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Compositional sequence distribution in unsaturated polyesters as revealed by ^{13}C n.m.r. spectroscopy

J. Grobelny and the late A. Kotas
Institute of Polymer Chemistry, Polish Academy of Sciences, 41-800 Zabrze, Poland
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A series of model unsaturated polyesters derived from maleic anhydride and various diols were synthesized and a study of their structures was carried out by means of ^{13}C n.m.r. spectroscopy. The n.m.r. spectra of polyesters produced by different procedures are reported and interpreted in terms of variety in the arrangement of diol components. Both fumarate and ester carbon atoms were found to be sensitive to compositional differences in the polyester chains. Diversity of the diol–fumarate–diol sequences was evidenced to account for the observed splitting of the resonances. Assignment of the peaks to different compositional sequences was accomplished through systematic alterations in polyester composition. The contributions of individual sequences were calculated assuming random and block distribution of diol units and compared with the experimental results. The comparison confirmed the validity of the assignment as well as the efficiency of the approach in the description of diol unit distribution in unsaturated polyesters.

(Keywords: unsaturated polyesters; compositional sequence distribution; nuclear magnetic resonance)

INTRODUCTION

Unsaturated polyesters are well known to offer excellent physical properties for many technological applications. They are commonly prepared by polycondensation of maleic and/or phthalic anhydride with various diols followed by copolymerization with vinyl monomers. Mechanical and thermal behaviours of the final products are greatly influenced by the structure of the unsaturated prepolymers as well as by the structure of the crosslinked network[1].

Considerable interest has been focused on maleate (*cis*)–fumarate (*trans*) isomerization in unsaturated polyesters[2–4]. It was found that the degree of *cis–trans* interconversion depends strongly on the nature of the diols, the presence of aromatic dibasic acids as well as on the reaction time and temperature. A higher reactivity of the *trans* isomers in subsequent copolymerization reactions appears to be decisive in the mechanical and thermal characteristics of the crosslinked materials.

Double bond saturation reactions during the synthesis of unsaturated polyesters were extensively examined by several authors[5–8]. The extent of saturation via the addition of diols to double bonds may reach 10–20%. Double bond consumption leads to the formation of branched structures and is claimed to modify the mechanical properties of the styrene-crosslinked final products.

When two or more different kinds of diol are used to synthesize unsaturated polyesters, the arrangement of diol units along the chains is believed to affect the properties of the crosslinked final products. Appropriate ways of synthesis employing various monomers may result in polyesters exhibiting the specific structures[1] that account for the desired thermal, mechanical and chemical properties of polyesters utilized in many significant areas. It would thus be essential to provide direct evidence of the structure of the polyester chains in terms of the distribution of diol structural units.

The major goal of this work was to develop a general method for monitoring and verifying an assumed structure of unsaturated polyesters produced from maleic anhydride and different diols via various synthetic routes.

EXPERIMENTAL

Materials

Several unsaturated polyester prepolymers were prepared by the standard high-temperature melt polycondensation[1,2,8] using maleic anhydride and selected diols. In all cases the polyesterification process was carried out under a nitrogen atmosphere by melting the reaction mixture and raising the temperature, the liberated water being distilled off. The following diols were used for the syntheses: propylene glycol (PG), an oligomer of propylene oxide with $M_n \approx 550$ and $M_w/M_n = 1.2$ (PO, trademark Rokopol 7p) and a product of addition of bisphenol A to propylene oxide (PD, propoxylated Dian, trademark Dianol 33). Rokopol 7p and Dianol 33 were supplied by NZPO 'Rokita' Co., Poland. Propylene glycol was used in a small excess (5–10%). No catalyst was employed. The progress of the reaction was monitored by measuring the acid number of samples periodically withdrawn from the reaction mixtures. The time of the reaction depended on the desired molecular mass (calculated from the acid number) and varied between 18 and 30 h, while the maximum reaction temperature was 205°C.

The polyester samples will be abbreviated as M*xyz* with *x*, *y* and *z* standing for the average numbers of PD, PO and PG, respectively.

Polyesters were obtained by one-stage or three-stage procedures. In the former case maleic anhydride was mixed with one, two or three diols with 1:1 molar ratio of the anhydride to the overall diol content. The reactions were stopped at acid numbers indicating desired molecular masses. Three-stage processes involved two separate syntheses of maleic anhydride with different kinds and amounts of diols followed by joining appropriate components together. The procedure was expected to afford polyesters of the same overall compositions as those prepared in the conventional, one-stage method but differing in distribution of the diol units.

Measurements

^1H and ^{13}C n.m.r. spectra of monomers and polyesters in $CDCl_3$ were recorded at 20°C on a Varian VXR-300 multinuclear pulsed n.m.r. spectrometer operating at the ^1H resonance frequency of 300 MHz and the ^{13}C resonance frequency of 75 MHz. Chemical shifts were referenced to tetramethylsilane serving as an internal standard. In order to obtain a satisfactory signal-to-noise ratio, about 30 000 scans were accumulated for ^{13}C spectra.

Convolution difference weighting (governed by convolution difference time constant and constant for convolution difference) was applied to the free induction decay (FID) in order to enhance spectral resolution.

Molecular masses of polyesters were determined by vapour-phase osmometry; for most samples they were found to correlate with the values derived from the acid numbers.

RESULTS AND DISCUSSION

Structure determination of substrates

Prior to the study of polyesters it was essential to establish the structure of the components utilized for their preparation.

Figure 1a displays the ^1H n.m.r. spectrum of the product of the reaction of bisphenol A with propylene oxide. This product will be referred to throughout the paper as PD. In order to determine the chemical structure of PD, assignment of the resonance signals was made by analysing the spectral changes observed upon the addition of trichloroacetyl isocyanate (TAI). This method is known to be a valuable aid in determining structures of hydroxy components[9,10]; moreover, the reaction with TAI should induce similar spectral changes to those expected by reacting such compounds with the maleic anhydride being used in the syntheses of unsaturated polyesters under study. The ^1H n.m.r. spectrum of the TAI derivative of PD is shown in *Figure 1b*. Taking into account the relative magnitudes of the downfield shifts of the multiplets due to methine, methylene and methyl protons as well as the integrated intensities of the signals (including those due to aromatics), it was found that the analysed product is in fact a mixture of the compounds formed via β- and α-opening of the propylene oxide ring.

In addition, the values of integrated intensities of the respective signals thus assigned indicate that the β-opening (a cleavage of the CH_2–O bond) prevails and the contribution of CH–OH groups formed due to this mode of reaction is about 85%. Formation of the product bearing one or two CH_2–OH groups results from cleavage of the CH–O bond (the α-opening) and the number of CH_2–OH groups is 15%.

The structure of PD was confirmed by ^{13}C n.m.r. study. *Figures 1c* and *d* present the ^{13}C spectra of PD and its TAI derivative. The observed directions and magnitudes

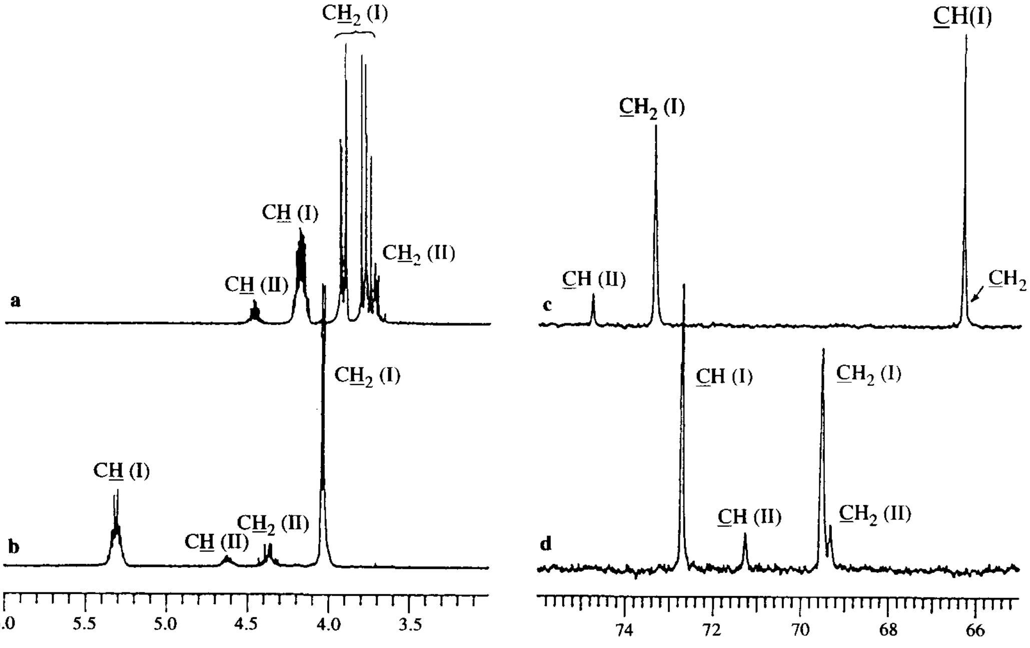


Figure 1 ^1H (a,b) and ^{13}C (c,d) n.m.r. spectra of CHO and CH_2O groups of PD (a,c) and its TAI derivative (b,d). I, $OCH_2CH(CH_3)OH$; II, $OCH(CH_3)CH_2OH$

of the shifts of the resonances due to CHO and CH_2O carbons reveal unambiguously that both secondary and primary carbinol carbons are present, the former type being predominant in the system. The expected changes in the methyl carbon region after the addition of TAI were also observed. The assignment of the signals was supported by ^{13}C undecoupled and DEPT (Distortionless Enhancement by Polarization Transfer) spectra.

