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Tetrad Distribution of an Aromatic Copolyterephthalate by ^{1}H NMR

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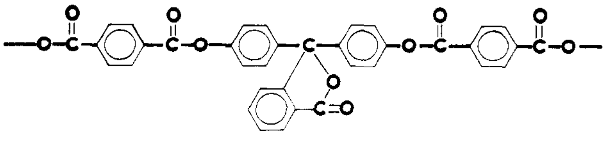
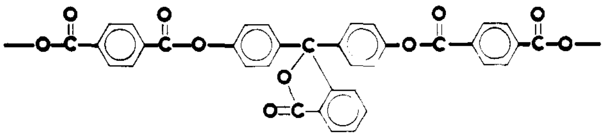
Received February 23, 1983

ABSTRACT: A method for the complete analysis of the compositional tetrad distribution of 3,3′-dimethylbisphenol A–phenolphthalein copolyterephthalate (PDT/FT) by ^{1}H NMR spectroscopy with a lanthanide-shift reagent is presented. The signal of the terephthalic protons in the 100-MHz ^{1}H NMR spectrum of the copolyterephthalate recorded in the presence of Eu(fod)$_3$ has been found to exhibit separate lines for compositional tetrads. A theoretical model of the tetrad signal spectrum has been proposed, and computer simulation has been performed to calculate probabilities of the tetrads. The data obtained for an equimolar PDT/FT copolymer synthesized at 240 °C indicate significant deviation from a random distribution of comonomer units with a tendency to form block segments along the copolymer chain.

Determination of the comonomer sequence distribution of copolyterephthalates by means of ^{1}H NMR spectroscopy has been shown to be possible utilizing for the analysis the signals of the terephthalic protons.[1-3] However, the standard ^{1}H NMR spectra, up to 100 MHz, can be successfully used for the analysis in those few cases when comonomers are sufficiently different from one another, and as far as it is known comonomer sequences longer than dyads have not yet been recorded. In the case of a fully aromatic copolyterephthalate the standard spectra are useless for this purpose because the terephthalic signals of each homosequence occupy nearly the same position at about 8.40 ppm. The standard 100-MHz ^{1}H NMR spectra of the aromatic copolyterephthalate obtained from terephthaloyl chloride, being an intermonomer, and equimolar amounts of 3,3′-dimethylbisphenol A and phenolphthalein as comonomers (PDT/FT) were found to be useless for sequence analysis because terephthalic signals of PDT/FT as well as the signals of corresponding homopolyterephthalates exhibit a single terephthalic signal at 8.36 ppm (Figure 1). Application of Eu(fod)$_3$ lanthanide shift reagent was found to be a useful method for separating the terephthalic proton singlet of PDT/FT into signals of three compositional dyads,[3] while the methyl signal of a D unit in the PDT/FT chain was found to show only traces of splitting into signals of compositional triads.[4]

Since the PDT/FT copolymer is derived from symmetrical monomers which can be incorporated in only one way into the polymer chain, there is no head-to-head and head-to-tail isomerism. The small anisotropic effect of the phenolphthalein unit can also be neglected as shown by investigations of the homopolyterephthalate of phenolphthalein.[4] Hence, configurational sequences need not be taken into account. Differences in the copolyterephthalate microstructure are due only to comonomer unit distribution while the intermonomer units introduce no differentiation and can be omitted in the description for the sake of clarity. Henceforth the term "sequence" stands for compositional sequence.





Experimental Section

3,3′-Dimethylbisphenol A/phenolphthalein copolyterephthalate (50:50) (PDT/FT) was prepared at 240 °C by polycondensation of terephthaloyl chloride (Fluka AG) as intermonomer and equimolar amounts of 3,3′-dimethylbisphenol A and phenolphthalein (POCh, Poland) as comonomers in solution of redistilled α-chloronaphthalene (Reachim, USSR) under an argon atmosphere.

The molecular weight of the sample was about 16 000 as determined in THF by the Knauer vapor pressure osmometer and the Waters Associates Instruments ALC/GPC-202/401 chromatograph. Thus, the degree of polymerization was about 45 since for the equimolar PDT/FT copolymer sample, an average molecular weight of the repeating unit, $\bar{m}$, can be calculated according to

$$\bar{m} = (M_{\text{-D-}} + 2M_{\text{-T-}} + M_{\text{-F-}})/2 \qquad (1)$$

where $M_{\text{-D-}}$, $M_{\text{-T-}}$, and $M_{\text{-F-}}$ are the molecular weights of the 3,3′-dimethylbisphenol A, terephthalic, and phenolphthalein units in the chain, respectively.

^{1}H NMR spectra were recorded on a Varian 100-MHz XL-100 spectrometer by using 5 wt % solutions in CDCl$_3$ (Merck) at room temperature. Eu(fod)$_3$ (Fluka AG) was used as a lanthanide shift reagent (LSR).

