Sequence Analysis of Poly(ethylene terephthalate) Terpolyesters Containing Isophthalic and *tert*-Butylisophthalic Units by ^{13}C NMR

Darwin P. R. Kint, Antxon Martínez de Ilarduya, and Sebastián Muñoz-Guerra*

Departament d'Enginyeria Química, Universitat Politècnica de Catalunya, ETSEIB, Diagonal 647, Barcelona 08028, Spain

Received July 2, 2001

Introduction

Because of its excellent general pattern of basic properties, poly(ethylene terephthalate) (PET) is today the thermoplastic of choice for an increasingly wide variety of applications. Transparency, one of its more outstanding properties, is however restricted to thin films and sheets due to the proclivity of PET to crystallize. Industrially used PET copolymers containing minor amounts of isophthalic units (PETI) are known to be less crystallizable than the PET homopolymer.[1−3] Unfortunately, the glass-transition temperature T_g of these copolyesters is lower than that of PET, which constitutes a serious drawback for expanding the use of this material to higher demanding applications. Recently, we have shown that the incorporation of *tert*-butylisophthalic acid as a third comonomer in PETI leads to poly(ethylene terephthalate-*co*-isophthalate-*co*-*tert*-butyl isophthalate) terpolyesters, abbreviated PETI^{t}BI, with a markedly repressed tendency to crystallize while showing higher T_g than PET.[4] Furthermore, it was found that the thermal and crystallization properties of these terpolymers can be accurately adjusted as a function of the comonomer composition.

The microstructure of heteropolymers has to be known in order to understand their molecular mobility dependent properties. This is the case of PETI^{t}BI where three aromatic units largely differing in their associate free volume coexist along the polymer chain. It is well-known that NMR spectroscopy is the appropriate methodology for the determination of the sequence distribution and randomness of copolymers like copolyamides[5] or PET copolyesters.[6,7] Thus, the microstructure of PETI has been analyzed by both ^{1}H and ^{13}C NMR methods.[8−10] More recently, we have shown that ^{13}C NMR analysis of these copolymers dissolved in deuterated trifluoroacetic acid (TFA-d_1) affords exceptional spectral resolutions for the nonprotonated aromatic carbons for PETI, which enabled us to determine the dyad and triad sequence distribution with high accuracy.[11] To our knowledge, no NMR studies addressing the characterization of the microstructure of PET-based terpolyesters have been carried out so far, probably due to the difficulty entailed in the assignment of the spectral resonances.

In the present note, we would like to report on the analysis of the microstructure of PETI^{t}BI by ^{13}C NMR. The fact that spectra taken in a mixture of chloroform and trifluoroacetic acid were found to show splitting for all nonprotonated aromatic carbons at the level of triads allowed us to determine the comonomer sequence distribution in these terpolymers.

* Corresponding author. E-mail munoz@eq.upc.es; Tel (+34) 93 401 66 80; Fax (+34) 93 401 7150.

Experimental Section

The terpolyesters used in this work were prepared by transesterification of mixtures of dimethyl terephthalate, dimethyl isophthalate, and *tert*-butylisophthalic acid with ethylene glycol and subsequent polycondensation. A detailed report on the synthesis, characterization, and properties of these novel terpolymers has been recently published.[4] The chemical structure of these terpolyesters with indication of the notations used for NMR assignments is depicted in Figure 1. The composition of the feed from which the terpolymer is produced is expressed as the molar ratio by the appropriate subscripts in the corresponding abbreviation, e.g., $PET_{60}I_{30}{}^tBI_{10}$. A series of PETI^{t}BI with a fixed content of 60 mol % in terephthalic units and the isophthalic to *tert*-butylisophthalic molar ratio ranging from 40/0 to 0/40 were selected for this study. All these terpolyesters are amorphous with T_g ranging from 69 up to 82.5 °C and have intrinsic viscosities higher than 0.5 dL g^{-1}, corresponding to number-average molecular weights above 10 000.[12] The values of these parameters are specified for each terpolymer in Table 1.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25.0 ± 0.1 °C, operating at 300.1 and 75.5 MHz, respectively. The polyesters (50 mg of sample) were dissolved in 0.7 mL of a mixture of $CDCl_3$/TFA-d_1 (8/1 v/v), and chemical shifts were internally referenced to tetramethylsilane (TMS). For the ^{13}C NMR spectra, the pulse and spectral widths were 4.3 μs (90°) and 18 kHz, respectively, and the relaxation delay was 2 s. From 5000 up to 15 000 FIDs were acquired with 64K data points and 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 computer software. The 2D ^{13}C−^{1}H heteronuclear shift correlation spectrum (HETCOR) was recorded by means of the *hxco* pulse sequence implemented in the Bruker NMR instrument package.

