

# Kinetic Studies on Copolycondensation Processes.

## VI. Influence of Copolycondensation Temperature on Tetrad Distribution of the PDT/FT Aromatic Copolyterephthalate by $^1\text{H-NMR}$ Spectroscopy

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### Synopsis

$^1\text{H-NMR}$  and  $\text{Eu}(\text{fod})_3$  lanthanide shift reagent were used to determine tetrad distribution of comonomer units of the PDT/FT copolyterephthalate obtained from terephthaloyl chloride (intermonomer) and 3,3'-dimethylbisphenol A and phenolphthalein (comonomers). Computer simulations of the terephthalic proton signal split into the lines of compositional tetrads were performed to obtain quantitative data. To characterize the microstructure of the copolymer samples synthesized at different temperatures, the degree of randomness and the degree of alternation were calculated. It was shown that the latter can differentiate the chains which seemed to be identical concerning the diad distribution only.

### INTRODUCTION

This paper is a sequel to the previous one<sup>1</sup> concerning the calculations of diad distribution for the low-molecular weight samples of the PDT/FT copolyterephthalate (former abbreviation DTF) obtained from terephthaloyl chloride as intermonomer and equal amounts of 3,3'-dimethylbisphenol A and phenolphthalein as comonomers. Development of a method for recording tetrad signals,<sup>2</sup> calculating tetrad distribution in this copolymer,<sup>3</sup> and the characterizing microstructure of a polymer chain based on the probabilities of sequences longer than diads<sup>4</sup> enabled us to perform tetrad distribution determination on PDT/FT samples synthesized at different temperatures, in the range covering the isokinetic temperature of the system, i.e. 200°C.<sup>5</sup>

### EXPERIMENTAL

The samples of poly[4,4'-isopropylidene(3,3'-dimethyl)diphenylene-4,4'-phthalidylidenediphenylene terephthalate 50:50] (PDT/FT) were obtained from 3,3'-dimethylbisphenol A and phenolphthalein (POCh, Poland) and terephthaloyl chloride (Fluka AG) used in the molar ratio 1:1:2, respectively. The high-temperature polycondensations were carried out in redistilled  $\alpha$ -chloronaphthalene (Reachim, USSR) at 200°C (the isokinetic temperature of the system<sup>5</sup>), 220°C and 240°C.

The molecular weight of the samples was determined in THF by the Knauer Vapour Pressure Osmometer and the Waters Associates Instruments ALC/GPC-202/401 Chromatograph.

$^1\text{H-NMR}$  spectra were recorded at 100 MHz on a Varian XL-100 Spec-

TABLE I  
 Parameters of the PDT/FT Samples

Reaction temp (°C)	Molecular weight	Degree of polymerization	Fractions of diads			Degree of randomness
			$x_{DD}$	$x_{DF}$	$x_{FF}$	
200	12500	35.4	0.226	0.452	0.321	0.91
220	13900	39.4	0.242	0.454	0.302	0.91
240	16000	45.3	0.260	0.449	0.291	0.90

trometer for 5 wt % solutions in  $\text{CDCl}_3$  (Merck) at room temperature.  $\text{Eu}(\text{fod})_3$  (Fluka AG) was used as a lanthanide shift reagent.

Simulations of tetrad fine splittings were performed by means of a Wang 2200 desktop computer equipped with a Wang 2212 X-Y plotter.<sup>3</sup>

## RESULTS AND DISCUSSION

The PDT/FT copolymer samples chosen for investigations are characterized in Table I. The values of the degree of randomness listed in Table I were calculated based on diad probabilities, according to the method previously described.<sup>1</sup>

As can be seen from Table I, the data obtained for samples prepared at different temperatures did not yield any significant differences in the value of the degree of randomness. The above finding may be regarded either as