A similar characterization procedure was employed for the oligomer of propylene oxide (PO), another diol component of the unsaturated polyesters under study. Both ^1H and ^{13}C n.m.r. spectra (*Figure 2*) are very complex, reflecting a great diversity in local environments (including the effects of structural and configurational isomerism discussed for poly(propylene oxide)[11]). The reaction with TAI (or MA) was observed to induce in the ^1H n.m.r. spectrum a downfield shift of the multiplet centred at about 3.9 ppm. This resonance can be assigned to protons alpha to secondary hydroxyl groups when taking into account the extent of the shift. Unlike the case of PD, there is no evidence for the existence of CH_2OH end groups in PO oligomer.

The assignment of the ^{13}C n.m.r. resonances of PO was made with the aid of a DEPT experiment. The results of such an approach are shown in *Figures 2c* and *d*. The peaks which are pointing up arise from methine carbons whereas those pointing down are ascribed to methylene carbons. The most upfield peaks are evidently due to CH–OH carbons as they shift to lower magnetic field for the TAI derivative. This is accompanied by an upfield shift of the resonances arising from CH_2 carbons of terminal units. On the other hand, the most downfield peaks, which are also found to arise from CH carbons, shift to higher magnetic field. However, this resonance cannot be ascribed to $-OCH(CH_3)CH_2OH$ end groups for the following reasons:

(1) the extent of the discussed CH carbon shift is less than expected for methine carbon adjacent to primary carbinol carbon, and
(2) no concomitant downfield shift of any of the peaks due to CH_2 carbons is observed.

Both ^1H and ^{13}C n.m.r. analysis thus revealed the PO diol to contain exclusively $-OCH_2CH(CH_3)OH$ end groups.

It is worth noting that the spectral changes observed for PD (*Figure 1*) and PO (*Figure 2*) upon the reaction with TAI are similar to those produced by maleic anhydride. In particular, the positions of the signals due to methine protons of terminal groups are very close to those in ^1H n.m.r. spectra of polyesters derived from MA and the two diols. Thus the areas of the multiplets centred at 5.3 and 5.1 ppm for PD and PO, respectively (*Figures 1c* and *2c*), can be considered as a measure of a number of different ester linkages present in unsaturated polyesters containing both PO and PD units.

However, methine protons of PG, when additionally present in polyester chains, also give rise to signals at 5.3 ppm $[-OCH_2CH(CH_3)O-]$ and 5.1 ppm $[HOCH_2CH(CH_3)O-]$. A direct observation of the

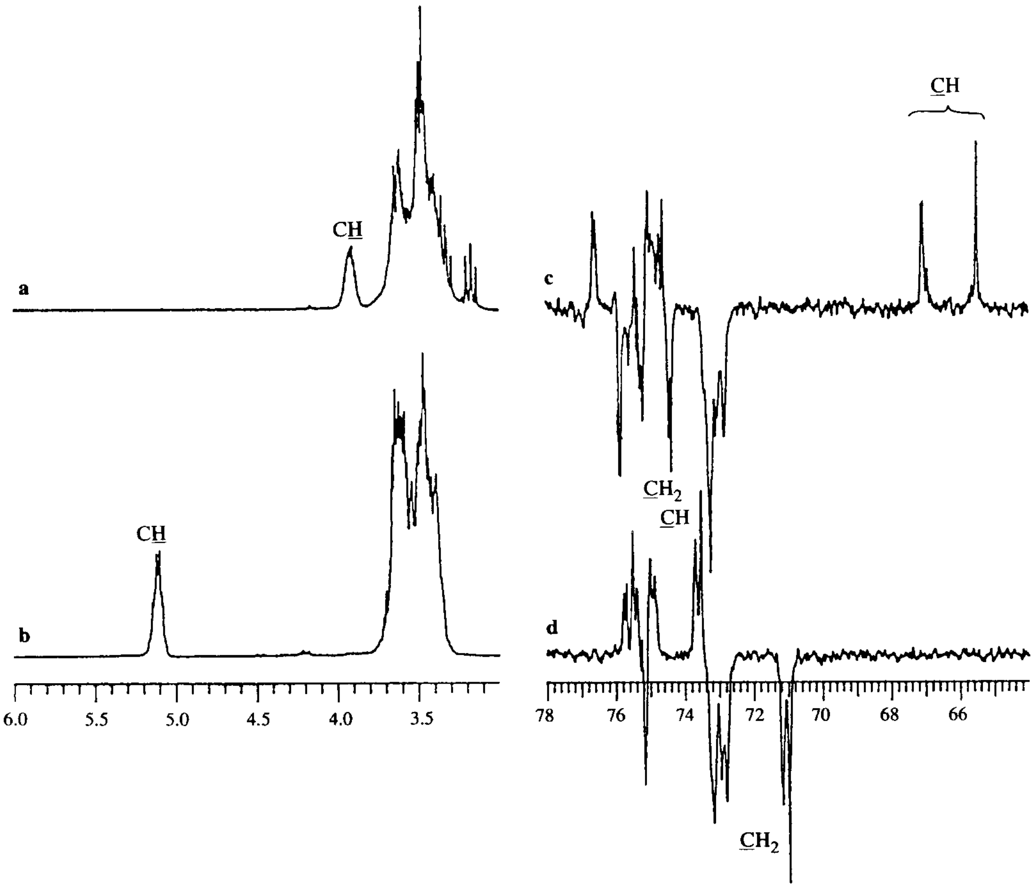


Figure 2 ^1H (a, b) and ^{13}C DEPT (c, d) n.m.r. spectra of CHO and CH_2O groups of PO (a, c) and its TAI derivative (b, d); the assignment refers to ultimate units of PO

