°C. GPC analyses were performed in a Waters system equipped with both refractive-index and light scattering detectors. Two 7.8 × 300 mm Styragel columns packed with divinylbenzene crosslinked polystyrene (pore size 10³ and 10⁴ Å) in series were used for the analysis. The flow rate of the eluent was 0.5 mL min⁻¹. Molecular weights and molecular weights distributions were estimated against monodisperse poly (methyl methacrylate) standards using the Maxima 820 software.

Carboxylic end-group was determined by potentiometric titration using a Metrohm 726 titroprocessor. For that, 0.5 g of OET or OEI oligomers were dissolved in 20 mL of *o*-cresol to which 50 mL of chloroform were added. The solution was titrated with 0.1M tetrabutyl ammonium hydroxide and the [COOH] was expressed in meq kg⁻¹.

NMR spectra were recorded at 25°C ± 0.1°C on a Bruker AMX-300 spectrometer operating at 300.1 MHz and 75.5 MHz for ¹H and ¹³C, respectively. 10 mg (¹H-NMR) and 50 mg (¹³C-NMR) of sample were dissolved in 1 mL of deuterated trifluoroacetic acid or a mixture of deuterated chloroform/trifluoroacetic acid (9/1 v/v) solvents for



Scheme 1 Synthetic route to obtain PET_{xI_y} copolyesters: (a) First step: esterification and (b) Second step: polycondensation.

NMR analysis. The spectra were internally referenced to the signal of tetramethylsilane (TMS). Sixty-four scans were acquired for 1H and 5,000–10,000 for ^{13}C with 32 and 64K data points, respectively. For the analysis of the microstructure, ^{13}C -NMR spectra were Fourier transformed (FT) with 128K providing a digital resolution of 0.27 Hz per point. Integration of the overlapping signals was made by Lorentzian deconvolution of the spectra using the Bruker 1D WIN-NMR software.

DSC experiments were performed on a Perkin-Elmer Pyris 1 instrument calibrated with indium. Thermograms were obtained from 4 to 6 mg samples at heating and cooling rates of $10^\circ C \text{ min}^{-1}$ under a nitrogen flow of 20 mL min^{-1} , except for determination of glass-transition temperatures, where the heating rate was $20^\circ C \text{ min}^{-1}$. Isothermal crystallization studies were performed on amorphous quenched films at different temperatures. Thermogravimetric analysis (TGA) were carried out on a PerkinElmer TGA-6 thermobalance at a heating rate of $10^\circ C \text{ min}^{-1}$ under a nitrogen atmosphere.

RESULTS AND DISCUSSION

The PET_{xI_y} copolyesters described in this work were prepared by a two-step melt polycondensation reaction as indicated in Scheme 1.

First, the ethylene terephthalate and ethylene isophthalate oligomers were produced separately. This step requires working at a slight over-pressure to increase the reaction temperature to the value at which both the terephthalic and isophthalic acids become almost soluble in EG. The chemical structure of the oligomeric fractions was characterized by NMR and their sizes were determined using end-group data afforded by NMR and carboxyl end-

group titration. The content in hydroxyl end groups expressed in meq kg^{-1} was estimated by integration of the signals at 4.8 and 4.2 ppm arising from the oxyethylene and hydroxyethylene end groups, respectively, using the following expression:

$$[\text{OH}] = [\text{CH}_2\text{OH}] = 1000 \times 1000 / 192.2 \times a / 2 / b / 4$$

where a and b are the integrals at 4.2 and 4.8, respectively.

The content in carboxylic end groups were measured by titration with tetrabutyl ammonium hydroxide.

From the values of $[\text{OH}]$ and $[\text{COOH}]$, the number average degree of polymerization (x_n) can be calculated using the following expression:

$$x_n = [\text{UR}] / 1/2[\text{GT}] \\ = 1000 \times 1000 / 192.2 / 1/2([\text{OH}] + [\text{COOH}])$$

where $[\text{UR}]$ and $[\text{GT}]$ are the repeating units and terminal groups concentrations, respectively.