Computer simulation of tetrad signals was performed by means of a Wang 2200 desk top computer equipped with a Wang 2212 X–Y plotter. The experimental spectra were compared with the simulated ones drawn by the plotter by means of a program for superposition of 28 Lorentzian–Gaussian lines.

Recording of Tetrad Signals. At higher concentration of Eu(fod)$_3$, the highly resolved terephthalic proton signals

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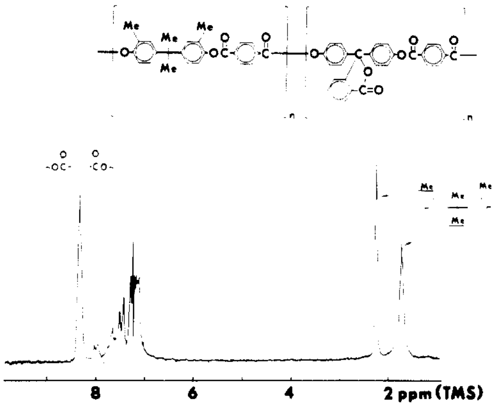


Figure 1. 100-MHz ^{1}H NMR standard spectrum of 3,3′-dimethylbisphenol A/phenolphthalein copolyterephthalate (PDT/FT) (5 wt % solution in CDCl$_3$).

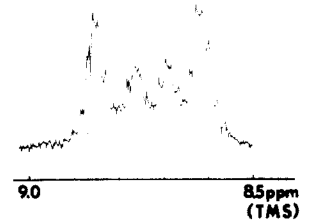


Figure 2. Tetrad splittings of 100-MHz ^{1}H NMR terephthalic signal of PDT/FT copolyterephthalate recorded in the presence of Eu(fod)$_3$ ([Eu(fod)$_3$]/[T] = 1.2).

of dyads were found to exhibit further splitting (Figure 2) which can be assigned to higher sequences. It is possible to clearly separate the outside signals by about 0.4 ppm. On further increasing the Eu(fod)$_3$ concentration the phenolphthalein signals, which are more shifted, superimpose on the terephthalic signals. The Eu(fod)$_3$ concentration was calculated from the NMR spectrum as a molar ratio of Eu(fod)$_3$ with respect to the terephthalic units in the copolymer chain according to the following equation:

$$[\mathrm{Eu(fod)_3}]/[\mathrm{T}] = 4I_{t\text{-Bu}}/27I_{\mathrm{T}} \tag{2}$$

where $I_{t\text{-Bu}}$ and I_{T} are the relative intensities of the Eu(fod)$_3$ *t*-Bu signal and terephthalic signal, respectively, in the ^{1}H NMR spectrum. Pr(fod)$_3$, shifting upfield, has also been examined, and though the induced signal separation was comparable with that of Eu(fod)$_3$, the broadening caused by Pr was greater and the tetrad fine splittings were not resolved.

Evaluation of the Theoretical Tetrad Spectrum

Out of 16 possible tetrads only 10 can be observed with NMR spectroscopy. In the case of a copolyterephthalate with symmetrical comonomers only four symmetrical tetrads, AAAA, BAAB, ABBA, and BBBB, give singlet signals, while the remainder give quartets, due to AB splittings. (Because the terephthalic system is analogous to the symmetrical 1,4-substituted benzene ring and the meta and para splittings are relatively small and because polymer signals are rather broad, it seems justifiable to adapt the simpler AB rules instead of the AA′BB′ rules.)

To calculate the lanthanide-induced shifts (LIS) of the terephthalic protons in every tetrad it can be assumed that the LIS value is influenced by four flanking units, two on each side of the central terephthalic unit in the tetrad. In the presence of the LSR the differences in dyad shifts are due to the influences of the two nearest units, α_{F} or α_{D}, one on each side. When the signal is sensitive to tetrads it means that the influence of the next two neighboring units, β_{F} and β_{D}, should be considered (Figure 3).

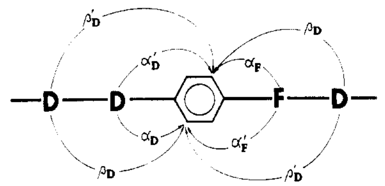


Figure 3. Influence of α and β flanking units on the LIS of terephthalic protons in the presence of LSR.

In the first approach, additivity of influences can be assumed, and LIS values can be calculated for every tetrad as a combination of α and β increments, added to the original chemical shift of the terephthalic protons in the standard spectrum, δ_0.

