^{13}C and ^{1}H n.m.r. study of the polyesterification of maleic anhydride and 1,2-propylene glycol

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The reaction steps of the polyesterification of maleic anhydride and 1,2-propylene glycol were followed by ^{13}C and ^{1}H n.m.r. spectroscopy. The number and structure of mono- and diesters of both maleates and fumarates in the reaction mixture are determined by the possible glycol unit configurations. The structure of the growing polyester chain reflects a statistical distribution of approximately equal numbers of symmetric and asymmetric arrangements of the polymer sequences.

Keywords ^{13}C nuclear magnetic resonance; ^{2}H nuclear magnetic resonance; polyesterification; *cis–trans* isomerization; maleic anhydride; 1,2-propylene glycol

INTRODUCTION

The polyesterification of maleic anhydride and *cis–trans* isomerization, depending on the temperature, reaction time and the type of glycol, have been widely studied concerning the properties of maleate and fumarate polyesters[1,2]. Nuclear magnetic resonance proved to be very useful in the determination of the *cis–trans* isomerization and the chain composition of polyesters[3-8].

The purpose of the present paper is to analyse the microstructure of the polyester chain and the *cis–trans* isomerization at different stages of the polycondensation reaction of maleic anhydride and 1,2-propylene glycol. ^{13}C in combination with ^{1}H n.m.r. was applied.

The sensitivity of ^{13}C chemical shifts to the slight environmental differences and the already known rules for substituent chemical shifts of related compounds[9,10] enable one to describe both the sequence of monomer units in the polyester backbone including configurational characteristics of the glycol unit and *cis–trans* isomerizations.

EXPERIMENTAL

The polyesterification of equivalent amounts of reagent grade 1,2-propylene glycol (Fluka), used without further purification, and maleic anhydride (Aldrich), recrystallized from benzene solution, was carried out without catalyst in a melt and under nitrogen gas with continuous stirring.

The reaction temperature was increasing during the polymerization stepwise up to 220°C. The aliquots were taken from the reaction mixture at different temperatures. For each aliquot the acid number of polyester was determined by a standard method and the corresponding molecular mass by osmometric measurements in methyl ethyl ketone solution on a Perkin-Elmer MWA 115 osmometer.

^{13}C n.m.r. spectra were recorded at 25.05 MHz on a JEOL FX-100 spectrometer using the internal deuterium lock. The spectral width was 6000 Hz, giving a digital resolution of 1.47 Hz for 8000 sampling and transformation points. The samples, dissolved in deuteroacetone immediately after the aliquots were taken, were measured at room temperature in 5 mm tubes with tetramethyl silane (TMS) as internal standard. All the samples were measured under exactly the same instrumental conditions, except in specific cases for which the appropriate parameters are given in the text. The assignments were based on proton noise and gated decoupled spectra.

^{1}H n.m.r. spectra of the same samples were recorded at 89.55 MHz on a JEOL FX-90Q spectrometer under similar conditions as for ^{13}C spectra. The spectral width was 1000 Hz and digital resolution 0.24 Hz.

RESULTS AND DISCUSSION

Table 1 lists the numbers of samples at given times and temperatures with the corresponding molecular mass ($\bar{M}_n$), acid number and fumarate contents. Though polycondensation gives a regular monomer distribution along the chain (–acid–glycol–acid–glycol–), the asymmetry of 1,2-propylene glycol introduced a number of different configurations in the polymer chain. Owing to the complexity of n.m.r. spectra, two general regions will be discussed separately.

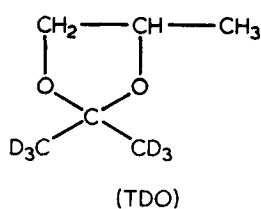### ^{13}C and ^{1}H n.m.r. spectra of 1,2-propylene glycol and related forms

The ^{13}C n.m.r. spectrum of sample No. 1, which is the mixture of 1,2-propylene glycol (PG) and maleic anhydride (MAn), is shown in *Figure 1*. The spectrum was recorded immediately after dissolving PG and MAn in acetone-d$_6$ (*Figure 1a*) and chloroform (*Figure 1b*). The methine, methylene and methyl ^{13}C chemical shifts of the pure PG in acetone-d$_6$ solution are listed in *Table 2*. However, in sample No. 1 in acetone solution three additional peaks in the PG region have been observed (*Figure 1a*). By the gated decoupling experiments these

Table 1 Reaction temperatures, molecular mass $(\overline{M}_n)$, acid numbers and fumarate contents of the samples
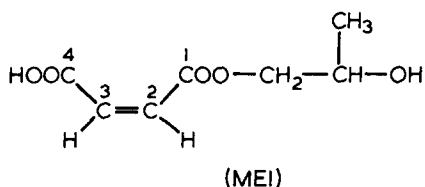
Sample no.	Time (min)	Temperature (°C)	$\overline{M}_n$	Acid number	Fumarate content[a] (%)
1	0	room	—	—	0
2	30	45	—	437	0
3	45	110	199	396	0
4	48	125	183	391	5
5	52	135	185	373	10
6	135	135	282	277	63
7	165	135	298	264	63
8	185	180	414	269	63
9	205	180	482	184	74
10	225	220	1210	110	90
11	245	220	1850	93	93
12	265	220	3062	71	95