As it can be seen in Table I, a number average of 5.7 and 5.4 repeating units were calculated for OET and OEI oligomers, for which around 15 and 20% of

TABLE I
Molecular Weights of Ethylene Terephthalate and Ethylene Isophthalate Oligomers

Oligoester	$[\text{COOH}]^a$ (meq kg^{-1})	$[\text{OH}]^b$ (meq kg^{-1})	x_n^c	M_n^c (g mol^{-1})
OET	393	1418	5.7	1095
OEI	271	1639	5.4	1045

^a Determined by potentiometric titration.

^b Values obtained by integration of CH_2OH and CH_2OOC signals in the 1H -NMR spectra.

^c $x_n = 10,405.8 / [\text{COOH}] + [\text{OH}]$.

TABLE II
Molecular Weights and Viscosities of PETI Copolyesters

Polyester	Feed composition ^a		Molecular weights			
	[OET]/[OEI]	[η] ^b	M_n^c	M_n^d	M_w^d	PD ^d
PET	100/0	0.86	30,600	43,200	103,700	2.4
PET ₉₄ I ₆	94/6	0.83	28,392	36,500	83,900	2.3
PET ₉₀ I ₁₀	90/10	0.82	27,600	34,400	78,600	2.4
PET ₇₅ I ₂₅	75/25	0.88	32,100	41,500	99,100	2.4
PET ₇₀ I ₃₀	70/30	0.88	32,100	47,000	113,100	2.4
PET ₆₀ I ₄₀	40/60	0.72	20,900	37,500	84,100	2.2
PET ₅₀ I ₅₀	50/50	0.70	19,700	38,100	83,200	2.2

^a Molar ratio in the initial feed.

^b Intrinsic viscosity (dL g⁻¹) measured in dichloroacetic acid at 25°C.

^c Number average molecular weight determined by solution viscometry using $a = 0.47$ and $K = 67 \times 10^{-4}$ as the Mark-Houwink parameters.²⁰

^d Number- and weight average molecular weights and polydispersity determined by GPC.

carboxylic end groups were found, respectively. These values are close to 5, which is the value theoretically calculated for a relation diacid/EG of 1/1.2.

In the second step, which was carried out in the polycondensation reactor, OET and OEI oligomers were blended in the required proportions to obtain the corresponding copolyesters with the chosen compositions. The reaction was carried out at higher temperature (290°C) and under vacuum to remove the excess of EG added in the feed. The copolyesters obtained are listed in Table II, where the feed content, viscosity, molecular weights, and polydispersity are given for each sample. The intrinsic viscosity of

the copolyesters was between 0.7 and 0.8 dL g⁻¹ indicating that the copolymers have moderate molecular weights. The GPC analysis afforded higher values but with a tendency fully consistent with the observed viscosities. They all have polydispersities around 2.

The chemical structure of the polyesters was ascertained by NMR spectroscopy. ¹H-NMR spectra in solution afforded clear differences in the chemical shifts of the signals arising from ET and EI units, which could be used to estimate the copolymer composition, ¹³C-NMR spectra were used to determine the microstructure of the copolymer chain. Figure 1

