

Kinetic Studies on Copolycondensation Processes. V. Investigations on Sequence Distribution of Fully Aromatic Copolyester by PMR Spectroscopy

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Synopsis

PMR spectroscopy and lanthanide shift reagents were used to determine sequence distribution of units of poly(dimethyldian-phenolphthalein)terephthalate. The calculated values of degree of randomness confirm the theory that the copolyester obtained at the isokinetic temperature (200°C) has random distribution of comonomer units and copolyesters obtained at temperatures above and below this temperature have a tendency to form block units along the macromolecular chain.

INTRODUCTION

In previous papers^{1,2} we suggested the hypothesis that copolyesters obtained at different temperatures differed in the structure of their macromolecular chain. The distribution of comonomer units along the macromolecular chains should vary considerably as the processing temperature varies within the range that includes the isokinetic temperature.² Thus, at the isokinetic temperature a copolymer with a random distribution of comonomer units should be formed, while above and below this temperature there should be a tendency to form block units along the macromolecular chain.

To confirm this hypothesis, i.e., to find the differences in the structure of macromolecular chains for the samples of copolyesters obtained at different temperatures, we used PMR spectroscopy.

EXPERIMENTAL

The low-molecular-weight samples (degree of polymerization about 10) of poly(dimethyldian-phenolphthalein)terephthalate (DTF) obtained from dimethyldian (D) and phenolphthalein (F) as comonomers and terephthaloyl chloride (T) as intermonomer were investigated (Fig. 1). The molar ratio of comonomers and intermonomer was 1:1:2. The samples of copolyesters were taken from three syntheses carried out in α -chloronaphthalene at 180, 200, and 220°C. The isokinetic temperature (t_{iso}) of this system was assigned to be 200°C.³ Homopolycondensations of D and F with T were performed at 220°C.

The PMR spectra were recorded at 60 MHz on a JEOL JNM-C-60H and at 100 MHz on a Varian XL-100 for 3–5 wt. % solutions in $CDCl_3$ at room temperature. $Eu(fod)_3$ from Fluka AG was used as the lanthanide shift reagent (LSR).

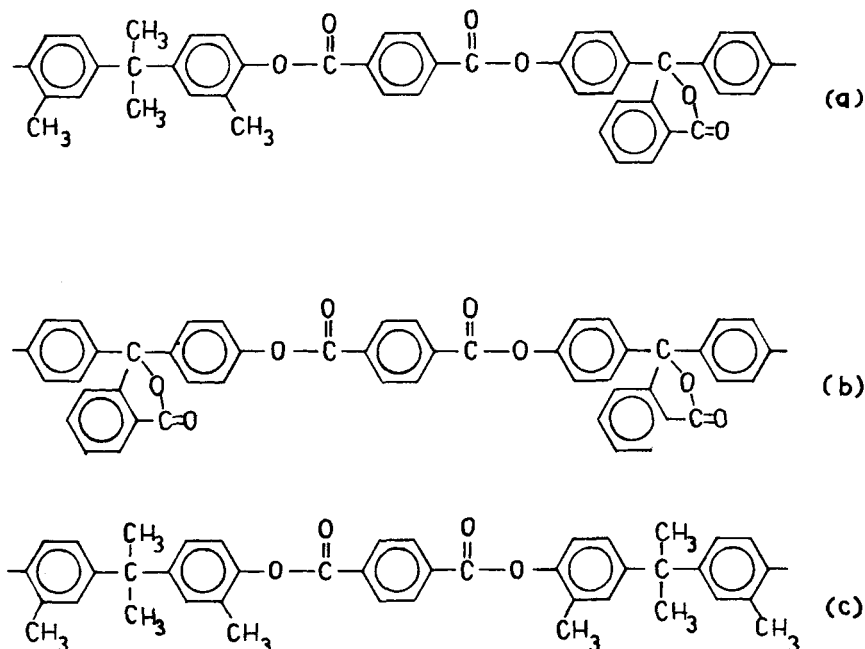


Fig. 1. Chemical structure of homo- and heterodyads: (a) -D-T-F- heterodyad; (b) -F-T-F- homodyad; and (c) -D-T-D- homodyad.