Results and Discussion

^{1}H and ^{13}C NMR spectra of $PET_{60}I_{30}{}^tBI_{10}$ are shown in Figure 2 for illustration. For the assignment of the signals, spectra of terpolymers with different compositions were compared among them and with those obtained from PETI and PET^{t}BI copolymers previously studied by us.[11,13] Definite support was given by well-defined correlation data provided by 2D NMR HETCOR spectra (Figure 3). The composition of the terpolyester could be precisely determined by relating the integrated signals of the terephthalic protons to those arising from the ortho-positioned protons, with respect to the ester groups, of the isophthalic and the *tert*-butylisophthalic units in the ^{1}H NMR spectra. ^{13}C NMR analysis corroborated the chemical structure of these terpolyesters. Under the applied experimental conditions, ^{13}C NMR spectra could be quantitatively used since the nonprotonated aromatic carbons of the three different aromatic units showed similar spin−lattice relaxation times (T_1) and nuclear Overhauser effects (NOE). Accordingly, the terpolyester compositions calculated by ^{13}C NMR were in full agreement with those obtained from ^{1}H NMR spectral data. It is worth noting that the correspondence of the copolymer composition with the composition of the feed is excellent. These results are shown in Table 1.

10.1021/ma011130a CCC: $22.00
Published on Web 12/04/2001

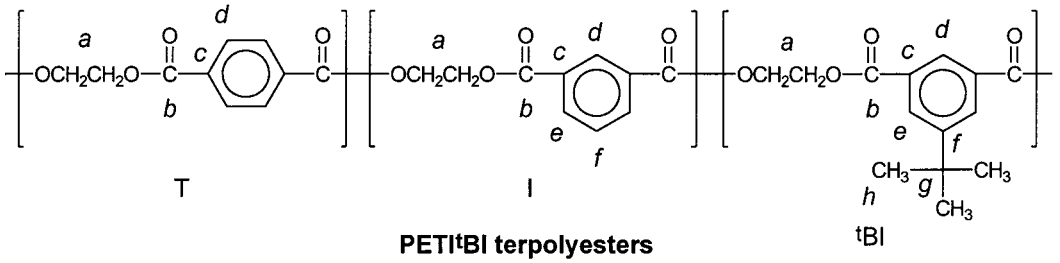

Figure 1. Chemical structure of PETI^{t}BI terpolyesters with notations used for NMR assignments.

Table 1. Viscosity, T_g, and Composition of PETI^{t}BI Terpolyesters

				copolyester composition (mol %)					
				X_T		X_I		X_{tBI}	
copolyester	$[\eta]^a$	$M_n{}^b$	T_g (°C)^c	^{1}H^d	^{13}C^e	^{1}H^d	^{13}C^e	^{1}H^d	^{13}C^e
$PET_{60}I_{40}$	0.70	19 800	68.8	60.2	60.1	39.8	39.9	0	0
$PET_{60}I_{30}tBI_{10}$	0.58	13 200	71.4	61.1	60.3	29.1	30.0	9.8	9.7
$PET_{60}I_{20}tBI_{20}$	0.50	9 700	74.6	60.4	60.5	19.7	19.7	19.9	19.8
$PET_{60}I_{10}tBI_{30}$	0.55	11 800	79.0	61.5	60.0	9.7	9.6	28.8	30.5
$PET_{60}{}^tBI_{40}$	0.57	12 800	86.5	61.7	59.7	0	0	38.3	40.3