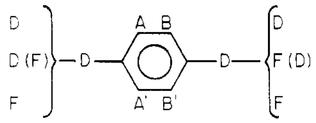
To calculate the positions of lines in the theoretical spectrum of terephthalic protons split in the presence of LSR, it is necessary to make the following assumptions. (1) The LIS value of the terephthalic proton signal depends on the influence of four neighboring units in the chain, whose influences are additive. (2) The influence of α neighboring units is greater than that of β ones; i.e., tetrad splitting is weaker than that of dyads. (3) The given increment, e.g., α_{F}, is constant at a given LSR concentration, independent of the kind of tetrad in which it is considered. (4) The influence across the terephthalic system (denoted by primes) are weaker than the direct ones; i.e., $\alpha' < \alpha$ and $\beta' < \beta$ (see Figure 3). (5) For β increments the unit between the terephthalic system and the second unit does not change the β value; e.g.,

$$\beta_{\mathrm{D}}(\text{over D}) = \beta_{\mathrm{D}}(\text{over F}) = \beta_{\mathrm{D}}, \text{ etc.} \tag{3}$$

The following notation will be used for calculations: $\delta_{\mathrm{A}}{}^{\mathrm{FF}}$ (ppm), chemical shift of A proton in the FF dyad, regarding only α and α' increments; $\delta_{\mathrm{A}}{}^{\mathrm{DFFF}}$ (ppm), chemical shift of A proton in the DFFF tetrad, regarding α, α', β, and β' increments; δ_0 (ppm), chemical shift of the terephthalic proton signal in the standard spectrum.

The positions of the lines of tetrads in the spectrum of the terephthalic protons split by Eu(fod)$_3$ can be calculated as shown below.

(a) For the DD dyad and the tetrads with a central DD dyad

possible sequences	spin system	signal
	A_4 $AA'BB' \cong AB$ A_4	singlet quartet singlet

The DD dyad shift is

$$\delta^{\mathrm{DD}} = \delta_{\mathrm{A}}{}^{\mathrm{DD}} = \delta_{\mathrm{B}}{}^{\mathrm{DD}} = \delta_0 + \alpha_{\mathrm{D}} + \alpha'_{\mathrm{D}} \tag{4}$$

The tetrad shifts are given by

$$\delta^{\mathrm{DDDD}} = \delta_{\mathrm{A}}{}^{\mathrm{DDDD}} = \delta_{\mathrm{B}}{}^{\mathrm{DDDD}} = \delta^{\mathrm{DD}} + \beta_{\mathrm{D}} + \beta'_{\mathrm{D}} \tag{5}$$

$$\delta_{\mathrm{A}}{}^{\mathrm{DDDF}} = \delta^{\mathrm{DD}} + \beta_{\mathrm{D}} + \beta'_{\mathrm{F}} \tag{6}$$

$$\delta_{\mathrm{B}}{}^{\mathrm{DDDF}} = \delta^{\mathrm{DD}} + \beta_{\mathrm{F}} + \beta'_{\mathrm{D}} \tag{7}$$

Because in NMR spectroscopy for symmetrical monomers the DDDF tetrad cannot be distinguished from FDDD and the chemical shifts of the reverse sequences are equal; i.e.,

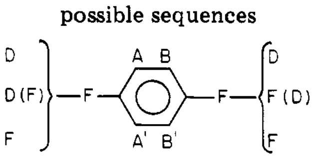
$$\delta_{\mathrm{A}}{}^{\mathrm{DDDF}} = \delta_{\mathrm{B}}{}^{\mathrm{FDDD}} \tag{8a}$$

$$\delta_{\mathrm{B}}{}^{\mathrm{DDDF}} = \delta_{\mathrm{A}}{}^{\mathrm{FDDD}} \tag{8b}$$

it is sufficient to determine only one shift for one sequence in the pair.

$$\delta^{\mathrm{FDDF}} = \delta_{\mathrm{A}}{}^{\mathrm{FDDF}} = \delta_{\mathrm{B}}{}^{\mathrm{FDDF}} = \delta^{\mathrm{DD}} + \beta_{\mathrm{F}} + \beta'_{\mathrm{F}} \tag{9}$$

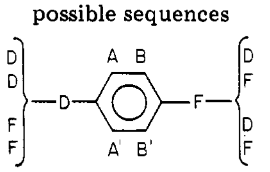
(b) For the FF dyad and the tetrads with a central FF dyad



spin system	signal
A_4	singlet
$AA'BB' \cong AB$	quartet
A_4	singlet

The calculations are the same as for tetrads with central DD dyads as shown for case a.

(c) For the $\overline{DF}$ dyad and the tetrads with a central $\overline{DF}$ dyad



spin system	signal
$AA'BB' \cong AB$	quartet
$AA'BB' \cong AB$	quartet
$AA'BB' \cong AB$	quartet
$AA'BB' \cong AB$	quartet

The $\overline{DF}$ dyad shift is

$$\delta_A{}^{DF} = \delta_B{}^{FD} = \delta_0 + \alpha_D + \alpha'_F \tag{10}$$

$$\delta_B{}^{DF} = \delta_A{}^{FD} = \delta_0 + \alpha_F + \alpha'_D \tag{11}$$

The tetrad shifts are

$$\delta_A{}^{DDFD} = \delta_B{}^{DFDD} = \delta_A{}^{DF} + \beta_D + \beta'_D \tag{12}$$

$$\delta_B{}^{DDFD} = \delta_A{}^{DFDD} = \delta_B{}^{DF} + \beta_D + \beta'_D \tag{13}$$

etc.