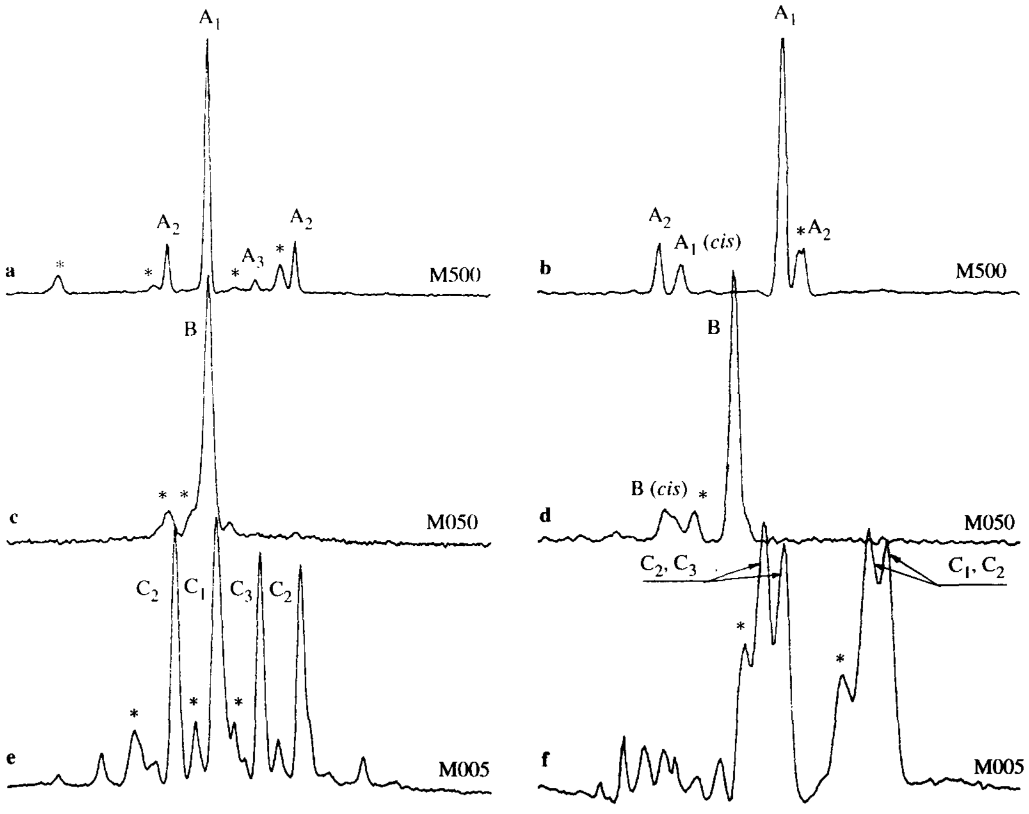


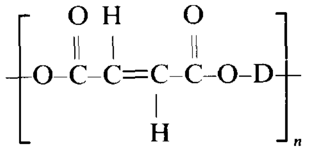
Figure 3 ^{13}C n.m.r. spectra of M500, M050 and M005 polyesters; the resonances are due to fumarate (a,c,e) and ester (b,d,f) carbons in the following sequences (see also *Table 1*): A_1, PD/PD(CH/CH), C1; A_2, PD/PD(CH/CH_2), C2 or C3; A_3, PD/PD(CH_2/CH_2), C4; B, PO/PO(CH/CH), C9; C_1, PG/PG(CH/CH), C12; C_2, PG/PG(CH/CH_2), C13 or C14; C_3, PG/PG(CH_2/CH_2), C15. The numbering of fumarate carbons C*n* refers to adjacent ester carbons in the spectra b, d and f; the resonances due to terminal sequences are marked with asterisks

resonances due to the formation of various ester linkages in polyesters containing PD, PO and PG diol units is thus no longer possible, making a structural analysis tedious.

Structure of polyesters

Having characterized the structure of the components used for the synthesis of polyesters, an attempt was made to determine the distribution of diol units in the polymer chains.

Figure 3 presents the expanded ^{13}C n.m.r. spectra of the olefinic and ester carbon regions of three unsaturated, predominantly fumarate (as revealed by ^{1}H n.m.r.) polyesters differing in the nature of the diol component. Their molecular masses correspond to $n \approx 5$ constituent repeat units:



$$\left[-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{C}=\underset{\underset{H}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-D-\right]_n$$

where D stands for PD, PO or PG.

The spectral regions exhibit splittings which reflect various chemical and magnetic environments 'seen' by fumarate and ester carbons. *Table 1* summarizes chemical structures of various sequences which can be found in the polyester chains along with the designations used throughout the paper, carbon numbering and the probabilities P^* calculated from the amounts of CHOH and CH_2OH groups in the diols.

As expected[6,8,12], when PG was used as a diol, four main peaks of almost equal intensity were observed. These peaks are known to be due to four non-equivalent unsaturated carbons which can be distinguished in various sequences of the PG–fumarate–PG type: PG/PG(CH/CH), PG/PG(CH/CH_2) + PG/PG(CH_2/CH) and PG/PG(CH_2/CH_2).

In the case of PD, owing to the presence of 15% primary and 85% secondary hydroxyl end groups, the relative proportions of PD/PD(CH/CH), PD/PD (CH/CH_2) + PD/PD(CH_2/CH) and PD/PD(CH_2/CH_2) sequences should be 0.7225, 0.2550 and 0.0225, respectively. In fact, the sequences were found to give rise to four peaks with experimental intensity ratio close to 72.25:12.75:12:75:2.25.

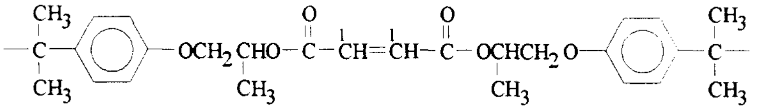
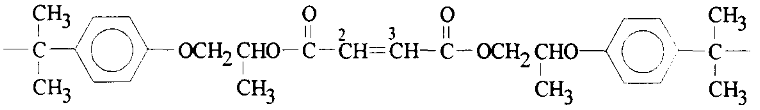
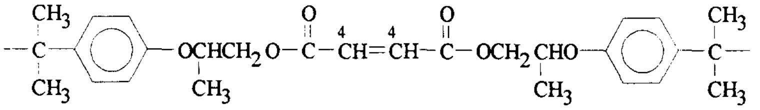
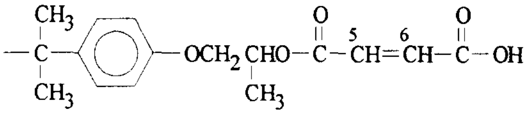
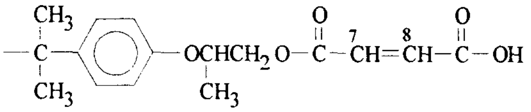
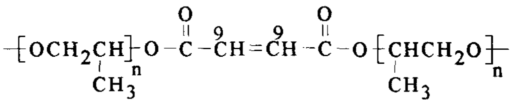
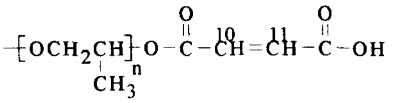
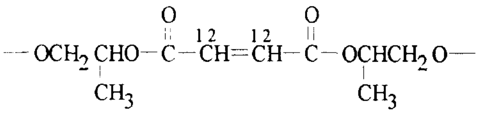
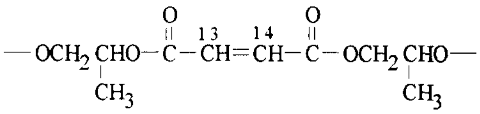
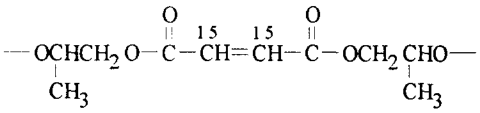
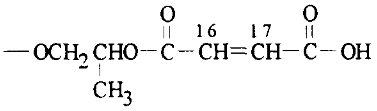
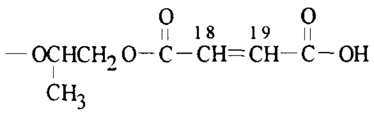
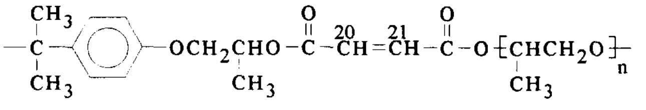
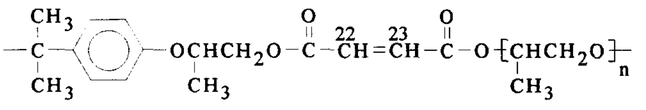
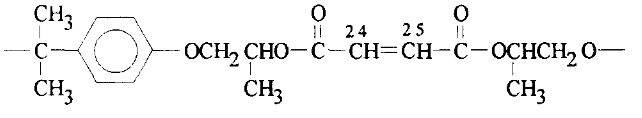
For PO only one main peak arising from the PO/PO(CH/CH) sequence was observed, consistent with the structure of this diol.

Likewise, the ester carbon regions of the three polyesters were found to reveal the effect of the compositional sequence distribution (*Figures 3b, d* and *f*).

Aside from the main peaks, the spectra of all the samples exhibit several other lines ascribed to terminal, diol–carboxyfumarate sequences. The intensities of the lines were observed to increase with decreasing molecular mass and to vanish completely for model dihydroxy polyesters having both chain ends capped by diol units, thus supporting the assignment.

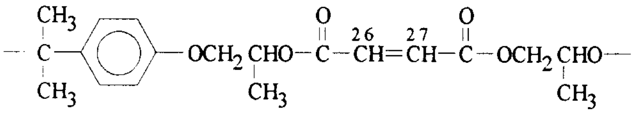
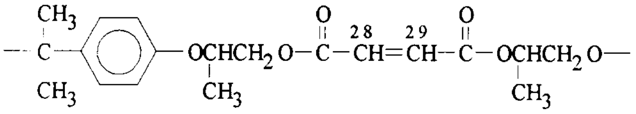
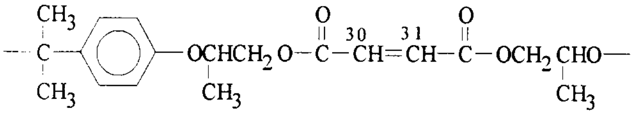
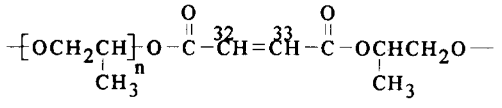
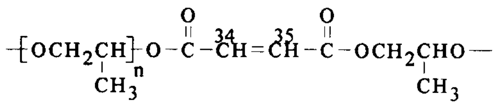
For PG-based polyester, additional peaks of low intensity resulting presumably from the vicinity of saturation sites were observed. The latter were evidenced

Table 1 A variety of diol–fumarate–diol sequences present in unsaturated polyesters and their relative contributions P^*