RESULTS AND DISCUSSION

PMR Spectra

In the PMR spectrum of each copolyester sample there are three groups of signals [Fig. 2(a)]:

1. Two singlets of methyl groups from dimethyldian:

$$\delta_{\text{CH}_3\text{-C}} = 1.74 \text{ ppm}$$

$$\delta_{\text{CH}_3\text{-Ar}} = 2.24 \text{ ppm (Me attached to aromatic ring)}$$

2. The region of aromatic signals of dimethyldian and phenolphthalein:

$$\delta_{\text{Ar}} = 7\text{--}8 \text{ ppm} \quad \begin{array}{l} (7.0\text{--}7.3 \text{ dimethyldian}) \\ (7.2\text{--}8.0 \text{ phenolphthalein}) \end{array}$$

3. The single signal of terephthalic protons:

$$\delta_{\text{T}} = 8.36 \text{ ppm}$$

The homopolyester spectra are relatively simpler [Fig. 2(b) and 2(c)].

Determination of Comonomer Fractions

The relative intensities of methyl, aromatic, and terephthalic signals were used to determine the fractions of comonomer units in the copolyester samples. The data are listed in the Table I. The fractions of comonomers in copolymer are

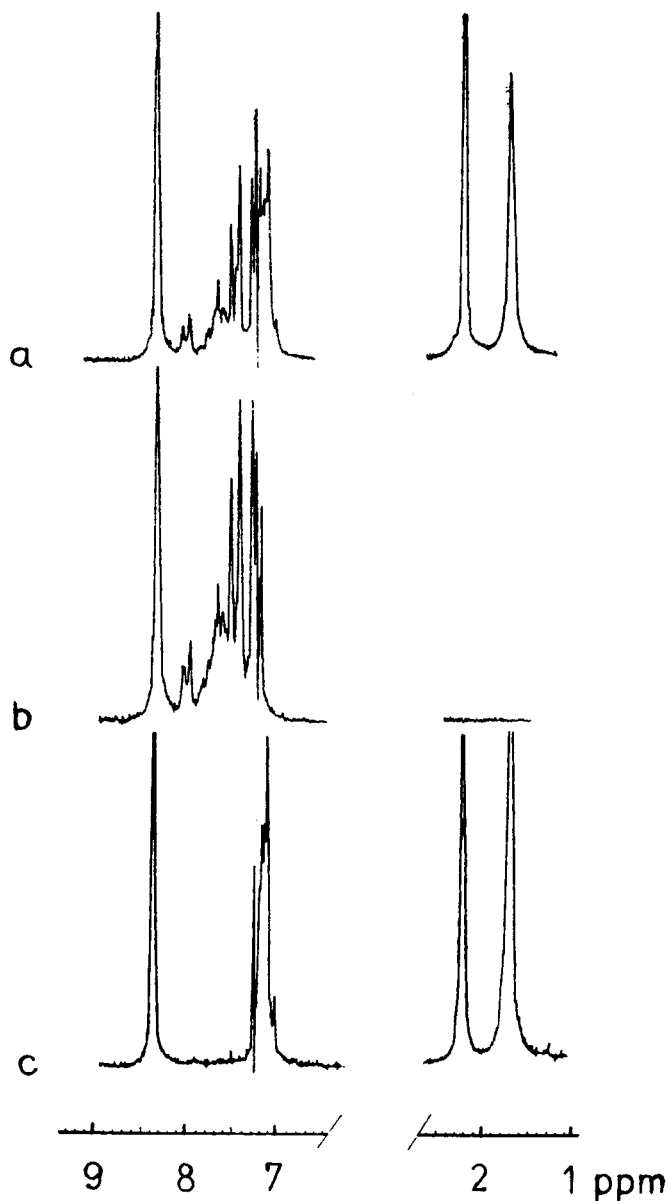


Fig. 2. 100-MHz PMR spectra of 3-5 wt. % solutions in CDCl_3 : (a) DTF copolyester; (b) FT homopolyester; and (c) DT homopolyester.

very close to equimolar, so it is the same ratio as for the original mixture of D and F.