For a given LSR concentration the values of α, α', β, and β' can be estimated and a theoretical spectrum, based on the model of α and β increments, can be calculated. On the basis of experimental data obtained for the PDT/FT copolymer spectrum, recorded in the presence of Eu(fod)$_3$,[4] it is reasonable to assume: (1) $\delta_0 = 8.36$ ppm, chemical shift of the terephthalic protons is given in the standard spectrum; (2) $\alpha_D > \alpha_F$, DD homodyad signal shift is greater than that of FF dyad; (3) $\beta_D > \beta_F$, the same direction of influences should be expected for β increments; (4) $\alpha \gg \beta$ and $\alpha' \gg \beta'$, tetrad splitting is much weaker than that of dyad; (5) $\alpha > \alpha'$ and $\beta > \beta'$, the influence "over" the terephthalic system is weaker than the direct one.

An estimation of relations between α and β values can be accomplished on the basis of analogy with an aliphatic copolymer. For instance, in the case of vinylidene chloride–isobutylene copolymer[5,6] the separations of the outermost signals, $\Delta\delta$, are

$$\Delta\delta_{dyad} = 2.5 \text{ ppm}$$

$$\Delta\delta_{tetrad} = 0.4 \text{ ppm}$$

$$\Delta\delta_{hexad} = 0.04 \text{ ppm}$$

i.e., $\Delta\delta_{dyad}$:$\Delta\delta_{tetrad}$:$\Delta\delta_{hexad}$ = 62.5:10:1.

It can be seen from this comparison that in aliphatic copolymers dyad signal separation is about 1 order of magnitude higher than for tetrads, and tetrad separation is 1 order of magnitude higher than for hexads. On the basis of this rough analogy it is possible, in a first approximation, to assume a similar relation in condensation copolymers, i.e. that α increments are about 1 order of magnitude higher than β increments. Thus, the theoretical spectrum of the terephthalic proton signal split in the presence of Eu(fod)$_3$ can be constructed according to the scheme presented in Figure 4.

According to the scheme, the theoretical spectrum was calculated for the following set of parameters, and additionally the simplest statistics (equal probability of each tetrad) was assumed to calculate the intensities of the lines: $\delta_0 = 8.36$ ppm; $\alpha_D = 0.91$ ppm; $\alpha'_D = 0.32$ ppm; $\beta_D = 0.06$ ppm; $\beta'_D = 0.03$ ppm; $\alpha_F = 0.47$ ppm; $\alpha'_F = 0.15$ ppm; $\beta_F = 0.02$ ppm; $\beta'_F = 0.01$ ppm. The theoretical spectrum obtained in this way (Figure 5) exhibits significant similarity with the experimental one (Figure 2).

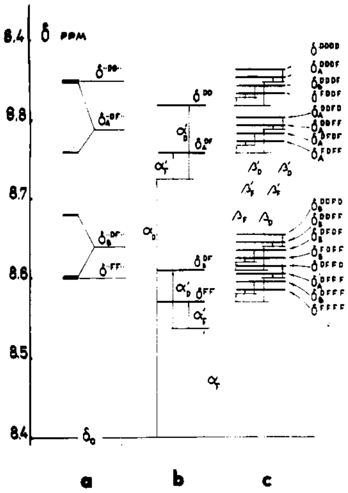


Figure 4. Scheme for calculation of the positions of tetrad lines in the theoretical spectrum of PDT/FT in the presence of Eu(fod)$_3$: (a) positions of experimental lines; (b) positions of theoretical lines regarding α influences only; (c) positions of theoretical lines regarding α and β influences.

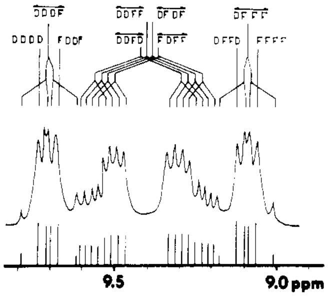


Figure 5. Theoretical spectrum of terephthalic protons of PDT/FT copolymer split by LSR.

Computer-Simulated Tetrad Spectrum

Computer simulation has been performed in order to confirm the agreement between the theoretical and experimental spectra of tetrad signals and to evaluate quantitative data on tetrad distribution. If the calculated and experimental spectra are in good agreement with each other, the tetrad probabilities can be readily calculated from the intensities of the components of simulated spectra.