^{a} Intrinsic viscosity (dL g^{-1}) measured in dichloroacetic acid at 25 °C. ^{b} Number-average molecular weight determined by solution viscometry using $a = 0.47$ and $K = 67 \times 10^{-4}$ as the Mark−Houwink parameters.[12] ^{c} Glass-transition temperature measured from melt-quenched samples by DSC at a heating rate of 30 °C.[4] ^{d} Determined from the aromatic proton resonances observed in ^{1}H NMR spectra. ^{e} Determined from integration of nonprotonated aromatic carbon signals in ^{13}C NMR spectra.

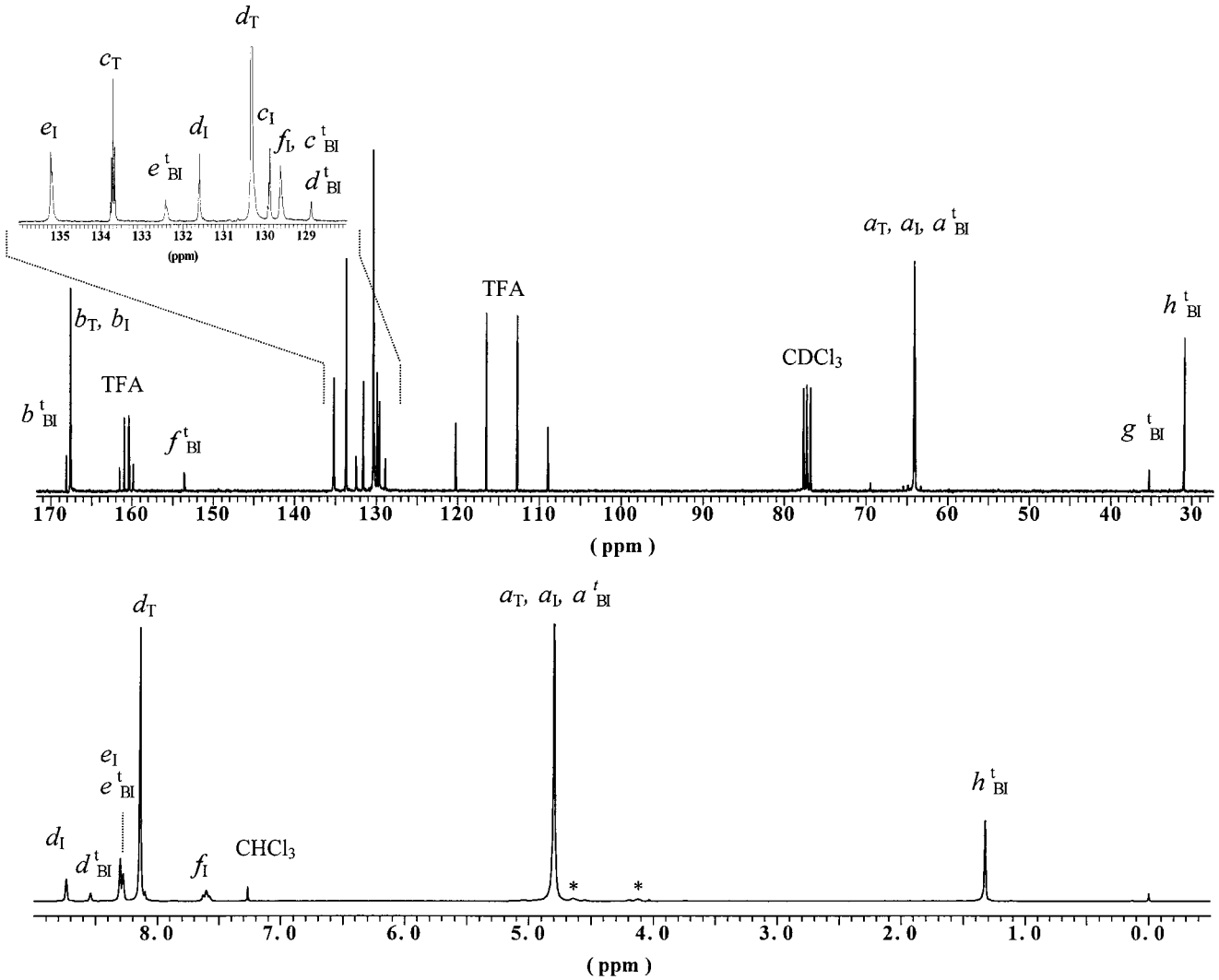

Figure 2. 300.1 MHz ^{1}H NMR (bottom) and 75.5 MHz ^{13}C NMR (top) spectra of $PET_{60}I_{30}{}^tBI_{10}$ recorded in $CDCl_3$/TFA. (*) Small signals at 4.3 and 4.7 ppm due to the presence of minor amounts (<2.5%) of diethylene glycol units and possible hydroxyethyl terminal groups.

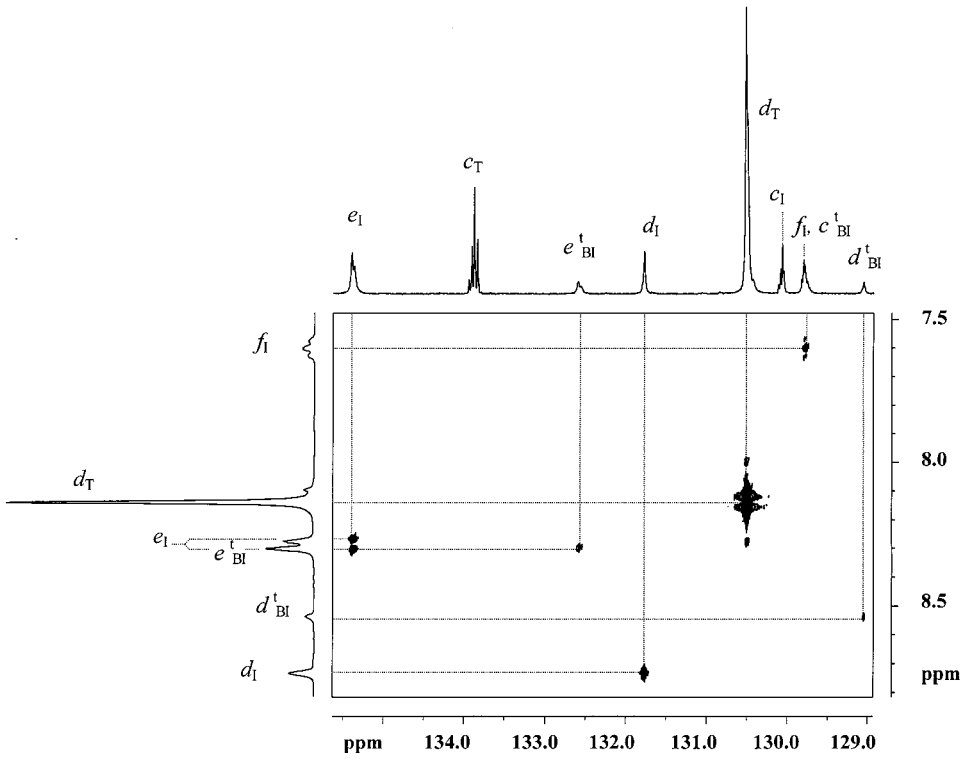

Figure 3. $^1H-^{13}C$ heteronuclear shift correlation spectrum (HETCOR) of $PET_{60}I_{30}{}^tBI_{10}$ recorded in $CDCl_3$/TFA.

