

## Paramagnetically Shifted High-Resolution NMR Spectra of Copolyesters by the Use of Tris(dipivalomethanato)europium(III).

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**ABSTRACT:** High-resolution NMR spectra of poly(ethylene terephthalate—iso-phthalate) are measured by the use of tris(dipivalomethanato)europium as a shift reagent. As a result, the peak assigned to the methylenic protons in glycol is separated into three peaks and they can be assigned to methylenes in terephthalate sequences, in the boundary between terephthalate and isophthalate, and in isophthalate sequences from downfield. This splitting allows the analysis of statistical properties of these practically important copolyesters. The composition ratios of the samples used are nearly equal to corresponding feed ratios, but the sequences of every monomer unit are somewhat stereoblock.

**KEY WORDS** Copolyester / Poly(ethylene terephthalate) / Poly-(ethylene isophthalate) / NMR / Shift Reagent / Tris(dipivalo-methanato)europium (III) / Sequence Length / Block /

The sequence lengths and other statistical properties of copolyesters were widely studied by Murano and his colleagues<sup>1-4</sup> from their high resolution nuclear magnetic resonance (NMR) spectra. In spite of their successful results, practically important copolyesters such as poly(ethylene terephthalate—iso-phthalate) cannot be analyzed by the NMR method, because there are no chemical shifts between the peaks assigned to the methylenic proton in glycol of the ethylene terephthalate unit and of the ethylene isophthalate unit. The above disadvantage may be closely related to the practical importance of the sample used. As is well known,<sup>5,6</sup> the degree of crystallinity in copolyesters made from ethylene terephthalate and ethylene isophthalate is much higher than in those made from the other glycol-dicarboxylic acid units. The disappearance of chemical shifts and high crystallinity may have resulted from the same cause, namely, the similarity in structure between the two kinds of monomer unit. A new method is therefore needed to analyze

the statistical properties of practically important copolyesters.

Recently, paramagnetic complexes containing the lanthanide such as Eu and Pr have been used to increase the chemical shift in NMR spectra.<sup>7,8</sup> The mechanism of the increase in chemical shift is considered to be the deshielding (Eu) or shielding (Pr) by the complexing to the shift reagent of the bases produced in ketones, ethers, esters and amines in the sample.<sup>9</sup> This mechanism suggests the use of a paramagnetic shift reagent in order to observe the NMR spectra of poly(ethylene terephthalate—iso-phthalate).

This paper deals with the NMR spectra of polyethylene terephthalate, polyethylene isophthalate and their copolymers with tris(dipivalomethanato)europium(III) (Hereafter, it is abbreviated in Eu(DPM)<sub>3</sub>), and the analysis of sequence distribution and other statistical properties of the copolymers on the basis of their NMR spectra.

### EXPERIMENTAL

The samples used are as follows:

1. poly(ethylene terephthalate)

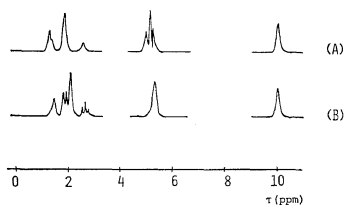
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2.	poly(ethylene terephthalate— isophthalate)	9 : 1 in feed
3.	"	8 : 2 "
4.	"	7 : 3 "
5.	"	6 : 4 "
6.	"	5 : 5 "
7.	"	4 : 6 "
8.	"	3 : 7 "
9.	"	2 : 8 "
10.	"	1 : 9 "
11.	poly(ethylene isophthalate)	