A computer program in BASIC, developed by Dworak[7] for a Wang 2200 desk-top computer, has been adopted to calculate and draw, by means of an X–Y plotter, a superposition of 28 lines, the positions, heights, and widths of which were fed to the computer as starting data. To obtain the shape of a single line the form between Gaussian and Lorentzian lines has been used:

$$S(f) = aL(f) + (1 - a)G(f) \tag{14}$$

where $S(f)$ is the single line shape, $L(f)$ and $G(f)$ are the Lorentzian and Gaussian lines, respectively, and a is the coefficient determining Gaussian and Lorentzian proportions in an experimentally observed signal.

To fit the simulated spectrum to the experimental spectrum of tetrads of PDT/FT copolyester, the following procedure was performed.

Line Assignment to the Respective Tetrads. (a) On the basis of the model of influences of α and β neighboring units and the theoretical spectrum shape, it is possible at first to assign the four signals of symmetrical sequences (singlets) and the two central lines of each asymetrical sequence signal (quartets) of both homodyads; i.e., DD and FF signals are split into the lines of the tetrads having the respective dyad in the center. Thus, in the signals of both homodyads the two central lines have been assigned to the asymetric tetrads, i.e. to the $\overline{\mathrm{DDDF}}$ tetrad in the DD homodyad signal and to the $\overline{\mathrm{FFFD}}$ tetrad in the FF homodyad signal. The next two lines in the region of each homodyad signal can be assigned now to symmetrical tetrads. On the basis of experimental results obtained for dyads,[4] i.e., that the DD dyad is more strongly shifted downfield than the FF dyad, it is reasonable to assume that the DDDD tetrad singlet is shifted downward with respect to the singlets of the FDDF tetrad. Analogously, in the region of the FF dyad signal the singlet at lower field may be assigned to the $\overline{\mathrm{DFFF}}$ tetrad and the other one to the FFFF tetrad. The central two lines of the $\overline{\mathrm{DF}}$ dyad quartet are split into further lines which can be assigned to the central lines of the quartets exhibited by tetrads having the central $\overline{\mathrm{DF}}$ dyad. The order of their occurrence in the spectrum can be determined by considering the influences of the α and β neighboring units on the LIS of terephthalic protons. In this way, from among 28 lines, the following 16 lines have been assigned and the positions of them can be taken directly from the experimental spectrum (the sequences are listed in order from lower to higher field): δ_{DDDD}, $\delta_{\mathrm{A}_2(\overline{\mathrm{DDDF}})}$, $\delta_{\mathrm{B}_2(\overline{\mathrm{DDDF}})}$, δ_{FDDF}; $\delta_{\mathrm{A}_2(\overline{\mathrm{DDFD}})}$, $\delta_{\mathrm{A}_2(\overline{\mathrm{DDFF}})}$, $\delta_{\mathrm{A}_2(\overline{\mathrm{FDFD}})}$, $\delta_{\mathrm{A}_2(\overline{\mathrm{FDFF}})}$; $\delta_{\mathrm{B}_2(\overline{\mathrm{DDFD}})}$, $\delta_{\mathrm{B}_2(\overline{\mathrm{DDFF}})}$, $\delta_{\mathrm{B}_2(\overline{\mathrm{FDFD}})}$, $\delta_{\mathrm{B}_2(\overline{\mathrm{FDFF}})}$; δ_{DFFD}, $\delta_{\mathrm{A}_2(\overline{\mathrm{DFFF}})}$, $\delta_{\mathrm{B}_2(\overline{\mathrm{DFFF}})}$, δ_{FFFF}.

(b) Due to the AB spin–spin splitting rules[8] the positions of the remaining lines, being the outer lines A_1 and B_1 of the asymmetric tetrad quartets, can be calculated. The value of J_{AB}, ranging from 4.6 to 5.2 Hz, can be estimated from the experimental spectrum as the distance between the central lines of the four tetrads $\overline{\mathrm{DDDF}}$, $\overline{\mathrm{DDFD}}$, $\overline{\mathrm{FDFF}}$, and $\overline{\mathrm{DFFF}}$ and their respective outer components, since some of them can be seen in the spectrum. The values, being in the range for the ortho constants for the terephthalic system, give the best match for the lines. In this way the positions of all 28 lines have been obtained.

Spectrum Calculation. (c) The positions of the lines, obtained according to paragraphs a and b, have been fed into the computer as starting parameters. On the basis of the experimental spectrum, approximate values of the line heights (h_i) and half-height widths (Δs_i) have been assumed.