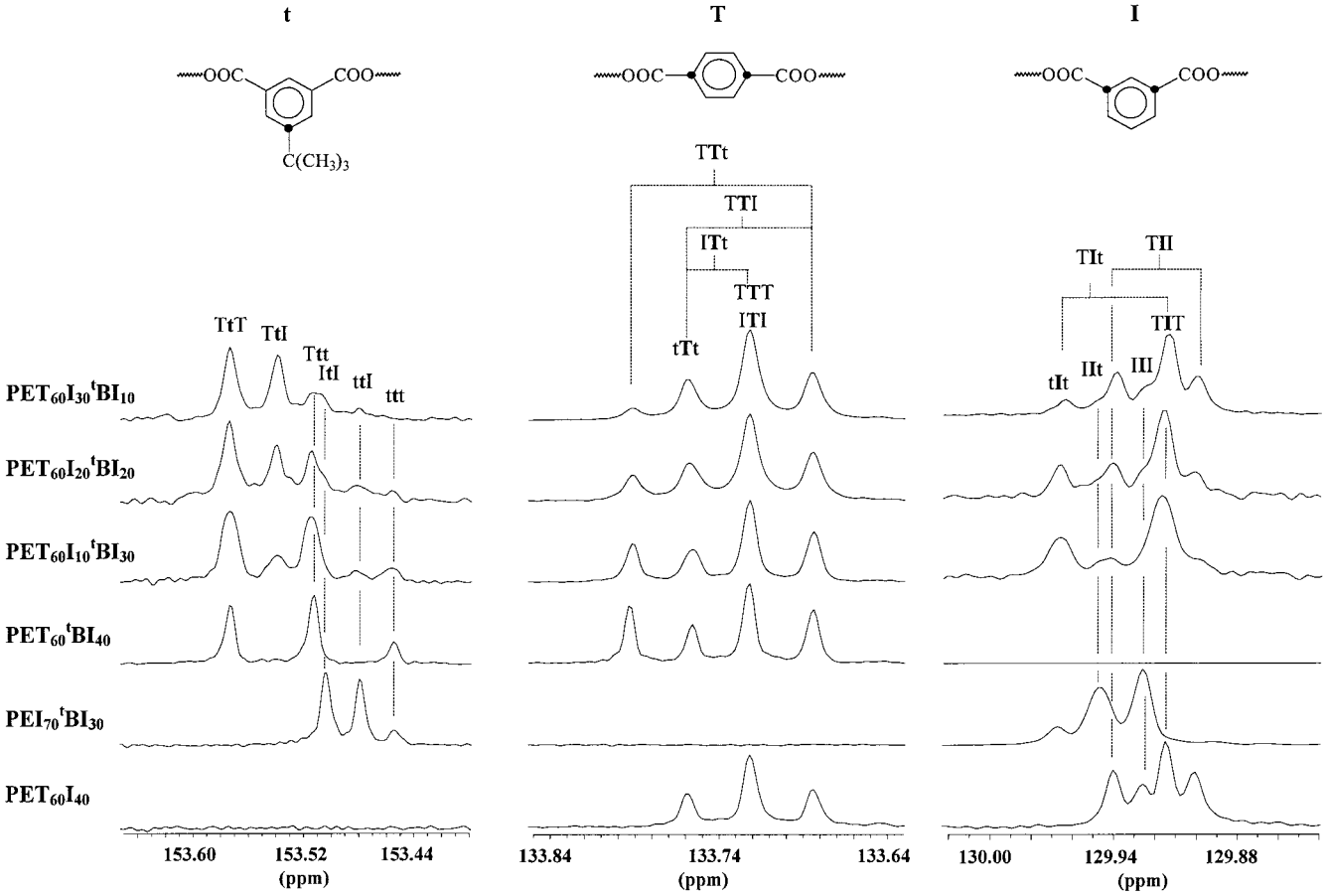

Figure 4. Comparison of ^{13}C NMR spectra of terpolyesters in the aromatic region showing the nonprotonated carbon splitting for the 5-*tert*-butylisophthalic, terephthalic, and isophthalic units.