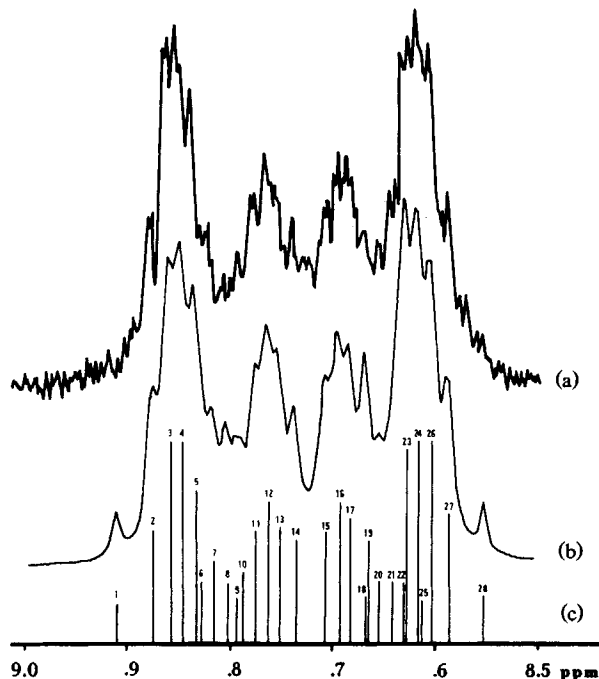


Fig. 1. 100 MHz  $^1\text{H}$ -NMR spectrum of the PDT/FT copolyterephthalate synthesized at the isokinetic temperature (200°C). The terephthalic proton signal split in the presence of  $\text{Eu}(\text{fod})_3$  (a) compared with the computer-simulated spectrum (b) and its components (c).  $[\text{Eu}(\text{fod})_3]/[\text{T}] = 1.2$ .

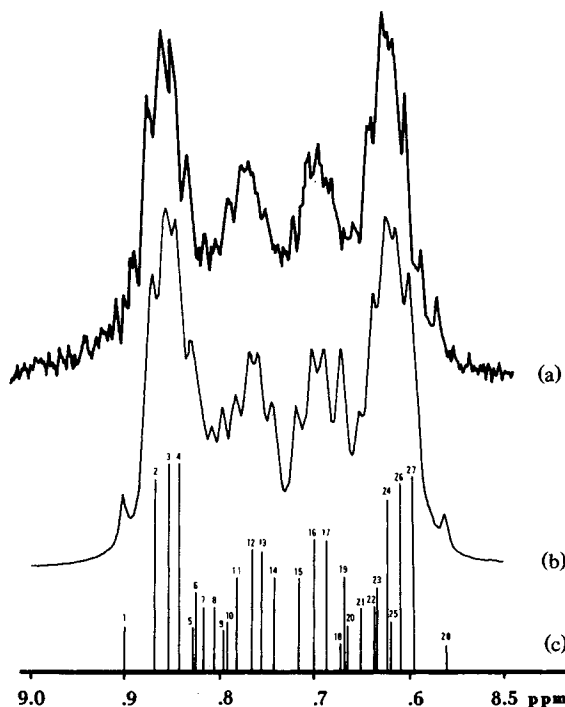


Fig. 2. 100 MHz  $^1\text{H-NMR}$  spectrum of the PDT/FT copolyterephthalate synthesized at  $220^\circ\text{C}$ . The terephthalic proton signal split in the presence of  $\text{Eu}(\text{fod})_3$  (a) compared with the computer-simulated spectrum (b) and its components (c).  $[\text{Eu}(\text{fod})_3]/[\text{T}] = 1.2$ .

a result, indicating no difference between the microstructure of the samples studied, or that the degree of randomness based on the diad probabilities only, is not sufficiently accurate and may be ambiguous. It was shown that the degree of randomness,  $B$ , based on the probabilities of diads only, should be regarded as the first approximation, and that it can assume the same value in spite of the differences in the microstructure of the macromolecular chain. To obtain a more accurate characterization, it is necessary to use parameters based on the probabilities of longer sequences.<sup>4</sup>

For the PDT/FT copolymer it was shown that using LSR, tetrad signals can be recorded<sup>2</sup> and the distribution of the tetrads can be calculated.<sup>3</sup>

The  $^1\text{H-NMR}$  spectra of the terephthalic proton signal of the PDT/FT copolymer, split in the presence of  $\text{Eu}(\text{fod})_3$ , are presented in Figures 1(a) and 2(a). The spectra were recorded for each sample at the same concentration of  $\text{Eu}(\text{fod})_3$  (calculated with respect to the terephthalic units<sup>3</sup>) equal to  $[\text{Eu}(\text{fod})_3]/[\text{T}] = 1.2$ ; hence, the lanthanide-induced shifts (LIS) of all spectra were nearly the same. In order to obtain quantitative data on tetrad distribution, a computer simulations were performed to fit the theoretical spectra to the experimental ones.

