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Notes

Sequence Analysis of Poly(ethylene terephthalate-*co*-isophthalate) Copolymers by ^{13}C NMR

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Introduction

Poly(ethylene terephthalate-*co*-isophthalate) copolyesters, abbreviated PETI, are materials of great industrial interest and extensive use. For a better understanding of the physical and mechanical properties of these copolymers, their microstructures should be characterized in full detail. It is generally accepted that NMR spectroscopy is the appropriate technique for the determination of sequence distribution and randomness of PETI copolyesters. Yamadera and Murano[1] anticipated that, under suitable experimental conditions, the methylene protons of the ethylene glycol unit could give rise to signals indicative of the chemical heterogeneity present in the copolyesters. Po' et al.[2−5] reported, however, that such protons showed a singlet at 4.78 ppm in the 300 MHz ^{1}H NMR spectra, revealing that the electronic and/or steric influences that they receive from terephthalic (T) and isophthalic (I) units are very similar. More recently, Ha et al.[6] found that the oxyethylene proton resonances for TT, TI, and II dyad sequences were undistinguishable, even in the 500 MHz ^{1}H NMR spectra. Although the aromatic region of these spectra appeared to be sensitive to microstructure effects, the resolution achieved was insufficient to measure the sequence lengths and distributions with accuracy and certainty.

Characterization of PETI copolyesters has been attempted by ^{13}C NMR spectroscopy too.[5] Although splitting of the terephthalic quaternary carbon signal into three peaks could be observed in ^{13}C NMR spectra, the unavailability of similar data relative to the isophthalic units prevented the determination of the microstructure by this method. In the present communication we wish to report on the analysis of PETI copolyesters by 75.5 MHz ^{13}C NMR carried out in 2% (w/v) deuterated trifluoroacetic acid (TFA-d_1) solution at 25.0 ± 0.1 °C. Under these experimental conditions, spectral resolutions higher than all others previously reported were attained. Information provided by such means has allowed us to describe with high accuracy and reliability the dyad and triad sequence distribution of these copolyesters.

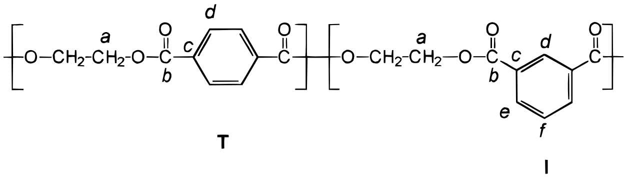

Figure 1. Chemical structure of PETI copolyesters with notations used for NMR assignments.

Experimental Section

This study covers a series of PETI copolyesters with terephthalic to isophthalic unit ratios (T/I) ranging from 94/6 to 60/40, in addition to poly(ethylene terephthalate) homopolyester (PET). The copolyester composition is denoted in the corresponding abbreviation by the appropriate subscripts, e.g. PET$_{60}$I$_{40}$. All polymers used in this work were kindly provided by Catalana de Polìmers S.L. (Barcelona, Spain) and they all were obtained by melt polycondensation.

Intrinsic viscosities of copolyesters were determined in dichloroacetic acid at 25.0 ± 0.1 °C using an Ubbelohde viscometer and found to be within the range of 0.63 to 0.71 dL g^{-1}. Their molecular weights were approximately estimated to range between 15 800 and 20 400 by applying the Mark−Houwink parameters reported in the literature for PET in the same solvent.[7]

^{1}H and ^{13}C NMR spectra were recorded with a Bruker AMX-300 spectrometer at 25.0 ± 0.1 °C, operating at 300.1 and 75.5 MHz, respectively. The copolyesters were dissolved in TFA-d_1 (2% w/v) and chemical shifts were measured with respect to tetramethylsilane (TMS). For ^{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 15000 FIDs were acquired with 64 K 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. 2D ^{13}C−^{1}H heteronuclear shift correlation spectra (HETCOR) were recorded by means of the *hxco* pulse sequence implemented in the Bruker NMR instrument package.