Sequence	Designation	Carbon no.	Probability, P^*
	PD/PD(CH/CH)	1	0.7225
	PD/PD(CH/CH$_2$)	2, 3	0.1275
	PD/PD(CH$_2$/CH)	3, 2	0.1275
	PD/PD(CH$_2$/CH$_2$)	4	0.0225
	PD/–(CH/–)	5, 6	0.85
	PD/–(CH$_2$/–)	7, 8	0.15
 $-[\underset{CH_3}{OCH_2CH}]_n-O-\overset{O}{\overset{\|}{C}}-\overset{9}{C}H=\overset{9}{C}H-\overset{O}{\overset{\|}{C}}-O-[\underset{CH_3}{CHCH_2O}]_n-$	PO/PO(CH/CH)	9	1
 $-[\underset{CH_3}{OCH_2CH}]_n-O-\overset{O}{\overset{\|}{C}}-\overset{10}{C}H=\overset{11}{C}H-\overset{O}{\overset{\|}{C}}-OH$	PO/–(CH/–)	10, 11	1
 $-OCH_2\underset{CH_3}{CH}O-\overset{O}{\overset{\|}{C}}-\overset{12}{C}H=\overset{12}{C}H-\overset{O}{\overset{\|}{C}}-O\underset{CH_3}{CH}CH_2O-$	PG/PG(CH/CH)	12	0.25
 $-OCH_2\underset{CH_3}{CH}O-\overset{O}{\overset{\|}{C}}-\overset{13}{C}H=\overset{14}{C}H-\overset{O}{\overset{\|}{C}}-OCH_2\underset{CH_3}{CH}O-$	PG/PG(CH/CH$_2$)	13, 14	0.25
	PG/PG(CH$_2$/CH)	14, 13	0.25
 $-O\underset{CH_3}{CH}CH_2O-\overset{O}{\overset{\|}{C}}-\overset{15}{C}H=\overset{15}{C}H-\overset{O}{\overset{\|}{C}}-OCH_2\underset{CH_3}{CH}O-$	PG/PG(CH$_2$/CH$_2$)	15	0.25
 $-OCH_2\underset{CH_3}{CH}O-\overset{O}{\overset{\|}{C}}-\overset{16}{C}H=\overset{17}{C}H-\overset{O}{\overset{\|}{C}}-OH$	PG/–(CH/–)	16, 17	0.5
 $-O\underset{CH_3}{CH}CH_2O-\overset{O}{\overset{\|}{C}}-\overset{18}{C}H=\overset{19}{C}H-\overset{O}{\overset{\|}{C}}-OH$	PG/–(CH$_2$/–)	18, 19	0.5
	PD/PO(CH/CH)	20, 21	0.85
	PO/PD(CH/CH)	21, 20	0.85
	PD/PO(CH$_2$/CH)	22, 23	0.15
	PO/PD(CH/CH$_2$)	23, 22	0.15
	PD/PG(CH/CH)	24, 25	0.425
	PG/PD(CH/CH)	25, 24	0.425

continued overleaf

Table 1 *Continued*

Sequence	Designation	Carbon no.	Probability, P*
	PD/PG(CH/CH$_2$)	26, 27	0.425
	PG/PD(CH$_2$/CH)	27, 26	0.425
	PD/PG(CH$_2$/CH)	28, 29	0.075
	PG/PD(CH/CH$_2$)	29, 28	0.075
	PD/PG(CH$_2$/CH$_2$)	30, 31	0.075
	PG/PD(CH$_2$/CH$_2$)	31, 30	0.075
 $-[OCH_2\underset{CH_3}{CH}]_n-O-\overset{O}{\overset{\parallel}{C}}-\overset{32}{C}H=\overset{33}{C}H-\overset{O}{\overset{\parallel}{C}}-O\underset{CH_3}{CH}CH_2O-$	PO/PG(CH/CH)	32, 33	0.5
	PG/PO(CH/CH)	33, 32	0.5
 $-[OCH_2\underset{CH_3}{CH}]_n-O-\overset{O}{\overset{\parallel}{C}}-\overset{34}{C}H=\overset{35}{C}H-\overset{O}{\overset{\parallel}{C}}-OCH_2\underset{CH_3}{CH}O-$	PO/PG(CH/CH$_2$)	34, 35	0.5
	PG/PO(CH$_2$/CH)	35, 34	0.5

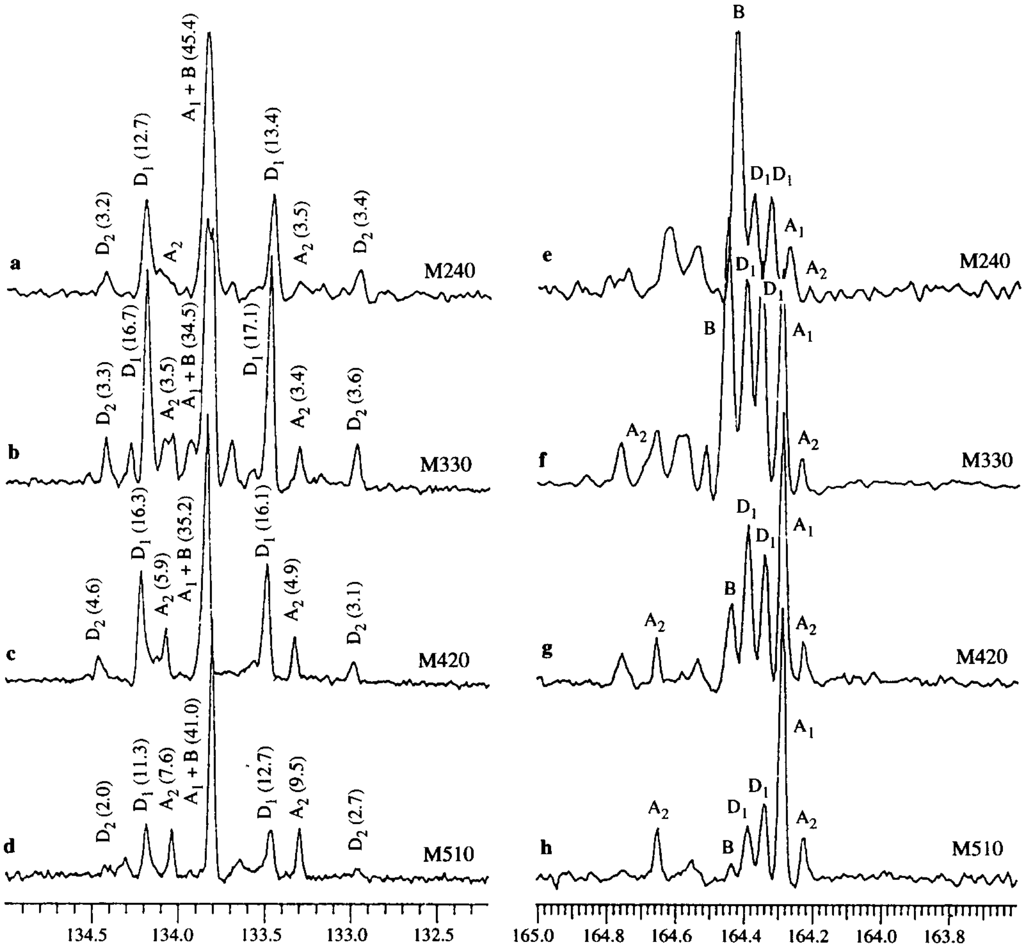


Figure 4 ^{13}C n.m.r. spectra of Mxy0 (x = PD, y = PO) polyesters with random distribution of diol units; the resonances are due to fumarate (a–d) and ester (e–h) carbons in the following sequences (see also *Table 1*): A$_1$, PD/PD(CH/CH), C1; A$_2$, PD/PD(CH/CH$_2$), C2 or C3; B, PO/PO(CH/CH), C9; D$_1$, PD/PO(CH/CH), C20 or C21; D$_2$, PD/PO(CH$_2$/CH), C22 or C23. The numbering of fumarate carbons Cn refers to adjacent ester carbons in the spectra e–h; the relative areas of the resonances due to internal sequences are given in brackets (to be compared with corresponding values from *Table 2*)

Table 2 Calculated values of the relative intensities (in %) of resonances due to fumarate carbons in polyesters of Mxy0 type (x = PD, y = PO)