As is shown in Figure 4, signal splitting due to triad sequence effects was observed for all the nonprotonated aromatic carbons. Assignment of the observed peaks was ascertained by comparison to the spectra of copolyesters $PET_{60}I_{40}$, $PEI_{70}{}^tBI_{30}$, and $PET_{60}{}^tBI_{40}$, in which triads composed of two comonomers could be unambigu-

ously identified. Using the relative integral values of the peaks included in the spectra of PETI^{t}BI, the distribution of the triads centered in terephthalic (I**T**I, I**T**t, t**T**t, T**T**T, T**T**I, and T**T**t), isophthalic (T**I**T, T**I**t, t**I**t, I**I**I, I**I**T, and I**I**t), and *tert*-butylisophthalic (T**t**T, T**t**I, I**t**I, t**t**t, t**t**T, and t**t**I) units could be estimated. Unfortunately, some terpolyester signals appeared overlapped, preventing the direct determination of the corresponding triad contents. Results were compared with those obtained for a Bernoullian statistical model where the contents in the different triad types were calculated using the following expressions:

$$[\mathrm{T}\mathbf{T}\mathrm{T}] = X_\mathrm{T}^3, \quad [\mathrm{I}\mathbf{T}\mathrm{I}] = X_\mathrm{T} X_\mathrm{I}^2, \quad [\mathrm{T}\mathbf{T}\mathrm{I}] = 2X_\mathrm{T}^2 X_\mathrm{I}$$

$$[\mathrm{I}\mathbf{T}\mathrm{t}] = 2X_\mathrm{T}X_\mathrm{I}X_\mathrm{tBI}, \quad [\mathrm{T}\mathbf{T}\mathrm{t}] = 2X_\mathrm{T}^2 X_\mathrm{tBI},$$

$$[\mathrm{t}\mathbf{T}\mathrm{t}] = X_\mathrm{T}X_\mathrm{tBI}^2$$

where X_T, X_I, and X_tBI are the mole fractions of the corresponding comonomer in the terpolymer as obtained from ^{1}H NMR spectra. The triads centered in either isophthalic or *tert*-butylisophthalic units were calculated in the same way. On the basis of such data, the estimated triad distribution of PETI^{t}BI could be compared with those calculated for a Bernoullian triad distribution for the different terpolyester compositions.

The number-average length for each comonomer sequence was calculated using the following equation:[7]

$$n_\mathrm{T} = \frac{[\mathrm{I}\mathbf{T}\mathrm{I}] + [\mathrm{I}\mathbf{T}\mathrm{t}] + [\mathrm{t}\mathbf{T}\mathrm{t}] + [\mathrm{T}\mathbf{T}\mathrm{T}] + [\mathrm{T}\mathbf{T}\mathrm{I}] + [\mathrm{T}\mathbf{T}\mathrm{t}]}{[\mathrm{I}\mathbf{T}\mathrm{I}] + [\mathrm{I}\mathbf{T}\mathrm{t}] + [\mathrm{t}\mathbf{T}\mathrm{t}] + {}^1/_2([\mathrm{T}\mathbf{T}\mathrm{I}] + [\mathrm{T}\mathbf{T}\mathrm{t}])}$$

For a terpolymer with a Bernoullian distribution, the number-averaged sequence length for each type of units is given by the following expression:

$$n_\mathrm{T} = 1/(X_\mathrm{I} + X_\mathrm{tBI}), \quad n_\mathrm{I} = 1/(X_\mathrm{T} + X_\mathrm{tBI}),$$

$$n_\mathrm{tBI} = 1/(X_\mathrm{T} + X_\mathrm{I})$$

A detailed account of the content of PETI^{t}BI in each type of triads is provided as Supporting Information for this note. An excellent correlation was observed between experimental values and those calculated for a Bernoullian statistical model. Theoretical and experimental values for the average sequence length and degree of randomness for each terpolymer are compared in Table 2, revealing that PETI^{t}BI have a random microstructure. Copolymerization is therefore essentially ideal, showing no preference either in the incorporation of the different comonomers or in their distribution along the polymer chain. It should be noted however that transesterification reactions known to take place along the course of polycondensation might contribute to the randomization of the terpolymer. The methodology here described appears to be highly efficient for the characterization of the microstructure PET terpolymers constituted by terephthalic, isophthalic, and *tert*-butylisophthalic units and of potential utility in the analysis of other related PET terpolymers.