The parameters of computer-simulated tetrad spectra are presented in Table II and Table III for the PDT/FT samples synthesized at  $200^\circ\text{C}$  and  $220^\circ\text{C}$ , respectively. The corresponding data for the sample prepared at  $240^\circ\text{C}$  were already presented elsewhere.<sup>3</sup>

For the calculated spectra criteria of correct tetrad assignment are as follows<sup>3</sup>:

## PDT/FT-200°C

$$\begin{aligned}
 (1) \quad \overleftarrow{P(\overrightarrow{DDDF})} + 2P(\overrightarrow{FDDF}) &= \overleftarrow{P(\overrightarrow{DDFD})} + \overleftarrow{P(\overrightarrow{DDFF})} \\
 52.7 &= 46.9 && \text{(discrepancy 6\%)} \\
 (2) \quad \overleftarrow{P(\overrightarrow{DFFF})} + 2P(\overrightarrow{DFFD}) &= \overleftarrow{P(\overrightarrow{FFDF})} + \overleftarrow{P(\overrightarrow{FFDD})} \\
 50.7 &= 48.1 && \text{(discrepancy 5.4\%)}
 \end{aligned}$$

## PDT/FT-220°C

$$\begin{aligned}
 (1) \quad \overleftarrow{P(\overrightarrow{DDDF})} + 2P(\overrightarrow{FDDF}) &= \overleftarrow{P(\overrightarrow{DDFD})} + \overleftarrow{P(\overrightarrow{DDFF})} \\
 43.0 &= 43.2 && \text{(discrepancy 0.5\%)} \\
 (2) \quad \overleftarrow{P(\overrightarrow{DFFF})} + 2P(\overrightarrow{DFFD}) &= \overleftarrow{P(\overrightarrow{FFDF})} + \overleftarrow{P(\overrightarrow{FFDD})} \\
 42.6 &= 43.6 && \text{(discrepancy 2.4\%)}
 \end{aligned}$$

TABLE II

The Parameters of Computer-Simulated Tetrad Spectra for the PDT/FT Sample Synthesized at 200°C (the Isokinetic Temperature of the System)

Line no.	Position (ppm)	Relative height	Half-width (Hz)	Relative intensity
1	8.910	2.00	0.8	1.60
2	8.874	5.50	1.2	6.60
3	8.858	10.00	1.5	15.00
4	8.846	10.00	1.5	15.00
5	8.833	7.50	1.3	9.75
6	8.828	2.50	1.1	2.75
7	8.816	4.00	1.1	4.40
8	8.803	3.90	1.1	4.29
9	8.794	2.00	0.8	1.60
10	8.788	2.40	1.0	2.40
11	8.774	5.50	1.3	7.15
12	8.762	7.50	1.5	11.25
13	8.751	5.80	1.3	7.54
14	8.735	5.00	1.2	6.00
15	8.707	5.50	1.3	7.15
16	8.694	7.50	1.5	11.25
17	8.682	6.20	1.3	8.06
18	8.668	2.25	0.8	1.80
19	8.666	5.00	1.2	6.00
20	8.653	2.50	1.1	2.75
21	8.641	3.40	1.1	3.74
22	8.630	3.45	1.1	3.79
23	8.628	9.00	1.2	10.80
24	8.617	10.00	1.4	14.00
25	8.613	2.40	1.0	2.40
26	8.603	10.00	1.3	13.00
27	8.586	6.50	1.3	8.45
28	8.552	2.25	0.8	1.80

TABLE III  
The Parameters of Computer-Simulated Tetrad Spectra for the PDT/FT Sample Synthesized at 220°C

Line no.	Position (ppm)	Relative height	Half-width (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	8.793	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

TABLE IV  
Relative Intensities of the Tetrads for the PDT/FT Samples Synthesized at 200°C and 220°C