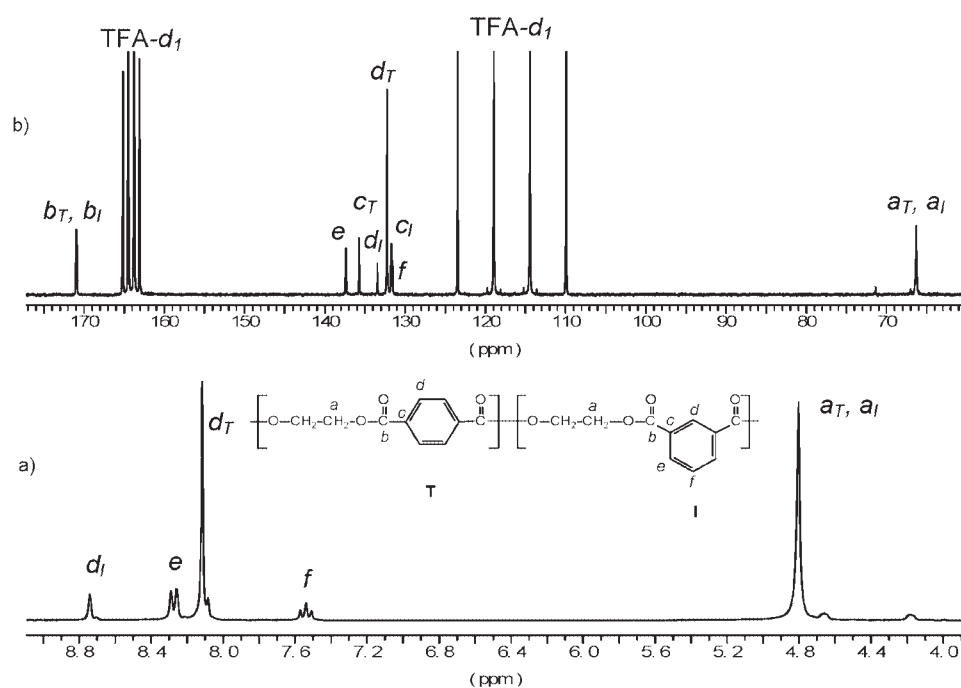


Figure 1 ¹H- (a) and ¹³C- (b) NMR spectra of PET₆₀I₄₀.

TABLE III
Composition,^a Diethylene Glycol Content, and Microstructure^b of PETI Copolyesters

Copolyester	Composition ^a		DEG ^c (mol%)	Triads (mol %)			Dyads (mol %)		Number average sequence length		Randomness ^B
	X _T	X _I		TTT	ITT	ITI	IT	II	n _T	n _I	
PET ₉₄ I ₆	94.1	5.9	5.5	84.5 (83.3)	9.6 (10.4)	0.0 (0.3)	5.9 (5.6)	0.0 (0.3)	15.1 (16.9)	1.0 (1.1)	1.07 (1.00)
PET ₉₀ I ₁₀	89.9	10.1	5.6	72.1 (72.6)	13.8 (16.3)	3.9 (0.9)	9.1 (9.1)	1.0 (1.0)	9.7 (9.9)	1.1 (1.1)	1.00 (1.00)
PET ₇₅ I ₂₅	75.5	24.5	5.1	43.8 (43.4)	27.6 (27.9)	4.1 (4.5)	18.4 (18.5)	6.1 (6.0)	4.1 (4.1)	1.3 (1.3)	0.99 (1.00)
PET ₇₀ I ₃₀	70.3	29.7	5.4	33.7 (34.7)	28.9 (29.4)	7.6 (6.2)	20.1 (20.9)	9.6 (8.8)	3.4 (3.4)	1.5 (1.4)	0.97 (1.00)
PET ₄₀ I ₆₀	60.7	39.3	4.9	21.5 (22.4)	28.4 (29.0)	10.8 (9.4)	23.4 (23.9)	15.9 (15.4)	2.5 (2.5)	1.7 (1.6)	0.99 (1.00)
PET ₅₀ I ₅₀	50.7	49.2	4.9	14.3 (13.0)	24.6 (25.3)	11.8 (12.3)	24.9 (24.9)	24.3 (24.2)	2.1 (2.0)	2.0 (2.0)	0.98 (1.00)

^a Determined from the aromatic proton resonances observed in ¹H-NMR spectra.

^b Experimental values obtained by deconvolution of ¹³C-NMR signals and equations taken from Ref. 21. Theoretical values (in brackets) were calculated on the basis of a random distribution using the copolyester composition data given in this table.

^c Determined from the ¹H-NMR spectra.

shows the ¹H and ¹³C-NMR spectra of PET₆₀I₄₀ copolyester obtained with peak assignments as a representative example of the family. Signal *f* and *d* of isophthalic and terephthalic protons, respectively, were used to calculate the copolymer composition. As it can be seen in Table III, a good correlation between the feed and final compositions was found in all cases. Additionally, ¹H-NMR spectra showed small peaks at 4.1 and 4.7 ppm due to the presence of diethylene glycol units presumably resulting from side reactions taking place along both esterification and polycondensation steps. The content of these units was estimated to be around 5% in all cases.

To investigate the microstructure of the resulting copolyesters, the evolution of ¹³C-NMR spectra with polycondensation time was recorded. As it was reported earlier,²² the nonprotonated aromatic carbons of isophthalic and terephthalic units were sensitive to sequence distribution at the level of dyads and triads, respectively. These signals were therefore used to estimate the number average sequence lengths and randomness of the copolymer that was generated as the reaction proceeded. Figure 2 shows the ¹³C-NMR spectra for the PET₅₀I₅₀ copolyester, the initial mixture of the OET γ OEI oligomers, the product resulting at the end of the esterification step and the copolymer formed at progressively longer polycondensation times.