Results and Discussion

The chemical structure of PETI copolyesters with indication of the notation used in this work for NMR assignments is shown in Figure 1. ^{1}H and ^{13}C NMR spectra of PET$_{60}$I$_{40}$ are reproduced in Figure 2 for illustration. Signal assignment was accomplished by comparison of spectra obtained for different copolymer compositions and it was supported by correlation data provided by 2D NMR HETCOR spectra (Figure 3). Chemical shifts of all peaks appearing in such spectra together with their respective assignments are given in Table 1. The signal at 4.94 ppm appearing as a singlet in the ^{1}H NMR spectra of PETI indicates that the CH$_2$ oxyethylene protons associated with TT, TI, and II dyad sequences are magnetically equivalent. No splitting of

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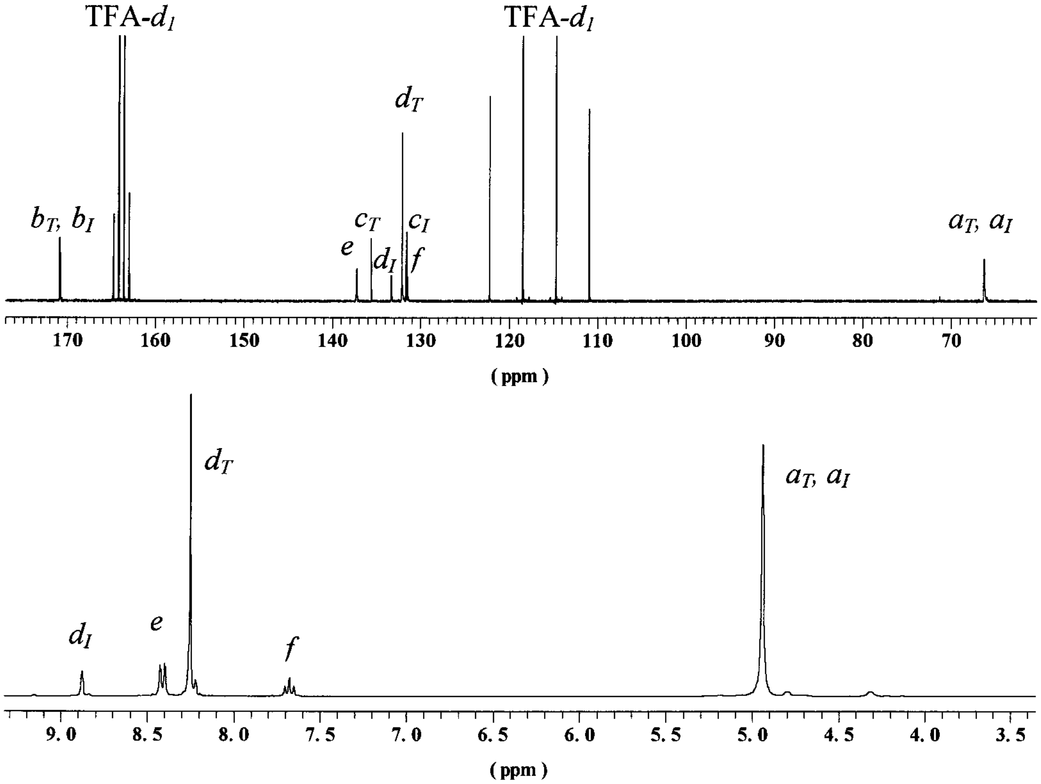

Figure 2. ^{1}H (bottom) and ^{13}C NMR (top) spectra of $PET_{60}I_{40}$ recorded in TFA-d_1.