Tetrad intensity	Relative intensities	
	200°C	220°C
$I_{\text{DDDD}}$	$I_2 = 6.60$	$I_2 = 15.3$
$I_{\text{DDDF}}$	$I_1 + I_3 + I_4 + I_9 = 33.2$	$I_1 + I_3 + I_4 + I_9 = 34.2$
$I_{\text{FDDF}}$	$I_5 = 9.75$	$I_6 = 4.4$
$I_{\text{DDFD}}$	$I_6 + I_{11} + I_{15} + I_{20} = 19.7$	$I_5 + I_{11} + I_{15} + I_{20} = 16.6$
$I_{\text{DDFF}}$	$I_7 + I_{12} + I_{16} + I_{21} = 31.3$	$I_7 + I_{12} + I_{16} + I_{21} = 25.7$
$I_{\text{DFDF}}$	$I_8 + I_{13} + I_{17} + I_{22} = 22.9$	$I_8 + I_{13} + I_{17} + I_{22} = 25.8$
$I_{\text{FDFD}}$	$I_{10} + I_{14} + I_{19} + I_{25} = 16.8$	$I_{10} + I_{14} + I_{19} + I_{25} = 17.0$
$I_{\text{DFFD}}$	$I_{23} = 10.8$	$I_{23} = 5.8$
$I_{\text{DFFF}}$	$I_{18} + I_{24} + I_{26} + I_{28} = 29.1$	$I_{18} + I_{24} + I_{26} + I_{28} = 31.0$
$I_{\text{FFFF}}$	$I_{27} = 8.45$	$I_{27} = 15.7$
	$\sum_{i=1}^{28} I_i = 188.6$	$\sum_{i=1}^{28} I_i = 191.6$

TABLE V  
Tetrad Probabilities for the PDT/FT Copolymer Synthesized at Different Temperatures

Tetrad probability	Reaction temperature		
	200°C	220°C	240°C
$P(\overrightarrow{DDDD})$	0.035	0.080	0.063
$P(\overrightarrow{DDDF})$	0.176	0.178	0.192
$P(\overrightarrow{FDDF})$	0.052	0.023	0.025
$P(\overrightarrow{DDFD})$	0.105	0.087	0.084
$P(\overrightarrow{DDFF})$	0.166	0.134	0.154
$P(\overrightarrow{DFDF})$	0.121	0.135	0.103
$P(\overrightarrow{FDFD})$	0.089	0.089	0.082
$P(\overrightarrow{DFFD})$	0.057	0.030	0.016
$P(\overrightarrow{DFFF})$	0.154	0.162	0.209
$P(\overrightarrow{FFFF})$	0.045	0.082	0.072

Good agreement between computer-simulated and the experimental spectra enabled us to use the values of relative intensities of corresponding components of the simulated spectra for calculating the probability of individual sequences. Relative intensities of the tetrad signals are listed in Table IV, and tetrad probabilities for all the samples are presented in Table V. Probabilities of shorter sequences, i.e., triad, diad, and monad (composition), calculated from the data obtained for the tetrads are listed in Table VI.

The sequence probabilities presented in Tables V and VI were used to calculate first-, second-, and third-order conditional probabilities<sup>6</sup> for each PDT/FT sample and are listed in Table VII. From these data first-, second-, and third-order degree of alternation and the averaged degree of alternation<sup>4</sup> were calculated and listed in Table VIII.

On examining the results obtained the values of degree of alternation and averaged degree of alternation up to third order may be seen to differ for samples obtained at the various reaction temperatures applied. The

TABLE VI  
Triad, Diad, and Monad (Composition) Probabilities Calculated from the Tetrad Distributions for the PDT/FT Copolyterephthalate Synthesized at Different Temperatures

Sequence probability	Reaction temperature		
	200°C	220°C	240°C
$P(\overrightarrow{DDD})$	0.123	0.169	0.159
$P(\overrightarrow{DDF})$	0.275	0.223	0.240
$P(\overrightarrow{FDF})$	0.105	0.112	0.092
$P(\overrightarrow{DFD})$	0.113	0.111	0.093
$P(\overrightarrow{DFF})$	0.262	0.222	0.239
$P(\overrightarrow{FFF})$	0.122	0.163	0.177
$P(\overrightarrow{DD})$	0.263	0.281	0.280
$P(\overrightarrow{DF})$	0.481	0.445	0.423
$P(\overrightarrow{FF})$	0.256	0.274	0.297
$P(\overrightarrow{D})$	0.503	0.504	0.492
$P(\overrightarrow{F})$	0.497	0.496	0.508