As it is shown in Figure 2, the signals that in the physical mixture appear as single peaks (labeled as 1), at the end of the esterification step were split in 4 and 2 peaks for the quaternary aromatic carbons of terephthalate and isophthalate units, respectively

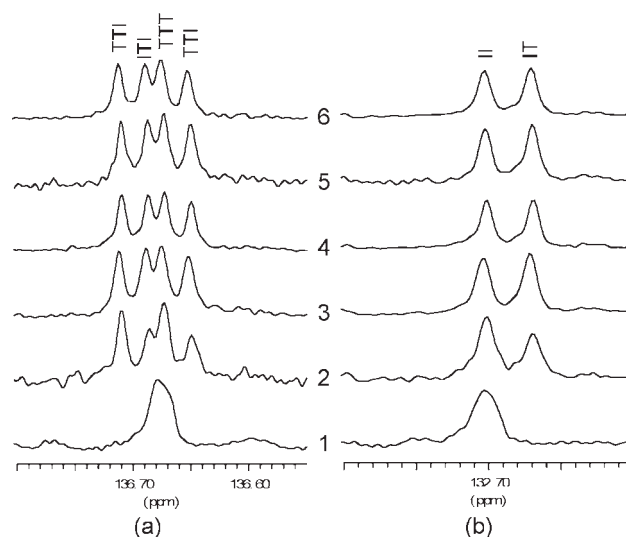


Figure 2 Evolution of ¹³C-NMR spectra of PET₅₀I₅₀ with time. 1, mixture of equimolar amounts of the two oligomers before reaction; 2, product resulting at the end of the esterification step; 3, 4, 5, and 6, copolyesters obtained at 15, 30, 45, and 90 min of polycondensation reaction.

TABLE IV
Evolution of Microstructure^a and Randomness Degree of PET₅₀I₅₀ Copolyester with Reaction Time

Copolyester	Polycondensation time (min)	Triads (mol %)			Dyads (mol %)		Number average sequence length		Randomness <i>B</i>
		TTT	ITT	ITI	IT	II	<i>n_T</i>	<i>n_I</i>	
PET ₅₀ I ₅₀	0	17.6	25.8	6.5	17.3	32.7	2.7	2.8	0.73
	15	12.4	24.7	12.9	26.3	23.7	2.0	1.9	1.03
	30	13.3	25.0	11.7	24.1	25.9	2.1	2.1	0.96
	45	12.5	25.0	12.6	25.3	24.7	2.0	2.0	1.00
	90	14.3	24.6	11.8	24.9	24.3	2.1	2.0	0.98

^a Experimental values obtained by deconvolution of ¹³C-NMR signals and equations taken from Ref. 21.

(labeled as 2 and 6). By integration of such peaks the evolution of the average sequence lengths and randomness of the copolymer could be evaluated as a function of reaction time. As it can be observed in Table IV, the copolyesters obtained at the end of the esterification step display a certain blocky microstructure, whereas those obtained after polycondensation were almost random even after short reaction times. These results evidence that the transesterification processes leading to randomization occur very fast at 290°C in these low-viscosity oligoesters. As a consequence, the resulting PET_{*x*}I_{*y*} copolyesters have a microstructure practically undistinguishable from that present in these type of copolyesters obtained by polycondensation of the monomers.²³

The thermal behavior of PET_{*x*}I_{*y*} of copolyesters was examined by DSC and TGA. As it can be seen in Table V, both melting temperature and enthalpy decrease as the content in isophthalate units increase to the point that the copolyester becomes unable to

crystallize when the contents of these units is higher than 25%. Due to the amorphous nature of these copolyesters with high contents in isophthalate units, they showed improved solubility in organic solvents, being soluble in CHCl₃, where PET was observed to be not soluble. The effect of composition on *T_g* is similar; this temperature gradually decreases with the content of isophthalate units taking values in the range limited by the *T_g* of PET and PEI homopolymers. The polymers were thermally stable upto almost 400°C and no remarkable differences could be observed among the components of the series.