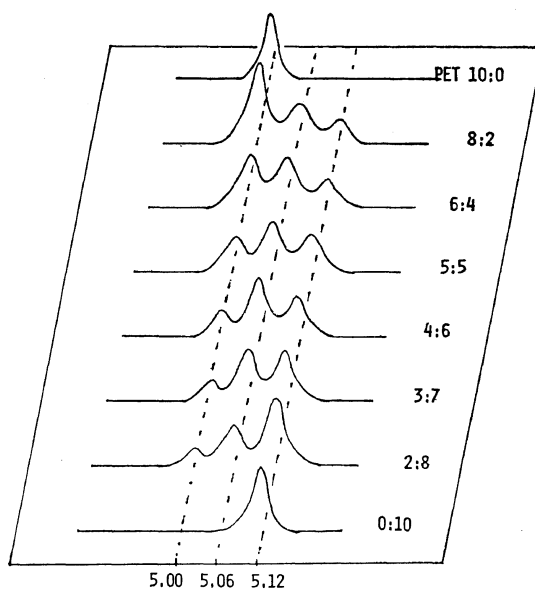
All samples were polymerized at Katata Research Institute, Toyobo Co., Ltd. and supplied by the courtesy of Dr. M. Murano of the institute. Twenty five mg of each sample was dissolved in 5 cc of 1,1,2,2-tetrachlorethane with 30 mg of  $\text{Eu}(\text{DPM})_3$ . This solvent is not good in general for polyesters, but appears to be the best for the present purpose, because a nonpolar solvent must be chosen to avoid coordination of the solvent to the shift reagent. Each of the solutions was set in an NMR spectrometer JNM 4H 100 and its spectrum was measured at 80°C.

## RESULTS AND DISCUSSION

Figure 1 (A) shows the spectrum of the sample 6 with  $\text{Eu}(\text{DPM})_3$  and Figure 1 (B) the spectrum without the shift reagent of the same sample. Complex peaks around  $\tau=2.2$  which are assigned to phenylene protons of the sample are somewhat broadened by an addition of the shift reagent. On the other hand, the single peak located at  $\tau=5.5$ , which is assigned to the methylenic protons in glycol, was clearly separated into three peaks. This separation is reproduced for most of the samples in Figure 2.



**Figure 1.** High resolution NMR spectra of poly(ethylene terephthalate—isophthalate) (5 : 5 in feed): (A) with  $\text{Eu}(\text{DPM})_3$ ; (B) without  $\text{Eu}(\text{DPM})_3$ .



**Figure 2.** High resolution NMR spectra of glycol regions in poly(ethylene terephthalate—isophthalate) of various feed ratios.

This separation was not observed for the samples 2, 4 and 10, so the reproductions of the spectra of these samples are omitted in Figure 2. From the comparison of the spectra of the samples 1 and 11, three peaks located at  $\tau=5.00$ , 5.06 and 5.12 can be assigned to the methylenic protons in  $T-G-T$ ,  $T-G-I$  (and  $I-G-T$ ) and  $I-G-I$  sequences, respectively. The symbols  $T$ ,  $I$  and  $G$  are the abbreviations of terephthalic acid, isophthalic acid and glycol, respectively. The reason why the corresponding peak in the sample 2 was not separated is probably due to relatively small amounts of  $T-G-I$  and  $I-G-I$  sequences. The sample 10 is in a similar circumstance. However, the reason why the corresponding peak in the samples 4 was not separated is, as yet, an unsolved problem.

Statistical data obtained from the relative intensities of NMR peaks from the methylenic protons in glycol are summarized in Table I. Rows 1, 2 and 3 show the placement probabilities of  $T-G-T$ ,  $T-G-I$  (and  $I-G-T$ ), and  $I-G-I$  sequences, respectively, which were obtained from the intensities in a straightforward way. Rows 4 and 5 are the probabilities which

**Table I.** Statistical data of poly(ethylene terephthalate—*isophthalate*)

Feed ratio, <i>T</i> : <i>I</i>	$P_{T-G-T}$ , %	$P_{T-G-I}$ , %	$P_{I-G-I}$ , %	$P_T$ , %	$P_I$ , %	$\langle T \rangle_n$	$\langle I \rangle_n$	$\frac{4P_{T-G-T} \cdot P_{I-G-I}}{(P_{T-G-I})^2}$
8:2	57.8	30.3	11.9	73.0	27.0	4.81	1.78	3.00
6:4	44.6	38.1	17.3	63.7	36.3	3.34	1.91	2.13
5:5	28.0	39.0	33.0	47.5	52.5	2.43	2.70	2.43
4:6	19.5	48.8	31.7	43.9	56.1	1.80	2.30	1.04
3:7	16.4	40.9	42.7	36.9	63.1	1.81	3.01	1.67
2:8	13.5	33.0	53.5	30.0	70.0	1.82	4.24	2.65