Carbon no.	Sequence	M510	M420	M420 'block'	M330	M330 'block'	M240	M240 'block'	M150
1	PD/PD(CH/CH)	41.8	26.8	36.1	15.0	24.1	6.7	12.0	1.7
2	PD/PD(CH/CH_2)	7.4	4.7	6.4	2.7	4.25	1.2	2.1	0.3
3	PD/PD(CH_2/CH)	7.4	4.7	6.4	2.7	4.25	1.2	2.1	0.3
4	PD/PD(CH_2/CH_2)	1.3	0.8	1.0	0.5	0.75	0.2	0.4	0.1
9	PO/PO(CH/CH)	2.3	9.2	16.7	20.8	33.3	37.1	50.0	57.8
20	PD/PO(CH/CH)	9.8	15.7	7.1	17.7	7.1	15.7	7.1	9.8
21	PO/PD(CH/CH)	9.8	15.7	7.1	17.7	7.1	15.7	7.1	9.8
22	PD/PO(CH_2/CH)	1.7	2.8	1.25	3.1	1.25	2.8	1.25	1.7
23	PO/PD(CH/CH_2)	1.7	2.8	1.25	3.1	1.25	2.8	1.25	1.7
5	PD/–(CH/–)	5.9	4.75	3.55	3.55	3.55	2.35	3.55	1.2
6		5.9	4.75	3.55	3.55	3.55	2.35	3.55	1.2
7	PD/–(CH_2/–)	1.05	0.85	0.65	0.65	0.65	0.4	0.65	0.2
8		1.05	0.85	0.65	0.65	0.65	0.4	0.65	0.2
10	PO/–(CH/–)	1.4	2.8	4.15	4.15	4.15	5.5	4.15	6.9
11		1.4	2.8	4.15	4.15	4.15	5.5	4.15	6.9

Table 3 Calculated values of the relative intensities (in %) of resonances due to fumarate carbons in polyesters of Mx0z type (x = PD, z = PG)

Carbon no.	Sequence	M501	M501 'block'	M402	M402 'block'	M303	M303 'block'	M204	M204 'block'	M105
1	PD/PD(CH/CH)	41.8	48.2	26.8	36.1	15.0	24.1	6.7	12.0	1.7
2	PD/PD(CH/CH_2)	7.4	8.5	4.7	6.4	2.7	4.25	1.2	2.1	0.3
3	PD/PD(CH_2/CH)	7.4	8.5	4.7	6.4	2.7	4.25	1.2	2.1	0.3
4	PD/PD(CH_2/CH_2)	1.3	1.5	0.8	1.1	0.5	0.75	0.2	0.4	0.1
12	PG/PG(CH/CH)	0.6	–	2.3	4.2	5.2	8.3	9.3	12.5	14.5
13	PG/PG(CH/CH_2)	0.6	–	2.3	4.2	5.2	8.3	9.3	12.5	14.5
14	PG/PG(CH_2/CH)	0.6	–	2.3	4.2	5.2	8.3	9.3	12.5	14.5
15	PG/PG(CH_2/CH_2)	0.6	–	2.3	4.2	5.2	8.3	9.3	12.5	14.5
24	PD/PG(CH/CH)	4.9	3.55	7.9	3.5	8.9	3.5	7.9	3.5	4.9
25	PG/PD(CH/CH)	4.9	3.55	7.9	3.5	8.9	3.5	7.9	3.5	4.9
26	PD/PG(CH/CH_2)	4.9	3.55	7.9	3.5	8.9	3.5	7.9	3.5	4.9
27	PG/PD(CH_2/CH)	4.9	3.55	7.9	3.5	8.9	3.5	7.9	3.5	4.9
28	PD/PG(CH_2/CH)	0.9	0.6	1.4	0.6	1.6	0.6	1.4	0.6	0.9
29	PG/PD(CH/CH_2)	0.9	0.6	1.4	0.6	1.6	0.6	1.4	0.6	0.9
30	PD/PG(CH_2/CH_2)	0.9	0.6	1.4	0.6	1.6	0.6	1.4	0.6	0.9
31	PG/PD(CH_2/CH_2)	0.9	0.6	1.4	0.6	1.6	0.6	1.4	0.6	0.9
5	PD/–(CH/–)	5.9	7.1	4.7	3.5	3.5	3.5	2.4	3.5	1.2
6		5.9	7.1	4.7	3.5	3.5	3.5	2.4	3.5	1.2
7	PD/–(CH_2/–)	1.05	1.25	0.8	0.6	0.6	0.6	0.4	0.6	0.2
8		1.05	1.25	0.8	0.6	0.6	0.6	0.4	0.6	0.2
16	PG/–(CH/–)	0.7	–	1.4	2.1	2.1	2.1	2.8	2.1	3.5
17		0.7	–	1.4	2.1	2.1	2.1	2.8	2.1	3.5
18	PG/–(CH_2/–)	0.7	–	1.4	2.1	2.1	2.1	2.8	2.1	3.5
19		0.7	–	1.4	2.1	2.1	2.1	2.8	2.1	3.5

by the presence of characteristic bands (appearing near 2.9 ppm in ^1H and in the 35–40 ppm region of ^{13}C n.m.r. spectra) reported as being due to chain branching[6,7].

In ester carbon regions some peaks due to residual *cis* isomers are present. Their existence was confirmed by analysing other spectral regions ($\sim$130 ppm in ^{13}C and $\sim$6.2 ppm in ^1H n.m.r. spectra).

For model polyesters with two or three different kinds of diol there are several other possible arrangements, presented also in *Table 1*. As mentioned in the Experimental section, the polymers will be designated as Mxyz, where x, y and z, respectively, denote the average numbers of PD, PO and PG units in the chain.

The ^{13}C n.m.r. spectra were recorded for a series of Mxy0 ($x+y=6$) and Mx0z ($x+z=6$) polyesters with x, y and z varying between 1 and 5 (*Figures 4* and *5*). The assignment was accomplished by observation of the changes in line intensities upon systematic variations in