Finally, the crystallization kinetic parameters of the crystallizable copolyesters PET₉₄I₆ and PET₉₀I₁₀ were determined from isothermal crystallizations experiments carried out at different temperatures (Table VI and Fig. 3). The Avrami exponent *n*, was shown to increase with temperature from values below 2 to values near to 3 revealing that a change in the crystal growth process from two-dimensional

TABLE V
Thermal Properties of PET, PEI, and PET_{*x*}I_{*y*} Copolyesters

Polyester	DSC							TGA		
	First heating ^a			Cooling ^a		Second heating ^a		° <i>T_d</i> ^c (°C)	<i>T_d</i> ^d (°C)	RW ^e (%)
	<i>T_g</i> ^b (°C)	<i>T_m</i> (°C)	Δ <i>H_m</i> (J g ⁻¹)	<i>T_c</i> (°C)	Δ <i>H_c</i> (J g ⁻¹)	<i>T_m</i> (°C)	Δ <i>H_m</i> (J g ⁻¹)			
PET	79.4	245.3	34.2	192.4	32.1	246.1	31.1	413	440	16.6
PET ₉₄ I ₆	77.4	231.2	32.1	165.9	23.8	230.5	33.1	409	441	12.8
PET ₉₀ I ₁₀	76.8	221.9	26.2	157.3	23.3	222.2	26.5	392	439	14.3
PET ₇₅ I ₂₅	72.7	–	–	–	–	–	–	411	437	18.8
PET ₇₀ I ₃₀	72.4	–	–	–	–	–	–	415	436	18.8
PET ₆₀ I ₄₀	71.4	–	–	–	–	–	–	412	440	14.8
PET ₅₀ I ₅₀	70.0	–	–	–	–	–	–	414	442	16.2
PEI	64.7	–	–	–	–	–	–	414	446	16.1

^a Melting (*T_m*) and crystallization (*T_c*) temperatures and their respective enthalpies (Δ*H_m*, Δ*H_c*) measured by DSC at heating/cooling rates of 10°C min⁻¹.

^b Glass-transition temperature taken as the inflection point of the heating DSC recorded at 30°C min⁻¹ from samples quenched from the melt.

^c Temperature at which a 10% weight loss was observed in the TGA traces recorded at 10°C min⁻¹.

^d Temperature of maximum degradation rate.

^e Remaining weight at 550°C.

TABLE VI
Crystallization Parameters of PET₉₄I₆ and PET₉₀I₁₀ Copolyesters at Different Temperatures

Crystallization temperature (°C)	PET ₉₄ I ₆				Crystallization temperature (°C)	PET ₉₀ I ₁₀			
	Avrami Parameters ^a					Avrami Parameters ^a			
	t_o^b	n	$\log k$	$t_{1/2}$		t_o^b	n	$\log k$	$t_{1/2}$
170	0.2	1.6	-0.4	1.6	150	0.1	1.5	-0.4	1.6
180	0.3	2.5	-0.9	2.2	160	0.2	1.7	-0.5	1.7
190	0.5	2.5	-1.6	3.7	170	0.4	2.3	-0.9	2.5
200	3.4	2.9	-2.5	10.1	180	1.1	2.6	-1.6	4.6

^a Avrami exponent n , constant of crystallization, and crystallization half-time $t_{1/2}$ (min).

^b Onset crystallization time (min).

to three-dimensional spherulitic growth likely took place with increasing in crystallization temperature. Comparison of the crystallization half-time for the two copolyesters for the same degree of undercooling revealed that crystallization was delayed in PET₉₀I₁₀. As expected, crystallizability is significantly repressed by the incorporation of isophthalate units in the copolyester. Similar conclusions were obtained in the work of Wu and Chang²⁴ on PETI copolyesters obtained from melt polycondensation.