monomer units were found in polymers, and were obtained from the relations

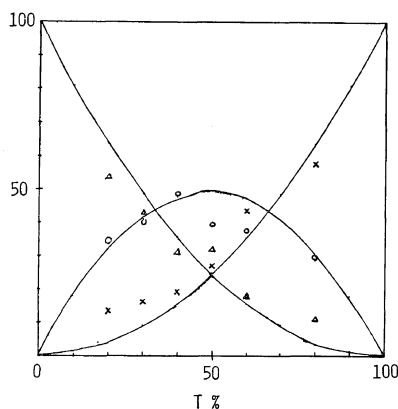
$$\begin{aligned} P_T &= P_{T-G-T} + P_{T-G-I}/2 \\ P_I &= P_{I-G-I} + P_{T-G-I}/2 \end{aligned} \quad (1)$$

under the assumption of statistical stationarity. These values are somewhat different from those of the corresponding feed ratios and the deviations seem to be random. The conclusion is made therefore that the composition ratios in the samples have not deviated from the corresponding feed ratios in a particular way, but both ratios are nearly equal with each other.

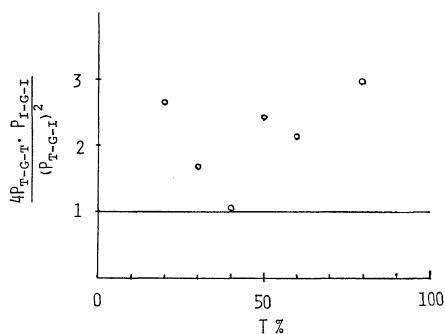
Rows 6 and 7 in Table I show the number-averaged sequence lengths of the samples which are obtained by similar fashion to the quantities in stereospecific polymers.<sup>10</sup> These relations are as follows:

$$\begin{aligned} \langle T \rangle_n &= 2P_T/P_{T-G-I} \\ \langle I \rangle_n &= 2P_I/P_{T-G-I} \end{aligned} \quad (9)$$

The last row in Table I is a measure of randomness of the sequences in the polymers. The quantity  $(4P_{T-G-T} \cdot P_{I-G-I})/(P_{T-G-I})^2$  is also obtained by a fashion similar to that in stereospecific polymers.<sup>11</sup> When this quantity is equal to unity, two kinds of monomer are taken into the polymer chain according to the Bernoulli trial. In other words, it corresponds to the azeotropic condition in an addition copolymer. As seen from Table I, all of the quantities are somewhat larger than unity in poly(ethylene terephthalate—*isophthalate*) and therefore the copolymer is to some degree a block copolymer system and the sequences in the polymer are also somewhat "block". This conclusion is different from that for the system of poly(ethylene terephthalate—*sebacate*).<sup>1</sup> This second conclu-



**Figure 3.** Dependence of the fractions of *T*—*G*—*T*, *T*—*G*—*I*, and *I*—*G*—*I* sequences on feed ratio: ×,  $P_{T-G-T}$ ; O,  $P_{T-G-I}$ ; Δ,  $P_{I-G-I}$ .



**Figure 4.** Dependence of the quantity,  $(4P_{T-G-T} \cdot P_{I-G-I})/(P_{T-G-I})^2$  on feed ratio.

sion can be visualized in the following two ways. The first is similar to Bovey's plot in stereospecific polymers,<sup>12</sup> and it is illustrated in Figure 3. The abscissa, *T*, in the figure is the fraction of ethylene terephthalate in feed and the ordinate is each of  $P_{T-G-T}$ ,  $P_{T-G-I}$  and

$P_{I-G-I}$ . The solid lines in the figure correspond to theoretical values expected for the case of Bernoulli trial. Experimental data certainly scatter from these lines. The second way is the plot of  $(4P_{T-G-T} \cdot P_{I-G-I}) / (P_{T-G-I})^2$  against  $T$ . This plot is illustrated in Figure 4. The second way is rather more sensitive to the deviation from the Bernoulli trial than the first.

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