[a] Determined from ^{1}H n.m.r. spectra

Figure 1 ^{13}C n.m.r. spectra of sample No.1 in (a) acetone-d_6 and (b) chloroform-d_1 solution

peaks were assigned as methine, methylene and methyl group absorptions, respectively. They appear only if the mixture is dissolved in acetone-d_6 but are missing in the chloroform solution (*Figure 1b*). Besides, there is an additional peak at 108.8 ppm corresponding to the quaternary carbon atom, and two methyl-d_6 multiplets centred at about 26.5 and 26.1 ppm. All these absorptions have their origin in 2,2,4-trimethyl-1,3-dioxolan[11] formed in the present case from acetone-d_6 and PG in the presence of maleic anhydride:

(TDO)

In this reaction a small amount of maleic acid (MAc) was also formed (*Figure 1a*). If the acetone solution of PG and MAn was left at room temperature for 1 h, a monoester was formed:

(MEI)

It was identified as ME1 on the basis of ^{13}C n.m.r. methylene carbon deshielding by adjacent carboxyl group and methine carbon shielding in comparison with the pure PG signals. Within several hours the second monoester ME2 was formed:
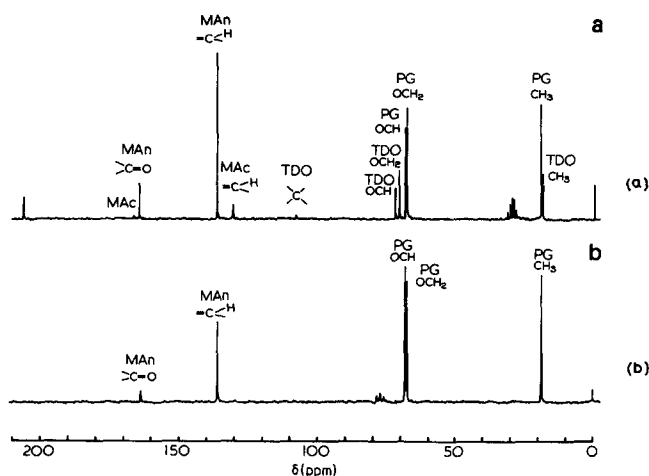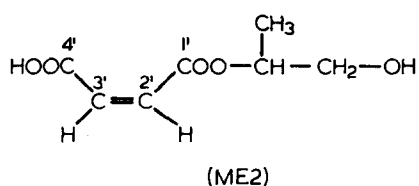

(ME2)

Table 2 ^{13}C chemical shifts (ppm from TMS) of the methine, methylene and methyl groups of PG region

| PG form | Group | | |
	Methine	Methylene	Methyl
1	PG	68.6	67.8	19.1
2	TDO	72.3	70.8	18.6
3	ME1	65.8	70.3	19.3
4	ME2	73.2	64.9	16.1
5	M–PG–M	69.6	66.8	16.2
6	FE1	65.8	70.5	19.3
7	FE2	73.4	64.9	16.1
8	M–PG–F	69.6–70.0	66.8–67.1	16.2
9	F–PG–F	70.0	67.1	16.2

The shielding effects of methine and methylene groups are reversed (*Table 2*), since methine carbon is in the α-position to the carboxyl group. It is interesting to note that the methyl carbon in ME2 is shielded by about 3 ppm. This appears to be the case in all di- and polyesters where the methyl group is in the β-position to carboxyl (*Table 2*).

The same monoesters ME1 and ME2 were confirmed in the spectrum of sample No. 2 (*Figure 2b*) which was taken from the reaction mixture at 45°C. In continuation of the reaction at 110°C (sample No. 3) only diester of PG was formed (M–PG–M). This is in accordance with earlier findings that in the first step of polyesterification monoesters and then diesters of glycol are formed[12]. The structure of M–PG–M was determined from the ^{13}C n.m.r. spectrum (*Figure 2c*):