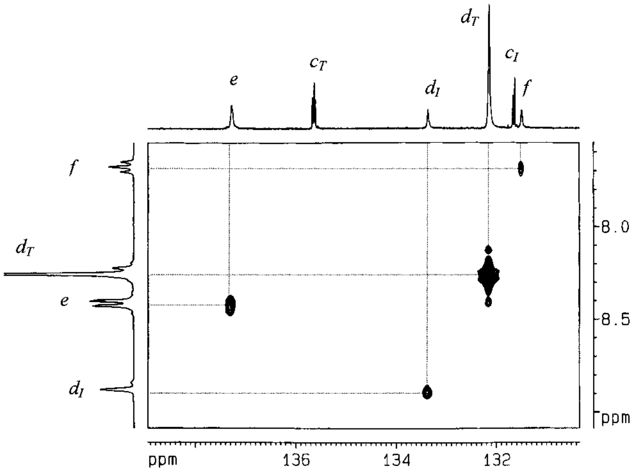

Figure 3. The^{1}H−^{13}C heteronuclear shift correlation spectrum (HETCOR) of $PET_{60}I_{40}$ recorded in TFA-d_1.

Table 1. ^{1}H and ^{13}C NMR Chemical Shifts (δ in ppm) of PET and PETI Copolyesters in TFA-d_1

	^{1}H Chemical Shifts					
	$^{T}H_a$	$^{T}H_d$	$^{I}H_a$	$^{I}H_d$	$^{I}H_e$	$^{I}H_f$
PET	4.94	8.25				
PETI	4.94	8.25	4.94	8.88	8.41	7.68

	^{13}C Chemical Shifts									
	$^{T}C_a$	$^{T}C_b$	$^{T}C_c$	$^{T}C_d$	$^{I}C_a$	$^{I}C_b$	$^{I}C_c$	$^{I}C_d$	$^{I}C_e$	$^{I}C_f$
PET	66.2	170.9	135.6	132.1						
PETI	66.2	170.9	135.6	132.1	66.2	170.8	131.6	133.4	137.3	131.5

signals due to sequence effects could be observed either in the aromatic region. The composition of the PETI copolyesters could be calculated straightforwardly by integration of the aromatic proton signals and results obtained by this means are reported in Table 2.

Table 2. Intrinsic Viscosity and Composition of Copolyesters

polyester	[η]^a (dL g^{-1})	M_n^{b} (g mol^{-1})	[T]/[I]^c ^{1}H^d	[T]/[I]^c ^{13}C^e
PET	0.63	15 800	100/0	100/0
$PET_{94}I_6$	0.71	20 400	93.9/6.1	94.6/5.4
$PET_{90}I_{10}$	0.65	16 900	90.1/9.9	92.4/7.6
$PET_{75}I_{25}$	0.70	19 800	74.8/25.2	77.1/22.9
$PET_{60}I_{40}$	0.70	19 800	60.2/39.8	60.1/39.9

[a] Intrinsic viscosity measured in dichloroacetic acid. [b] Number-average molecular weight calculated using the Mark−Houwink parameters reported for PET.[7] [c] Terephthalic to isophthalic molar ratio in the copolyester. [d] Determined from the aromatic proton resonances by ^{1}H NMR. [e] Determined from the aromatic quaternary carbon resonances by ^{13}C NMR.

As happens with the oxyethylene protons in the ^{1}H NMR spectra, a unique signal was observed for the oxyethylene carbons in the ^{13}C NMR spectra. It can be concluded that the oxymethylene units are nonsensitive to sequence effects and useless therefore for the determination of the microstructure of PETI copolyesters. On the contrary, a clear splitting into four and two peaks was observed for the quaternary carbon of the terephthalic and isophthalic units, respectively. The four peaks observed for the terephthalic quaternary carbon were attributed to TTT, TTI (two peaks), and ITI triad sequences, all of them centered at the terephthalic unit. The two peaks appearing for the isophthalic unit were assigned to IT and II dyad sequences (Figure 4). Several authors[8,9] had pointed out earlier that quaternary carbons are more sensitive to sequence effects than any other aromatic carbons due to the occurrence of through-space and through-bond interactions between neighboring units.