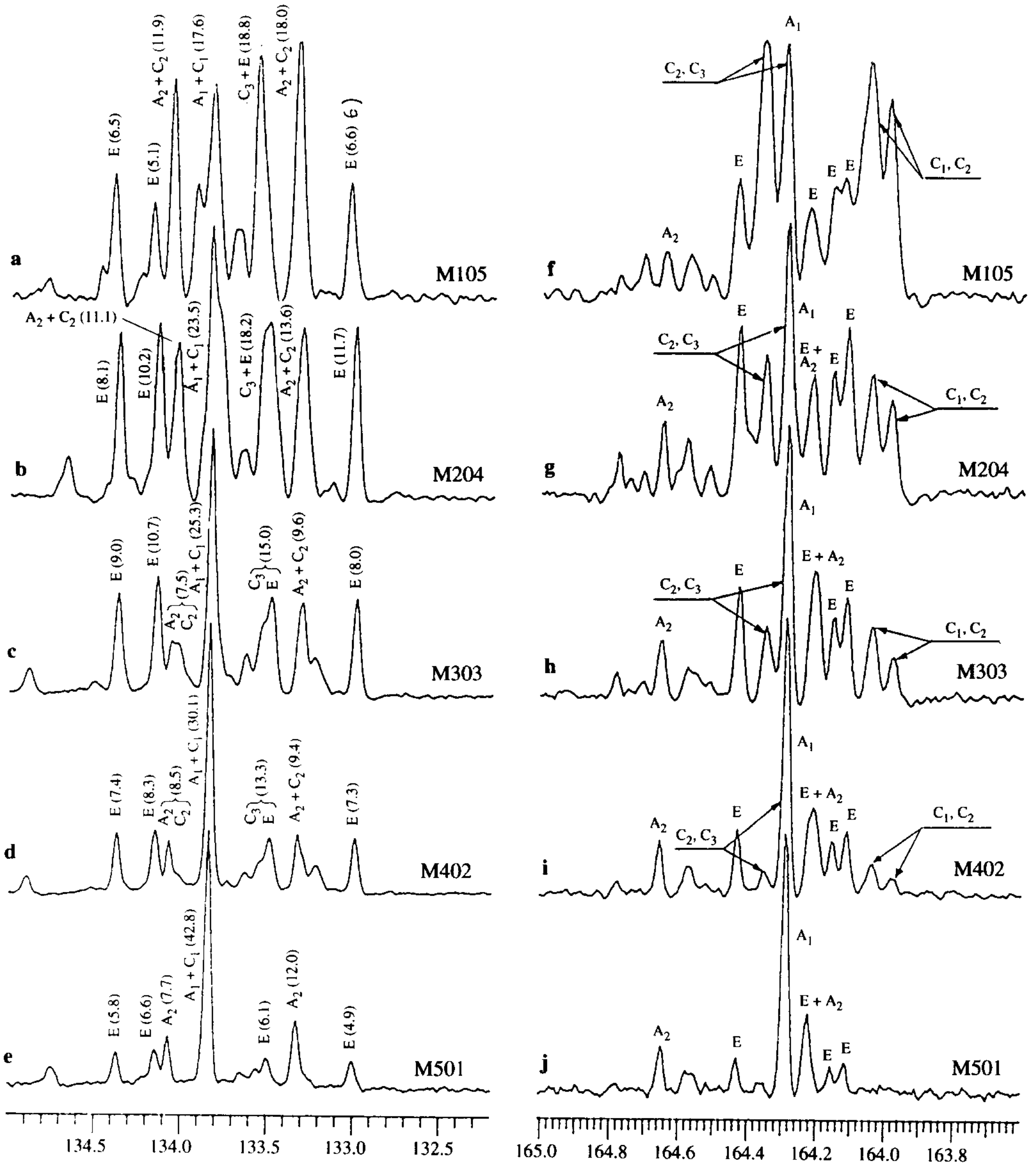


Figure 5 ^{13}C n.m.r. spectra of Mx0z (x = PD, z = PG) polyesters with random distribution of diol units; the resonances are due to fumarate (a–e) and ester (f–j) carbons in the following sequences (see also *Table 1*): A_1, PD/PD(CH/CH), C1; A_2, PD/PD(CH/CH_2), C2 or C3; C_1, PG/PG(CH/CH), C12; C_2, PG/PG(CH/CH_2), C13 or C14; C_3, PG/PG(CH_2/CH_2), C15; E, PD/PG(CH/CH) + PD/PG(CH/CH_2), C24 or C25 or C26 or C27. The numbering of fumarate carbons Cn refers to adjacent ester carbons in the spectra f–j; the relative areas of the resonances due to internal sequences are given in brackets (to be compared with corresponding values from *Table 3*)

Table 4 Calculated values of the relative intensities (in %) of resonances due to fumarate carbons in polyesters of Mxyz type (x = PD, y = PO, z = PG)

Carbon no.	Sequence	M411	M321	M312	M222	M231	M213	M141	M132	M123	M114
1	PD/PD(CH/CH)	26.0	15.0	15.0	6.7	6.7	6.7	1.7	1.7	1.7	1.7
2	PD/PD(CH/CH_2)	4.7	2.7	2.7	1.2	1.2	1.2	0.3	0.3	0.3	0.3
3	PD/PD(CH_2/CH)	4.7	2.7	2.7	1.2	1.2	1.2	0.3	0.3	0.3	0.3
4	PD/PD(CH_2/CH_2)	0.8	0.5	0.5	0.2	0.2	0.2	0.1	0.1	0.1	0.1
9	PO/PO(CH/CH)	2.3	9.2	2.3	9.2	20.8	2.3	37.1	20.8	9.2	2.3
12	PG/PG(CH/CH)	0.6	0.6	2.3	2.3	0.6	5.2	0.6	2.3	5.2	9.3
13	PG/PG(CH/CH_2)	0.6	0.6	2.3	2.3	0.6	5.2	0.6	2.3	5.2	9.3
14	PG/PG(CH_2/CH)	0.6	0.6	2.3	2.3	0.6	5.2	0.6	2.3	5.2	9.3
15	PG/PG(CH_2/CH_2)	0.6	0.6	2.3	2.3	0.6	5.2	0.6	2.3	5.2	9.3
20	PD/PO(CH/CH)	7.9	11.8	5.9	7.9	11.8	4.0	7.9	6.0	4.0	2.0
21	PO/PD(CH/CH)	7.9	11.8	5.9	7.9	11.8	4.0	7.9	6.0	4.0	2.0
22	PD/PO(CH_2/CH)	1.4	2.1	1.0	1.4	2.1	0.7	1.4	1.0	0.7	0.4
23	PO/PD(CH/CH_2)	1.4	2.1	1.0	1.4	2.1	0.7	1.4	1.0	0.7	0.4

continued

Table 4 *Continued*

Carbon no.	Sequence	M411	M321	M312	M222	M231	M213	M141	M132	M123	M114
24	PD/PG(CH/CH)	3.9	3.0	5.9	3.9	2.0	5.9	1.0	2.0	3.0	3.9
25	PG/PD(CH/CH)	3.9	3.0	5.9	3.9	2.0	5.9	1.0	2.0	3.0	3.9
26	PD/PG(CH/CH_2)	3.9	3.0	5.9	3.9	2.0	5.9	1.0	2.0	3.0	3.9
27	PG/PD(CH_2/CH)	3.9	3.0	5.9	3.9	2.0	5.9	1.0	2.0	3.0	3.9
28	PD/PG(CH_2/CH)	0.7	0.5	1.0	0.7	0.35	1.0	0.2	0.4	0.5	0.7
29	PG/PD(CH/CH_2)	0.7	0.5	1.0	0.7	0.35	1.0	0.2	0.4	0.5	0.7
30	PD/PG(CH_2/CH_2)	0.7	0.5	1.0	0.7	0.35	1.0	0.2	0.4	0.5	0.7
31	PG/PD(CH_2/CH_2)	0.7	0.5	1.0	0.7	0.35	1.0	0.2	0.4	0.5	0.7
32	PO/PG(CH/CH)	1.15	2.3	2.3	4.6	3.45	3.45	4.6	7.0	7.0	4.6
33	PG/PO(CH/CH)	1.15	2.3	2.3	4.6	3.45	3.45	4.6	7.0	7.0	4.6
34	PO/PG(CH/CH_2)	1.15	2.3	2.3	4.6	3.45	3.45	4.6	7.0	7.0	4.6
35	PG/PO(CH_2/CH)	1.15	2.3	2.3	4.6	3.45	3.45	4.6	7.0	7.0	4.6
5	PD/–(CH/–)	4.7	3.5	3.5	2.35	2.35	2.35	1.2	1.2	1.2	1.2
6		4.7	3.5	3.5	2.35	2.35	2.35	1.2	1.2	1.2	1.2
7	PD/–(CH_2/–)	0.8	0.6	0.6	0.4	0.4	0.4	0.2	0.2	0.2	0.2
8		0.8	0.6	0.6	0.4	0.4	0.4	0.2	0.2	0.2	0.2
10	PO/–(CH/–)	1.4	2.8	1.4	2.8	4.2	1.4	5.6	4.2	2.8	1.4
11		1.4	2.8	1.4	2.8	4.2	1.4	5.6	4.2	2.8	1.4
16	PG/–(CH/–)	0.7	0.7	1.4	1.4	0.7	2.1	0.7	1.4	2.1	2.8
17		0.7	0.7	1.4	1.4	0.7	2.1	0.7	1.4	2.1	2.8
18	PG/–(CH_2/–)	0.7	0.7	1.4	1.4	0.7	2.1	0.7	1.4	2.1	2.8
19		0.7	0.7	1.4	1.4	0.7	2.1	0.7	1.4	2.1	2.8