TABLE VII

First-, Second-, and Third-Order Conditional Probabilities Calculated from the Tetrad Distribution for the PDT/FT Copolyterephthalate Synthesized at Different Temperatures

Order	Conditional probability	Reaction temperature		
		200°C	220°C	240°C
III	$P(DDD/D)$	0.284	0.473	0.396
	$P(FDD/D)$	0.640	0.798	0.800
	$P(DFD/D)$	0.465	0.392	0.452
	$P(DDF/D)$	0.382	0.390	0.350
	$P(FFD/D)$	0.634	0.604	0.654
	$P(FDF/D)$	0.576	0.603	0.560
	$P(DFF/D)$	0.435	0.270	0.134
	$P(FFF/D)$	0.631	0.497	0.590
	$P(DDD/F)$	0.715	0.527	0.604
	$P(FDD/F)$	0.370	0.206	0.208
	$P(DFD/F)$	0.535	0.608	0.554
	$P(DDF/F)$	0.604	0.601	0.642
	$P(FFD/F)$	0.340	0.401	0.343
	$P(FDF/F)$	0.424	0.397	0.445
	$P(DFF/F)$	0.588	0.729	0.874
	$P(FFF/F)$	0.369	0.503	0.407
	II	$P(DD/D)$	0.468	0.601
$P(DF/D)$		0.470	0.503	0.440
$P(FD/D)$		0.572	0.501	0.567
$P(FF/D)$		0.512	0.405	0.402
$P(DD/F)$		0.523	0.397	0.428
$P(DF/F)$		0.545	0.499	0.565
$P(FD/F)$		0.437	0.503	0.435
I	$P(FF/F)$	0.477	0.595	0.596
	$P(D/D)$	0.523	0.558	0.569
	$P(D/F)$	0.481	0.445	0.423
	$P(F/D)$	0.481	0.445	0.423
	$P(F/F)$	0.515	0.552	0.585

largest difference was found to exist between the samples synthesized at the isokinetic temperature (200°C) and the sample prepared at the temperature of 240°C. It should be noted, however, that the values of degree of randomness, i.e., degree of alternation of first order, calculated from

TABLE VIII

First-, Second-, and Third-Order Degree of Alternation ( $A$ ) and Averaged Degree of Alternation ( $F$ ) Calculated for the PDT/FT Copolyterephthalate Synthesized at Different Temperatures

Parameter	Reaction temperature		
	200°C	220°C	240°C
$A_1 = F_1 = P(D/F) + P(F/D)$	0.96	0.89	0.84
$A_2 = P(FD/F) + P(DF/D)$	0.91	1.01	0.87
$A_3 = P(DFD/F) + P(FDF/D)$	1.11	1.22	1.11
$F_1 = A_1 = F(D/F) + P(F/D)$	0.96	0.89	0.84
$F_2 = \frac{A_1 + A_2}{2}$	0.93	0.95	0.86
$F_3 = \frac{A_1 + A_2 + A_3}{3}$	0.99	1.04	0.94

tetrad distribution differ significantly from those calculated from diad distribution only (cf. Table I). Now, after precise separation of the tetrad lines, the roughness of the previous method,<sup>1</sup> based on the simple integration of the diad signals, can be clearly seen, since some of the tetrad lines, being the components of the respective diad signals, can be found out of the spectral regions formerly ascribed to the respective diads [See Figs. 1(c) and 2(c)]. Hence, determination of tetrad distribution improves the accuracy of diad and triad distribution evaluation.

### CONCLUSIONS

It was shown in the work that the accuracy of characterization of macromolecular chain based on diad distribution only may be insufficient for differentiation between macromolecular chains and inspection of longer sequence distribution may reveal differences for those copolymer chains which were regarded as identical.

On the basis of the results obtained it may be therefore assumed that the reaction temperature of high-temperature copolycondensation in solution may have an observable effect on the microstructure of the chain of condensation copolymers. Similarly, as for low-molecular weight samples,<sup>1</sup> a conclusion that may be drawn from that observation is that at the isokinetic temperature, when reactivities of the two comonomers are equal, nearly random distribution of both comonomers in the chain is obtained. On the other hand, the higher the temperature difference, i.e., the higher the difference in comonomer reactivities, the more the chain microstructure deviates from the random arrangement, and the tendency to form blocks becomes more pronounced.

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