Determination of Sequence Distribution

Several examples of sequence distribution determinations in condensation copolymers studied by high-resolution pmr spectroscopy have already been described in the literature.⁴⁻⁸ These investigations showed that such determi-

TABLE I
Dimethyldian Fractions in DTF Copolyester Calculated from PMR Spectra

| Reaction Temperature (°C) | Reaction Time (min) | Extent of Reaction | Fraction of Dimethyldian |
|---------------------------|---------------------|--------------------|--------------------------|
| 180 ($t < t_{180}$) | 180 | 0.21 | 0.50 |
| | 240 | 0.59 | 0.49 |
| | 360 | 0.68 | 0.50 |
| 200 ($t = t_{180}$) | 30 | 0.24 | 0.56 |
| | 90 | 0.51 | 0.56 |
| | 180 | 0.70 | 0.49 |
| | 360 | 0.85 | 0.45 |
| 220 ($t > t_{180}$) | 30 | 0.46 | 0.55 |
| | 60 | 0.65 | 0.49 |
| | 90 | 0.71 | 0.47 |
| | 180 | 0.86 | 0.46 |
| | 300 | 0.91 | 0.45 |

nations are possible when the chemical shifts of the homolinkages and heterolinkage are sufficiently different from one another. Because of the large dimensions and relatively smaller influence of the neighboring units in condensation copolymers, only dyads can be distinguished.

For the DTF, the copolyester protons of the intermonomer, e.g., terephthalic protons, were found to exhibit a singlet at $\delta = 8.36$ ppm in both the DTF copolyester and the DT and FT homopolyester spectra (Figs. 2 and 3). To observe the separated signals of the homo- and heterodyads, we have used LSR in a method similar to that of Chujo et al.,⁹ because the standard DTF spectrum gives no information about sequence distribution. In the presence of $\text{Eu}(\text{fod})_3$ the signal of the terephthalic protons was found to be split into three parts. After the addition of a small amount of europium complex to the DTF sample, the terephthalic protons give three signals [Fig. 3(b)], and after the addition of a next portion of $\text{Eu}(\text{fod})_3$, the inner signal gives two peaks due to AA'BB' splittings [Fig. 3(c)]. 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 reasonable to adapt the simpler AB rules instead the AA'BB' ones.

It is possible to separate clearly the outside signals about 0.4 ppm, then after another addition of $\text{Eu}(\text{fod})_3$ the phenolphthalein signals, which are shifted stronger, superimpose with terephthalic ones. It would be possible to obtain larger separation using deuterophenolphthalein or LSR shifted upfield.

We have examined $\text{Pr}(\text{fod})_3$, but the maximum separation was smaller than for $\text{Eu}(\text{fod})_3$, and investigations with deuterocompounds were not performed.

We have assigned the two outside signals (singlets) to the homodyads -D-T-D- and -F-T-F- and the central quartet to the heterodyad -D-T-F-. The outer lines of the AB quartet give a common signal with the lines of homodyad signals.

The assignment of the outside signal to the respective -D-T-D- and -F-T-F- homodyads was carried out using the results of analogous experiments performed for the FT and DT homopolyesters. We observed the chemical shifts of the terephthalic protons of the DTF copolyester [Fig. 4(a)], each homopolyester [Fig.

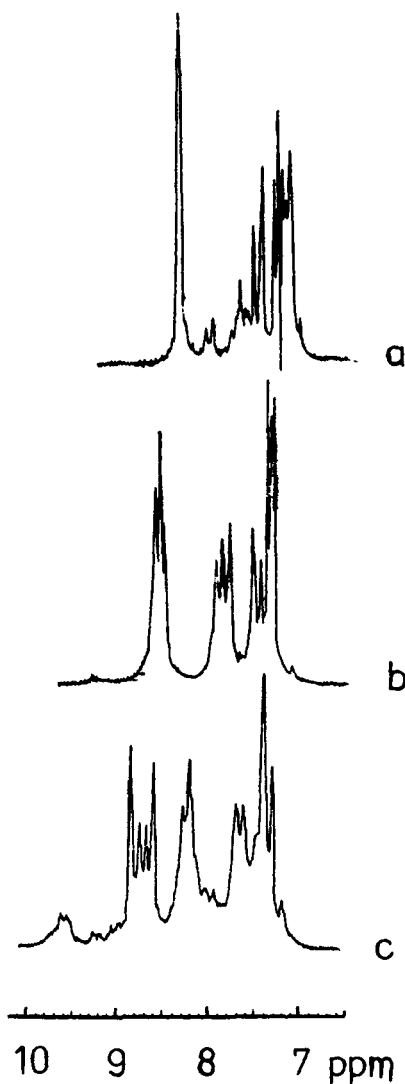


Fig. 3. The splittings of terephthalic 100-MHz PMR spectrum: (a) standard spectrum of DTF copolyester; (b) DTF copolyester spectrum after the addition of small amount of $\text{Eu}(\text{fod})_3$; and (c) DTF copolyester spectrum after another addition of $\text{Eu}(\text{fod})_3$.