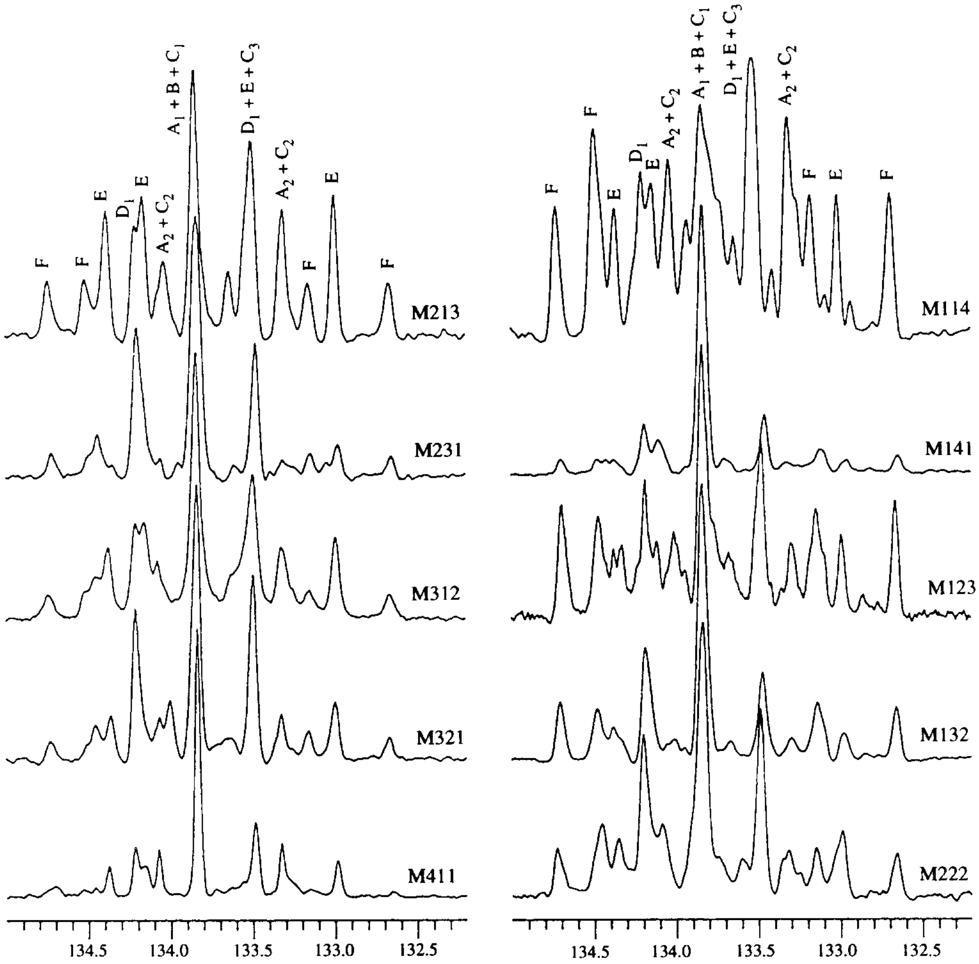


Figure 6 ^{13}C n.m.r. spectra of M*xyz* (x = PD, y = PO, z = PG) polyesters; the resonances are due to fumarate carbons in the following sequences (see also *Table 1*): A_1, PD/PD(CH/CH), C1; A_2, PD/PD(CH/CH_2), C2 or C3; B, PO/PO(CH/CH), C9; C_1, PG/PG(CH/CH), C12; C_2, PG/PG(CH/CH_2), C13 or C14; C_3, PG/PG(CH_2/CH_2), C15; D_1, PD/PO(CH/CH), C20 or C21; E, PD/PG(CH/CH) + PD/PG(CH/CH_2), C24 or C25 or C26 or C27; F, PO/PG(CH/CH) + PO/PG(CH/CH_2), C32 or C33 or C34 or C35

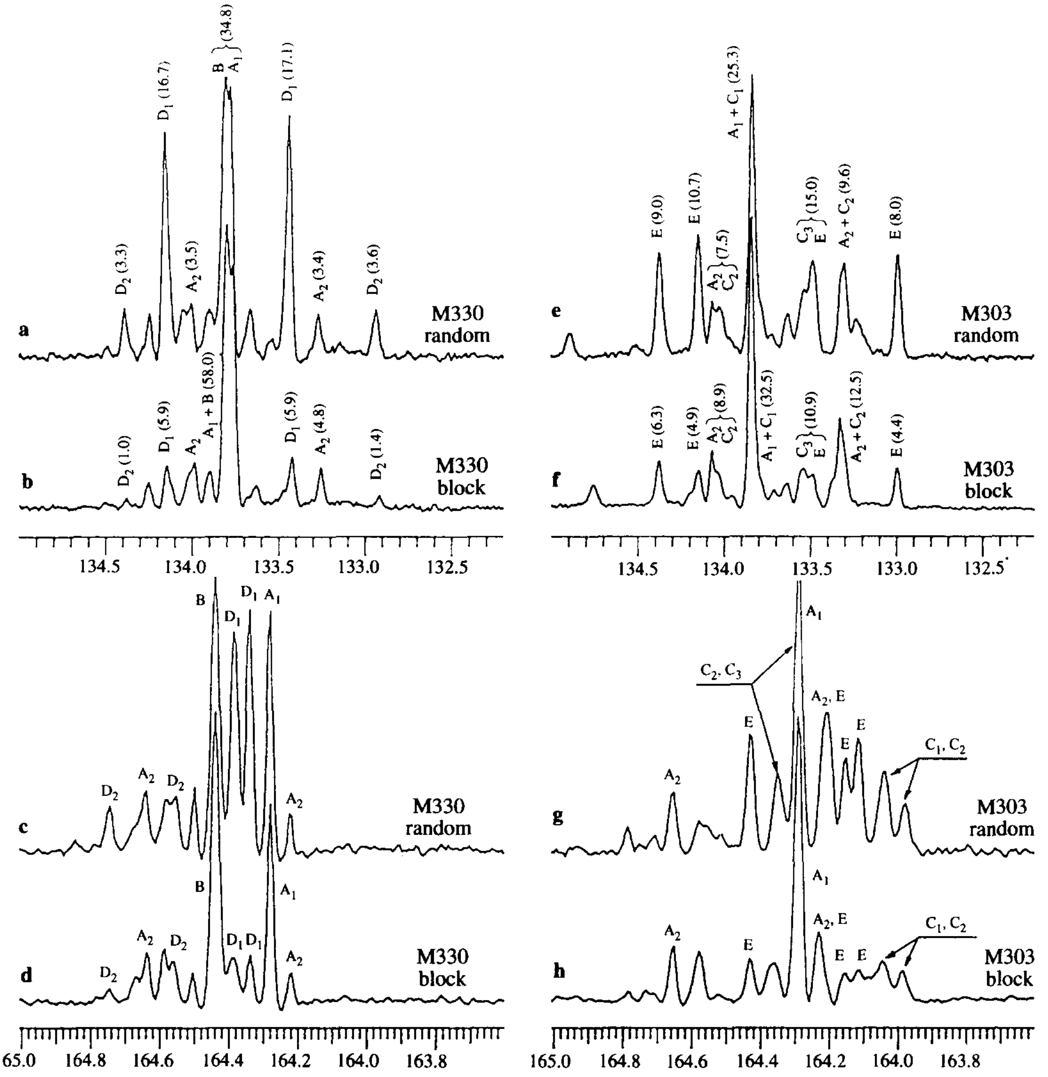


Figure 7 ^{13}C n.m.r. spectra of M330 and M303 polyesters with random and block distribution of diol units; the resonances are due to fumarate (a, b, e and f) and ester (c, d, g and h) carbons in the following sequences (see also *Table 1*): A_1, PD/PD(CH/CH), C1; A_2, PD/PD(CH/CH_2), C2 or C3; B, PO/PO(CH/CH), C9; D_1, PD/PO(CH/CH), C20 or C21; D_2, PD/PO(CH_2/CH), C22 or C23; C_1, PG/PG(CH/CH), C12; C_2, PG/PG(CH/CH_2), C13 or C14; C_3, PG/PG(CH_2/CH_2), C15; E, PD/PG(CH/CH) + PD/PG(CH/CH_2), C24 or C25 or C26 or C27. The numbering of fumarate carbons C*n* refers to adjacent ester carbons in the spectra c, d, g and h; the relative areas of the resonances due to internal sequences are given in brackets (to be compared with corresponding values from *Tables 2* and *3*)

polyester composition. It was found that, in addition to the signals observed for polyesters containing one kind of any diol, several new peaks appear in the regions of unsaturated and ester carbons. These new signals can unambiguously be ascribed to the sequences with the two different diol units adjacent to the fumarate moiety. Both the nature of the diol and the type of the resulting ester linkage give rise to a number of signals.

By assuming a random distribution of all the diol units in polyester chains, the contribution of each sequence was determined. The following parameters were used in the calculations:

(1) $P\{x\ [\text{or } y]\}$ – an unconditional probability of finding a given diol (x or y) unit in the polyester chain (equal to the mole fraction of that diol when the overall chemical composition of the polymer is assumed to be identical to the feed composition);

(2) $P\{x\ [\text{or } y]/x\ [\text{or } y]\}$ – a conditional probability of a diol–fumarate–diol sequence formation, regardless of the type of the resulting ester linkage;

(3) $P^*\{x\ [\text{or } y](\text{CH}\ [\text{or CH}_2])\}$ – a relative contribution of CH or CH_2 end groups in a given diol (x or y)

$$P^*\{\text{PG(CH)}\} = P^*\{\text{PG(CH}_2)\} = 0.5$$
$$P^*\{\text{PD(CH)}\} = 0.85 \qquad P^*\{\text{PD(CH}_2)\} = 0.15$$
$$P^*\{\text{PO(CH)}\} = 1 \qquad P^*\{\text{PO(CH}_2)\} = 0$$

(values for PD and PO being derived from ^1H n.m.r. spectra);

(4) $P^*\{x\ [\text{or } y]/x\ [\text{or } y](\text{CH}\ [\text{or CH}_2]/\text{CH}\ [\text{or CH}_2])\}$ – a relative contribution of a sequence formed by a given pair of diols with specified end groups adjacent to the fumarate unit.