Table 2. Experimental and Theoretical (in Parentheses) Average Sequence Lengths and Randomness of PETI^{t}BI Terpolyesters

copolyester	average sequence lengths			degree of randomness B
	n_T	n_I	n_tBI	
$PET_{60}I_{30}{}^tBI_{10}$	2.62	1.37	1.09	0.98
	(2.57)	(1.41)	(1.11)	(1.00)
$PET_{60}I_{20}{}^tBI_{20}$	2.50	1.24	1.22	0.99
	(2.52)	(1.24)	(1.24)	(1.00)
$PET_{60}I_{10}{}^tBI_{30}$	2.73	1.04	1.34	1.05
	(2.60)	(1.10)	(1.40)	(1.00)

Acknowledgment. The authors acknowledge the financial support received from CICYT with Projects MAT96-1181-CO-3 and 2FD97-1585. The authors are thankful to Catalana de Polìmers S.L. Barcelona (Spain) for their generous gift of the $PET_{60}I_{40}$ sample.

Supporting Information Available: Table showing experimental and theoretical sequence distribution and randomness of PETI^{t}BI terpolyesters. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Li, B.; Yu, J.; Lee, S.; Ree, M. *Eur. Polym. J.* **1999**, *35*, 1607. (b) Li, B.; Yu, J.; Lee, S.; Ree, M. *Polymer* **1999**, *40*, 5371. (c) Lee, S.; Ree, M.; Park, C. E.; Jung, Y. K.; Park, C. S.; Jin, Y. S.; Bae, D. C. *Polymer* **1999**, *40*, 7137.
(2) Wu, T. M.; Chang, C. C.; Yu, T. L. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, *38*, 2515.
(3) Karayannidis, G. P.; Sideridou, I. D.; Zamboulis, D. N.; Bikiaris, D. N.; Sakalis, A. J. *J. Appl. Polym. Sci.* **2000**, *78*, 200.
(4) Kint, D. P. R.; Martínez de Ilarduya, A.; Muñoz-Guerra, S., submitted.
(5) Kricheldorf, H. R.; Hull, W. E. *J. Polym. Sci., Part A: Polym. Chem.* **1978**, *16*, 2253. (b) Kricheldorf, H. R.; Joshi, S. V.; Hull, W. E. *J. Polym. Sci., Part A: Polym. Chem.* **1982**, *20*, 2791.
(6) Yamadera, Y.; Murano, M. *J. Polym. Sci., Part A1* **1967**, *5*, 2259.
(7) Randall, J. C. *Polymer Sequence Determination*; Academic Press: New York, 1977; p 71.
(8) Abis, L.; Po', R.; Bacchilega, G.; Occhiello, E.; Garbassi, F. *Makromol. Chem.* **1992**, *193*, 1859.
(9) Spera, S.; Po', R.; Abis, L. *Polymer* **1993**, *34*, 3380.
(10) Spera, S.; Po', R.; Abis, L. *Polymer* **1996**, *37*, 729.
(11) Martínez de Ilarduya, A.; Kint, D. P. R.; Muñoz-Guerra, S. *Macromolecules* **2000**, *33*, 4596.
(12) Moore, W. R.; Sanderson, D. *Polymer* **1968**, *3*, 153.
(13) Kint, D. P. R.; Martínez de Ilarduya, A.; Muñoz-Guerra, S. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1994.

MA011130A