4(b,c)], and a mixture of homopolyesters [DT:FT = 1:9 w/w, Fig. 4(d)] after the addition of the same amount of $\text{Eu}(\text{fod})_3$ to each sample.

In all cases the signal of terephthalic protons of the DT homopolyester was strongly shifted downfield. This fact enabled us to assign the downfield outside signal in the terephthalic proton region of the DTF copolyester spectrum recorded in the presence of $\text{Eu}(\text{fod})_3$ to the -D-T-D- homodyad.

Calculation of Sequence Distribution

The relative intensities of the terephthalic proton signals corresponding to the respective hetero- and homodyads were used to calculate the sequence distribution. Because the outside lines of the central quartet of the DTF copolyester

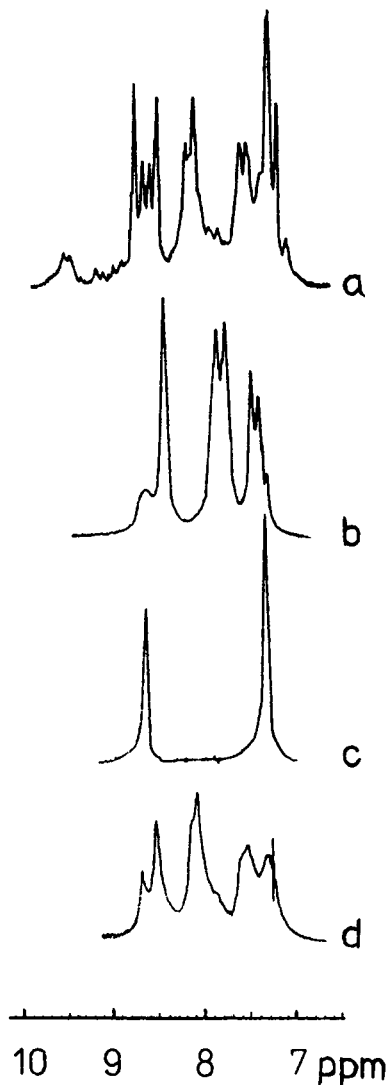


Fig. 4. Assignment of the terephthalic signals of the DTF copolyester to the respective dyads. The PMR spectra after the addition of the equal amounts of $\text{Eu}(\text{fod})_3$: (a) DTF copolyester; (b) FT homopolyester; (c) DT homopolyester; and (d) mixture of homopolyesters (DT:FT = 1:9 w/w) spectrum.

gave a common signal with the lines of homodyads, the relative intensities I_{DTD} , I_{DTF} , I_{FTF} obtained directly from the integration of the split terephthalic proton signals in the presence of LSR were corrected by assuming the signal of heterodyad to be the AB quartet. In calculating the proper intensities, we have used the well-known rules of AB splitting.¹⁰⁻¹² The real intensities of the homodyad signals I'_{DTD} and I'_{FTF} are lower and the heterodyad signal I'_{DTF} higher (Fig. 5). Because of the AB splitting rules, the inner (I_1) and the outer (I_2) intensities of the AB quartet lines are