(d) Calculation of the spectrum shape has been performed in two stages: the shape of an individual line has been calculated according to the equation

$$F_i(f) = aL_i(f) + (1 - a)G_i(f) \tag{15}$$

and the envelope curve of the total spectrum has been calculated according to the equation

$$S(f) = \sum_{i=1}^{n} F_i(f) \tag{16}$$

Computing and Matching Procedure. (e) The calculated and drawn spectra were compared with the experimental one, and the starting parameters were corrected repeatedly with respect to the overall changes (paragraph c) until satisfactory agreement was obtained. However, the changes in the starting parameters cannot be introduced arbitrarily because the relations between the intensities of the AB system must be obeyed (paragraph b) as well as the relations between tetrad probabilities (paragraph g). Every change in the height of one line involves necessary changes in the other related lines. After several approximations it was found that for the sake of optimum matching, the half-height widths of the signals should cover the range from 0.8 to 1.5 Hz, which is in good accordance with experimental results.

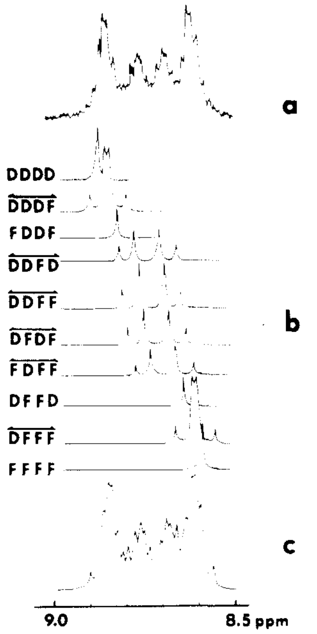


Figure 6. Comparison of the experimental spectrum of tetrad splittings of PDT/FT copolymer (a) with the computer-simulated spectrum (c) and its components (b).

Intensity Calculations. (f) Calculations of relative intensities, I_i, of the lines were performed according to the equation

$$I_i = h_i\Delta s_i / \sum_{i=1}^{n} h_i\Delta s_i \tag{17}$$

On the basis of relative intensities, obtained due to the above procedure, the probabilities of the tetrads can be calculated as a sum of the intensities of respective signals with respect to the total intensity of the terephthalic proton signal.

Checking of Correct Assignment and Spectrum Fitting. (g) Apart from the statistics of the chain, there are two independent equations, which must always be obeyed. Hence, these equations can be applied as a criterion for proper signal assignment and as a measure of discrepancy between the calculated and experimental spectra.

$$P(\overline{\mathrm{DDDF}}) + 2P(\mathrm{FDDF}) = P(\overline{\mathrm{DDFD}}) + P(\overline{\mathrm{DDFF}}) \tag{18}$$

$$P(\overline{\mathrm{DFFF}}) + 2P(\mathrm{DFFD}) = P(\overline{\mathrm{FFDF}}) + P(\overline{\mathrm{FF.\ \ D}}) \tag{19}$$

Accuracy of the presented line resolution has been confirmed by planimetry for a spectrum with well-defined distribution and was found to be better than 5%.[7]

Results and Discussion

Calculation of Tetrad Distribution of PDT/FT Copolyester. A fairly good agreement of the simulated spectrum with the experimental one was obtained for the set of parameters presented in Table I. The computer-simulated spectrum, its components, and the experimental spectrum are compared in Figure 6. The relative intensities, calculated from the simulated spectrum, and the tetrad probabilities calculated from these data are pres-

Table I
Parameters of the Computer-Simulated Tetrad Spectrum of Terephthalic Proton Signals in the 100-MHz ^{1}H NMR Spectrum of PDT/FT Copolyester Split with Eu(fod)$_3$

line no.	line position, ppm	relative height	line width,[a] Hz	relative intensity
1	8.900	2.30	0.8	1.84
2	8.869	10.20	1.5	15.30
3	8.854	11.00	1.5	16.50
4	8.842	11.00	1.5	16.50
5	8.828	2.30	1.0	2.30
6	8.825	4.00	1.2	4.80
7	8.818	3.30	1.1	3.63
8	8.806	3.40	1.1	3.74
9	8.796	2.30	0.8	1.84
10	9.793	2.50	1.0	2.50
11	8.781	5.00	1.2	6.00
12	8.767	6.50	1.3	8.45
13	8.756	6.50	1.3	8.45
14	8.742	5.00	1.2	6.00
15	8.717	5.00	1.2	6.00
16	8.701	7.00	1.4	9.80
17	8.688	7.00	1.4	9.80
18	8.673	1.40	0.8	1.12
19	8.670	5.00	1.2	6.00
20	8.667	2.30	1.0	2.30
21	8.651	3.50	1.1	3.85
22	8.638	3.50	1.1	3.85
23	8.636	4.80	1.2	5.76
24	8.624	9.20	1.5	13.80
25	8.620	2.50	1.0	2.50
26	8.611	10.00	1.5	15.00
27	8.596	10.50	1.5	15.75
28	8.562	1.40	0.8	1.12

[a] Line half-height width.