By combining equations (1)–(4) it is possible to calculate the probability of the occurrence of internal diol–fumarate–diol (equation (5)) or terminal diol–carboxy-fumarate (equation (6)) sequences with specified diol end groups (or group) adjacent to fumarate (or carboxy-fumarate) unit:

$$P\{x\ [\text{or } y]/x\ [\text{or } y](\text{CH}\ [\text{or CH}_2]/\text{CH}\ [\text{or CH}_2])\} \quad (5)$$

$$P\{x\ [\text{or } y]/\text{–}(\text{CH}\ [\text{or CH}_2]/\text{–})\} \quad (6)$$

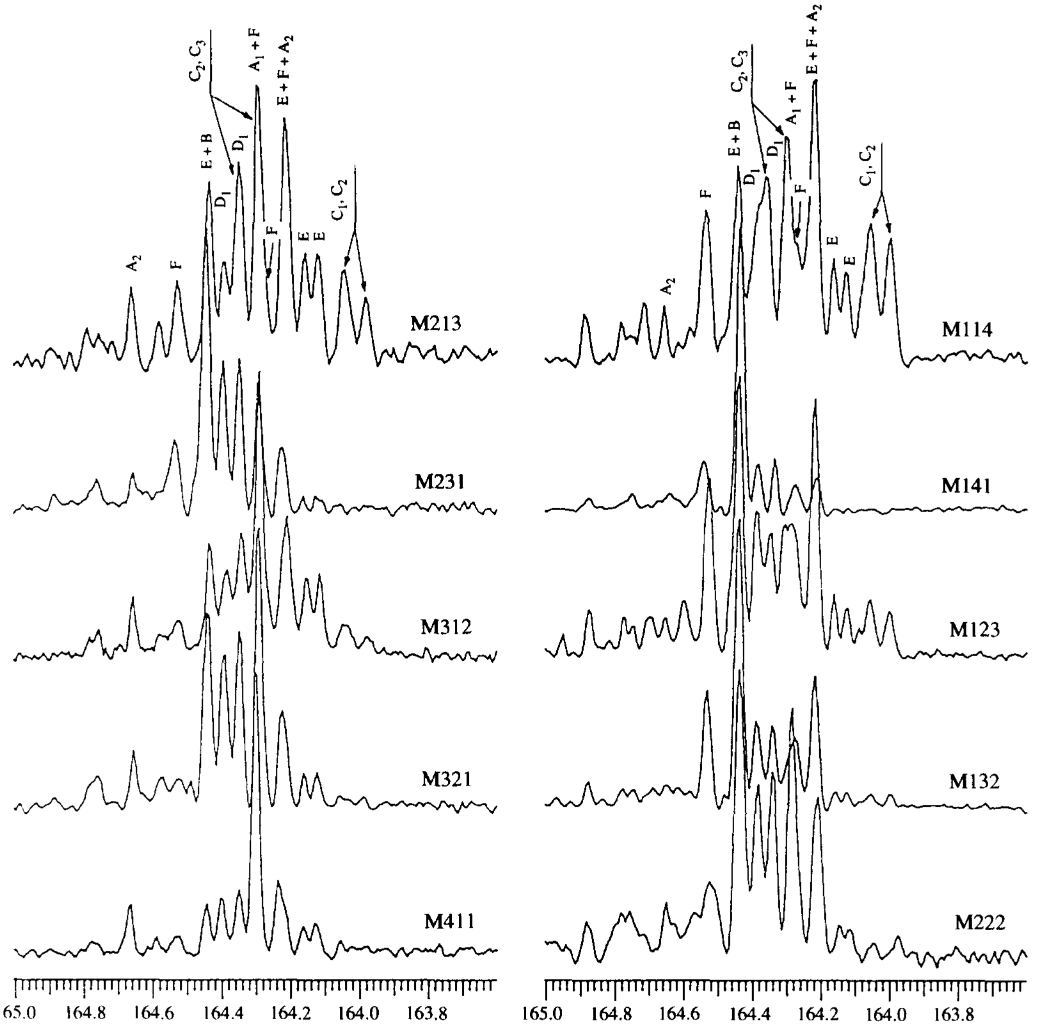


Figure 8 ^{13}C n.m.r. spectra of Mxyz polyesters (x = PD, y = PO, z = PG); the resonances are due to ester carbons in the sequences described in the caption to *Figure 6*

Finally, taking into account the contributions due to internal and terminal sequences in a chain of the assumed length, the probabilities (5) and (6) were converted into relative intensities of fumarate carbon resonances arising from the corresponding sequences.

The calculated values of the intensities for model fumarate polyesters containing PD and PO or PD and PG are presented in *Tables 2* and *3*, respectively. Once the resonance signals had been assigned, the calculated contributions could be compared with experimental values making the reasonable assumption of the same nuclear Overhauser enhancement (NOE) and relaxation times for all carbons in the analysed region. The observed values (given in the spectra, *Figures 4* and *5*) were found to be close to those expected for polyesters with random distribution of diol units of each kind.

Similar calculations were performed for polyesters Mxyz ($x+y+z=6$) composed of fumarate and three kinds of diol unit with x, y and z varying between 1 and 4 (*Table 4*). In spite of severe overlapping (*Figure 6*), it appears to be possible to discern the resonances arising from the sequences present in the polyesters of type Mxy0 and Mx0z from the four new peaks due to PO/PG sequences. The assignment of the latter was also supported by recording ^{13}C n.m.r. spectra of some model polyester samples containing PO and PG units.

Having confirmed a validity of the assignment it was possible to determine the structure of polyesters prepared in the three-stage method of synthesis. This time, theoretical values, summarized in *Tables 2* and *3*, were calculated assuming an ideal block arrangement of diol units and the same overall polymer and feed compositions. Some illustrative ^{13}C n.m.r. spectra given in *Figure 7* serve to highlight the utility of the proposed approach. This figure displays the spectra of selected polyesters (M330 and M303) obtained in the method which is expected to prefer a formation of polyesters with 'block' distribution of diol units; the spectral patterns of the corresponding polymers prepared in the conventional, one-stage route are given for the sake of comparison. A salient feature of the spectra is a considerable decrease in the intensities of the lines due to sequences with diverse kinds of diol units at both sides of the fumarate moiety in favour of those arising from the sequences composed of diol units of one kind. Such behaviour, observed also for other polyesters prepared in the three-stage procedure (M420, M240, M402, M204), confirms the assumed 'block' structure of these polymers.

Likewise, the diversity of the discussed sequences also accounts for the observed complexity of ester carbon spectral regions (*Figures 3–5*, *7* and *8*). The same general approach was applied to distinguish the signals and a comparison between experimental and calculated intensities was performed. The latter can be obtained by multiplying the corresponding data from *Tables 2–4* by 1.09, the factor resulting from the different contributions due to fumarate and ester carbons. Again, the peak areas (not provided in the spectra) were found to be consistent with a random or 'block' sequence distribution depending on the method of polyester preparation.

It should be stressed that the chemical shifts of the main signals arising from a given internal diol–fumarate–diol sequence are virtually the same regardless of the overall polyester composition and molecular mass. On the contrary, the lines ascribed to carbons in terminal, diol–carboxyfumarate sequences tend to shift upon variations in chain length and composition of the polyesters. This effect seems to be dependent on interactions between chain end groups, including possible formation of hydrogen bonds[13], and on the nature and concentration of the end groups.

CONCLUSIONS

An analytical method based on ^{13}C n.m.r. measurements was proposed which allows us to perform a detailed structural characterization of fumarate polyesters. The method is expected to be a useful and convenient aid in determining structure–property relationships as well as in monitoring and verifying the synthetic routes to well defined polyesters designed for specific applications.

REFERENCES

1 Jedliński, Z. J. in 'Handbook of Polymer Synthesis', Part A (Ed. H. A. Kricheldorf), Marcel Dekker, New York, 1991 and references therein
2 Curtis, L. G., Edwards, D. L., Simons, R. M., Trent, P. J. and Von Bramer, P. T. *Ind. Eng. Chem. Prod. Res. Dev.* 1964, **3**, 218
3 Bellenger, V., Mortaigne, B., Grenier-Loustalot, M. F. and Verdu, J. *J. Appl. Polym. Sci.* 1992, **44**, 643
4 Vancsó-Szmercsányi, I., Maros-Gréger, K. and Makay-Bödi, E. *J. Polym. Sci.* 1961, **53**, 241
5 Ordelt, Z. *Makromol. Chem.* 1963, **68**, 166
6 Judas, D., Fradet, A. and Maréchal, E. *Makromol. Chem.* 1984, **185**, 2583
7 Fradet, A. and Maréchal, E. *Makromol. Chem.* 1982, **183**, 319
8 Paci, M., Crescenzi, V., Supino, N. and Campana, F. *Makromol. Chem.* 1982, **183**, 377
9 Goodlett, V. W. *Anal. Chem.* 1965, **37**, 431
10 Bose, A. K. and Srinivasan, P. R. *Tetrahedron* 1975, **31**, 3025
11 Oguni, N., Shinohara, S. and Lee, K. *Polym. J.* 1979, **10**, 755
12 Bovey, F. A. 'NMR of Macromolecules', Academic Press, New York, 1969
13 Von Demmler, K. and Günzler, H. *Makromol. Chem.* 1966, **90**, 119