$$I_1 = 1 + \sin 2\theta$$

$$I_2 = 1 - \sin 2\theta$$

where

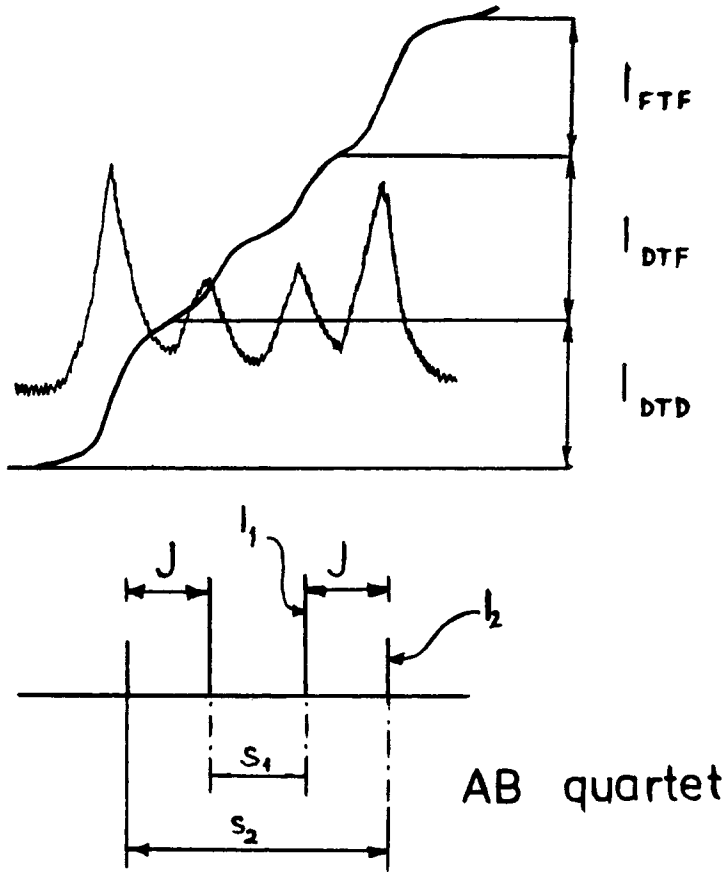


Fig. 5. Structure of AB splittings of the terephthalic proton spectrum.

$$\sin 2\theta = J_{AB}/(J_{AB}^2 + \gamma^2)^{1/2}$$

$$\gamma^2 = s_1 s_2$$

The value of J_{AB} was assumed to be $J_{ortho} = 9 \text{ Hz}$.¹³ The corrected values of the intensities are

$$I'_{DTD} = I_{DTD} - \frac{1}{2}\epsilon I_{DTF}$$

$$I'_{DTF} = I_{DTF} + \epsilon I_{DTF}$$

$$I'_{FTF} = I_{FTF} - \frac{1}{2}\epsilon I_{DTF}$$

where

$$\epsilon = I_1/I_2$$

The fractions of the respective dyads are

$$x_{DTD} = I'_{DTD}/I$$

$$x_{DTF} = I'_{DTF}/I$$

$$x_{FTF} = I'_{FTF}/I$$

TABLE II
 Degree of Randomness of DTF Copolyester Samples

| Reaction Temperature (°C) | Fractions of Dyads | | | Degree of Randomness |
|---------------------------|--------------------|------------------|------------------|----------------------|
| | x_{DTD} | x_{DTF} | x_{FTF} | |
| 180 | 0.275 | 0.435 | 0.290 | 0.87 |
| 200 | 0.255 | 0.505 | 0.245 | 1.00 |
| 220 | 0.280 | 0.430 | 0.280 | 0.87 |

where

$$I = I_{\text{DTD}} + I_{\text{DTF}} + I_{\text{FTF}} = I'_{\text{DTD}} + I'_{\text{DTF}} + I'_{\text{FTF}}$$

The fractions of the homo- and heterodyads were used to calculate the so-called degree of randomness (B)⁵:

$$B = \frac{x_{\text{DTF}}}{2x_{\text{DTD}} + x_{\text{DTF}}} + \frac{x_{\text{DTF}}}{2x_{\text{FTF}} + x_{\text{DTF}}}$$

B is equal to 0.0 for a mixture of homopolymers, 1.0 for a random distribution of units in a copolymer chain, and 2.0 for an alternating copolymer. The values of the dyad fractions and calculated degree of randomness for the DTF copolyester samples investigated are listed in the Table II.

For the DTF copolyester samples synthesized at the isokinetic temperature (200°C), a value of $B = 1.00$ was obtained, which would indicate the presence of a random sequence distribution in this copolyester. The B values for copolyesters synthesized at other temperatures (180 and 220°C) were equal to 0.87, which seems to suggest a tendency for the copolyester to form block units.

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