Table II
Relative Intensities of Tetrad Signals and Tetrad Probabilities Calculated from the Computer-Simulated Spectrum

relative intensities of tetrad signals	tetrad probability
$I_{\mathrm{DDDD}} = I_2 = 9.8$	$P(\mathrm{DDDD}) = 0.063$
$I_{\overline{\mathrm{DDDF}}} = I_1 + I_3 + I_4 + I_9 = 29.9$	$P(\overline{\mathrm{DDDF}}) = 0.192$
$I_{\mathrm{FDDF}} = I_5 = 3.8$	$P(\mathrm{FDDF}) = 0.025$
$I_{\overline{\mathrm{DDFD}}} = I_6 + I_{11} + I_{15} + I_{20} = 13.1$	$P(\overline{\mathrm{DDFD}}) = 0.084$
$I_{\overline{\mathrm{DDFF}}} = I_7 + I_{12} + I_{16} + I_{21} = 24.1$	$P(\overline{\mathrm{DDFF}}) = 0.154$
$I_{\overline{\mathrm{DFDF}}} = I_8 + I_{13} + I_{17} + I_{23} = 16.1$	$P(\overline{\mathrm{DFDF}}) = 0.103$
$I_{\overline{\mathrm{FDFF}}} = I_{10} + I_{14} + I_{19} + I_{25} = 12.8$	$P(\overline{\mathrm{FDFF}}) = 0.082$
$I_{\mathrm{DFFD}} = I_{22} = 2.5$	$P(\mathrm{DFFD}) = 0.016$
$I_{\overline{\mathrm{DFFF}}} = I_{18} + I_{24} + I_{26} + I_{28} = 32.6$	$P(\overline{\mathrm{DFFF}}) = 0.209$
$I_{\mathrm{FFFF}} = I_{27} = 11.2$	$P(\mathrm{FFFF}) = 0.072$
$\sum_{i=1}^{28} I_i = 156.0$	$\sum_{i=1}^{10} P_i = 1.000$

ented in Table II. For the calculated spectrum, criteria of correct tetrad assignment are as follows:

$$P(\overline{\mathrm{DDDF}}) + 2P(\mathrm{FDDF}) = P(\overline{\mathrm{DDFD}}) + P(\overline{\mathrm{DDFF}})$$
$$37.6 = 37.2 \text{ (discrepancy 1.1\%)}$$

$$P(\overline{\mathrm{DFFF}}) + 2P(\mathrm{DFFD}) = P(\overline{\mathrm{FFDF}}) + P(\overline{\mathrm{FFDD}})$$
$$37.6 = 36.9 \text{ (discrepancy 1.9\%)}$$

Tetrad probabilities calculated in this way can be used as starting parameters for further calculations of shorter sequence probabilities, i.e., triad, dyad, and monad (composition) (Table III), and the sequence probabilities can be used for calculation of conditional probabilities up to the third order (Table IV).

The composition of the copolymer, calculated from tetrad probabilities is in very good accordance with the overall composition of the copolymer, determined by means of a simple integration of the respective signals in the spectrum. This consistency can be regarded as an additional confirmation of a proper signal assignment.

Table III
Triad, Dyad, and Monad (Composition) Probabilities of the PDT/FT Copolymer Calculated from Tetrad Probabilities Obtained for the Computer-Simulated Spectrum

monads (composition of the copolymer)	dyads	triads
	$P(\mathrm{DD}) = 0.280$	$P(\mathrm{DDD}) = 0.159$
$P(\mathrm{D}) = 0.492$		$P(\overline{\mathrm{DDF}}) = 0.240$
	$P(\overline{\mathrm{DF}}) = 0.423$	$P(\mathrm{FDF}) = 0.092$
$P(\mathrm{F}) = 0.508$		$P(\mathrm{DFD}) = 0.093$
	$P(\mathrm{FF}) = 0.297$	$P(\overline{\mathrm{DFF}}) = 0.239$
		$P(\mathrm{FFF}) = 0.177$

Table IV
First-, Second-, and Third-Order Conditional Probabilities of the PDT/FT Copolymer Calculated from Tetrad Probabilities