The number of resonances that can be observed for a copolymer is given by the number of dyads, triads, and higher sequences in which the two monomers may be

Table 3. Experimental[a] and Theoretical[b] (in Parentheses) Sequence Distribution and Randomness in PETI Copolyesters

	composition[c]		triads (mol %)[d]			dyads (mol %)[d]		av sequence length		randomness
copolyester	X_T	X_I	T*T*T	T*T*I	I*T*I	*I*T	*I*I	$\bar{n}_T$	$\bar{n}_I$	R
$PET_{94}I_6$	93.9	6.1	89.1	10.9	0	92.6	7.4	17.1	1.1	0.97
			(88.2)	(11.5)	(0.4)	(93.9)	(6.1)	(16.4)	(1.1)	(1.00)
$PET_{90}I_{10}$	90.1	9.9	82.3	16.9	0.8	88.2	11.8	9.6	1.1	1.00
			(81.2)	(17.8)	(1.0)	(90.1)	(9.9)	(10.1)	(1.1)	(1.00)
$PET_{75}I_{25}$	74.8	25.2	58.8	36.5	4.7	73.8	26.2	4.0	1.4	0.96
			(56.0)	(37.7)	(6.3)	(74.8)	(25.2)	(4.0)	(1.3)	(1.00)
$PET_{60}I_{40}$	60.2	39.8	37.7	46.4	15.9	57.0	43.0	2.6	1.7	0.99
			(36.2)	(47.9)	(15.8)	(60.2)	(39.8)	(2.5)	(1.7)	(1.00)

[a] Experimental values were obtained from integration of ^{13}C NMR peaks and ref 11. [b] Theoretical values were calculated on the basis of a random distribution using the copolyester compositions given in this table. [c] Calculated from the aromatic proton resonances displayed in ^{1}H NMR spectra. [d] Triad and dyad contents relative to the total of sequences centered at the terephthalic and isophthalic units.

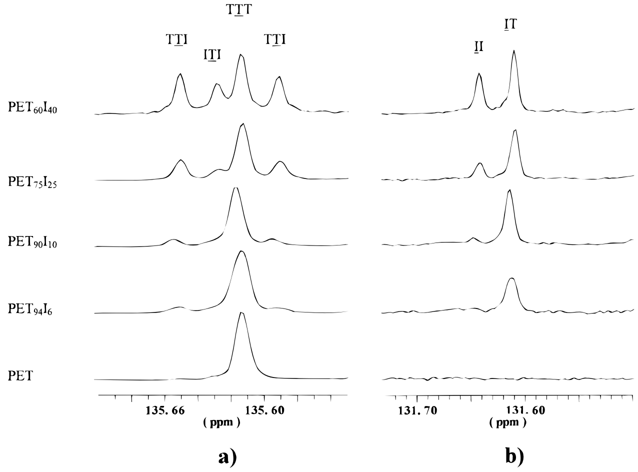

Figure 4. ^{13}C NMR spectra of PET and PETI copolyesters recorded in TFA-d_1. The aromatic region showing the quaternary carbon splitting for the terephthalic (a) an isophthalic units (b) is shown.

arranged. For an idealized random distribution of the two comonomers, the expected intensity of each peak can be calculated on the basis of a Bernoullian statistical model. If X_T and X_I represent the fractions of terephthalic and isophthalic units in the copolymer, X_T^2, $2X_TX_I$, and X_I^2 are the theoretical probabilities for the existence of TT, TI, and II dyad sequences in the copolymer. Comparison of theoretical and experimental data provides an estimation of the degree of randomness of the copolymer. For the same purpose, triad concentrations can be calculated by a similar procedure and compared with experimental data in the case that these were available. Table 3 shows the theoretical average sequence lengths and degree of randomness of PETI copolyesters calculated according to the methods reported in the literature[10,11] and using our ^{1}H NMR data. These results are compared with those obtained by integration of the terephthalic and isophthalic quaternary carbon signals. It was found that the experimentally determined average sequence lengths were in all cases in accordance with that predicted on the basis of ideal copolycondensation statistics with randomness close to unit. This is a highly expected result since melt copolycondensation tends to yield random copolyesters due to the occurrence of transesterification reactions in the molten phase.[1,12,13]

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