CONCLUSIONS

PET copolyesters containing different amounts of isophthalate units could be prepared from ethylene terephthalate and isophthalate linear oligomers. The copolyesters obtained showed a random microstructure which was attained since the earlier stages of polycondensation. The copolyesters were amorphous for contents in isophthalic units higher than 25%. It was shown that the melting temperature and

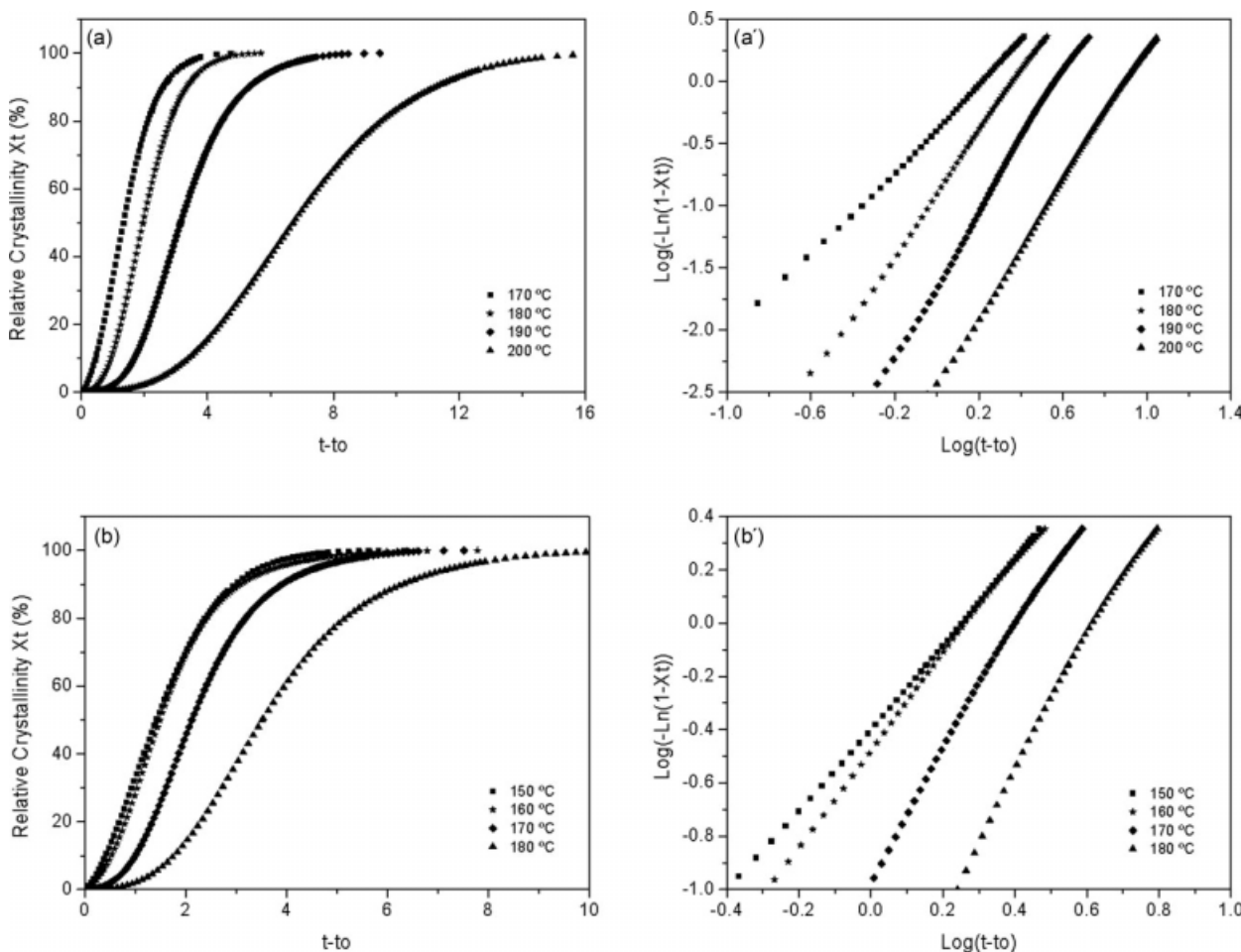


Figure 3 Relative crystallinity X_t versus crystallization time at different temperatures for isothermally crystallized PET₉₄I₆ (a) and PET₉₀I₁₀ (b) at the indicated temperatures, and their respective Avrami plots (a') and (b').

crystallinity decreased with the incorporation of isophthalic units as well as the crystallizability. Additionally, the copolymers showed glass-transition temperatures between the one of PET and PEI. These findings support that these copolymers have similar microstructure and properties to the ones obtained by the conventional two-stage melt polycondensation of terephthalic and isophthalic acids with ethylene glycol.

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