first order	second order	third order
$P(\mathrm{D/D}) = 0.569$	$P(\mathrm{DD/D}) = 0.568$	$P(\mathrm{DDD/D}) = 0.396$
		$P(\mathrm{FDD/D}) = 0.800$
	$P(\mathrm{FD/D}) = 0.567$	$P(\mathrm{DFD/D}) = 0.452$
		$P(\mathrm{FFD/D}) = 0.654$
$P(\mathrm{F/D}) = 0.423$	$P(\mathrm{DF/D}) = 0.440$	$P(\mathrm{DDF/D}) = 0.350$
		$P(\mathrm{FDF/D}) = 0.560$
	$P(\mathrm{FF/D}) = 0.402$	$P(\mathrm{DFF/D}) = 0.134$
		$P(\mathrm{FFF/D}) = 0.590$
$P(\mathrm{D/F}) = 0.423$	$P(\mathrm{DD/F}) = 0.428$	$P(\mathrm{DDD/F}) = 0.604$
		$P(\mathrm{FDD/F}) = 0.208$
	$P(\mathrm{FD/F}) = 0.435$	$P(\mathrm{DFD/F}) = 0.554$
		$P(\mathrm{FFD/F}) = 0.343$
$P(\mathrm{F/F}) = 0.585$	$P(\mathrm{DF/F}) = 0.565$	$P(\mathrm{DDF/F}) = 0.642$
		$P(\mathrm{FDF/F}) = 0.445$
	$P(\mathrm{FF/F}) = 0.596$	$P(\mathrm{DFF/F}) = 0.874$
		$P(\mathrm{FFF/F}) = 0.407$

The sequence probabilities and conditional probabilities can be used to calculate several "one-number" parameters, frequently used for the characterization of a copolymer chain.

(1) The average block length is given by

$$\bar{n}(\mathrm{D}) = \frac{1}{P(\mathrm{D/F})} = \frac{1}{0.423} = 2.364 = \bar{n}(\mathrm{F})$$

This value is a little higher than for a random copolymer and indicates a slight deviation toward a block chain.

(2) The persistence ratio,[9,10] developed for configurational sequence distributions, represents a measure of the deviation of the actual chain statistics from the simplest statistics possible, i.e., the Bernoullian statistics, and for the PDT/FT copolymer may be calculated as

$$\eta_{\mathrm{D}} = P(\mathrm{D})/P(\mathrm{F/D}) = 1.163$$

$$\eta_{\mathrm{F}} = P(\mathrm{F})/P(\mathrm{D/F}) = 1.201$$

The value of η increases from $^1/_2$ for a chain of purely alternating structure (...DFDFDF...) to unity, as the chain assumes a Bernoullian distribution of comonomers, and then increases without limit as the chain assumes more and more block character. Therefore, the values obtained for the PDT/FT copolymer sample investigated also indicate a deviation from Bernoullian statistics toward the block structure.

(3) The Ω parameter characterizes deviation from first-order Markov statistics.[11] Ω is equal to unity for the first-order Markov chain and increases for any deviation. For the copolymer investigated

$$\Omega_D = \frac{P(D)P(DDD)}{P(DD)^2} = 1.186$$

$$\Omega_F = \frac{P(F)P(FFF)}{P(FF)^2} = 1.019$$

Ω indicates a slight deviation from first-order Markov statistics.

(4) The degree of randomness[12] covers the range from 0.0 for a mixture of homopolymers to 2.0 for the purely alternating chain, and it is equal to unity for a random copolymer.

$$B = P(D/F) + P(F/D) = 0.846$$

For the PDT/FT copolymer, the value of the degree of randomness indicates significant deviation from random to block chain structure.

All the parameters calculated indicate that the PDT/FT copolymer synthesized at 240 °C exhibits deviation from the statistical distribution of comonomer units, and a significant tendency to form a block structure is observed. This is in good agreement with the isokinetic temperature theory, developed for high-temperature copolycondensations in solution.[3,13-16] According to the theory, for synthesis at the isokinetic temperature a random copolymer should be formed, while above and below this temperature increased reactivity of one of the comonomers should lead to a block structure of the copolymer chain. For the PDT/FT copolymer, the isokinetic temperature was determined to be 200 °C;[16] hence it is reasonable that at 240 °C a tendency to form block units is observed.

Conclusions

It is shown in this work that conventional NMR instruments operating at frequencies up to 100 MHz for protons and simultaneous application of lanthanide shift reagents can be combined to perform tetrad analysis of an aromatic copolyterephthalate. In such a system the standard spectrum (i.e., in the absence of the shift reagent) furnishes no information about the comonomer sequences. Among the various copolyterephthalates a system with similar comonomers is the most difficult for the NMR investigations, while in the case of significantly different comonomers the dyad separation can be observed even in the standard spectrum. Hence, the application of LSR can be regarded as a general method of evaluating comonomer sequences in various copolyterephthalates independent of comonomers, provided the copolymer is soluble in solvents suitable for LSR application.

It is shown in this paper that the theoretical spectrum of the terephthalic protons signal can be calculated on the basis of the assumption of an incremental influence of neighboring units in the sequence considered on a lanthanide-induced shift of these protons. For the PDT/FT copolymer investigated additivity of α and β increments was found, but for other systems thorough inspection of the assumptions must be undertaken.

The application of higher magnetic fields should also improve the separation of the various sequence signals;[17] therefore, the combination of these two methods, i.e. LSR application and the increase in magnetic field, may reveal signals of sequences longer than tetrads for the copolyterephthalates having significantly different comonomers.

Registry No. PDT/FT, 70876-98-1.

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