(M–PG–M)
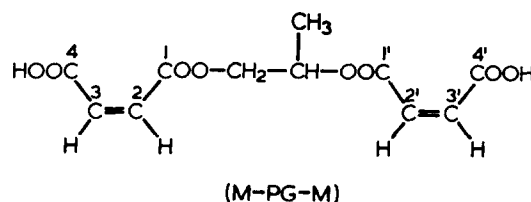
However, in the reaction mixture at 110°C all the previous forms of PG are also present as confirmed by ^{1}H n.m.r. spectra. Although the spectra of all the samples are very complex, some information can be deduced from the
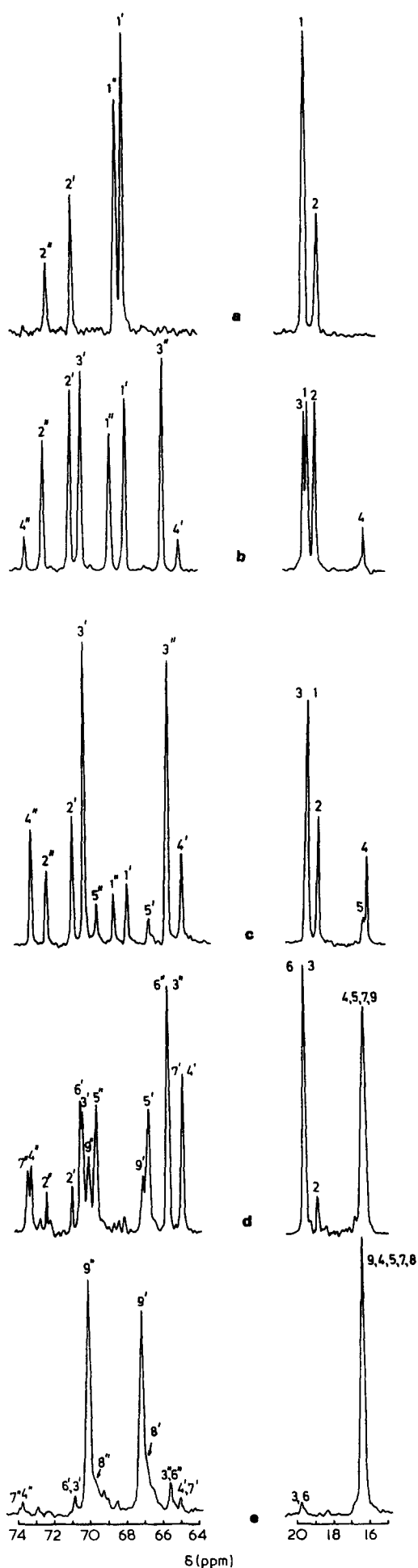
methyl absorption region. In the spectrum of sample No. 3, five methyl doublets were identified. The chemical shifts of methyl groups found in all the species during the reaction are listed in *Table 3*.

The assignment of the doublets corresponding to PG, ME1, ME2 and M–PG–M is based on the data by Birley *et al.*[13] for some related systems. The coupling constant J_{HH} of each doublet is about 6.5 Hz. An additional doublet centred at 1.19 ppm with coupling constant of about 5.8 Hz corresponds to TDO. This assignment was deduced by comparing this spectrum with that of sample No. 1 where only two PG forms were observed.

The *cis–trans* isomerization in the polycondensation of MAn and PG occurs predominantly at a very low degree of esterification[2]. Thus the fumarate esters appear already in sample No. 4 with the molecular mass corresponding mainly to the monoester structure.

At 135°C (sample No. 5) new peaks in [13]C n.m.r. spectra appeared (peaks 7″, 6″, 9″ and 9′ in *Figure 2d*). Since new peaks due to the fumarate appeared simultaneously in the olefinic region of the [13]C n.m.r. spectrum at 134 ppm, it was reasonable to assume that these four peaks in the PG region were also connected with the isomerization process. Their relative intensities were enhanced with increasing reaction time and temperature. To confirm this assignment, calcium chloride was added to the mixture of maleate monoesters in order to catalyse the isomerization process. At that instant the mixture was free of diesters and two fumarate monoesters FE1 and FE2 were formed:
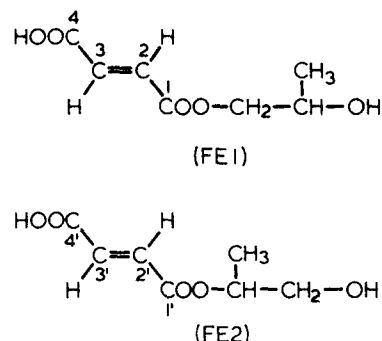

(FE1)

(FE2)

Table 3 ^{1}H chemical shifts (ppm from TMS) of methyl group of PG in different forms

PG form	Methyl doublet centre
PG	~1.12
ME1	1.16
FE1	1.18
TDO	1.19
ME2	1.23
FE2	1.26
M–PG–M	1.31
M–PG–F	1.33
F–PG–F	1.37

Figure 2 Expanded regions of PG absorptions for samples No.1 (a), 2(b), 3 (c), 5 (d) and 12 (e). The peaks are denoted by the same numbers of PG forms as in *Table 2*. The methylene peaks are marked with a prime and those of methine groups with a double prime; the methyl signals are not primed. Note that in sample No.12 each PG form is only a part of a polyester chain

The slight downfield shift of the FE1 methylene group by about 0.2 ppm confirms the *trans* configuration of the ester[10]. Accordingly, the methine group in FE2 is shifted downfield by the same amount, and the methyl group attached to it by about 0.1 ppm.

The molecular mass of samples Nos. 6 and 7 (at 135°C) corresponds predominantly to the diester structure. In these samples, together with the further isomerization of monoesters, the isomerization of the diester M–PG–M was also observed. The downfield shifts of both methine and methylene groups, in comparison with the M–PG–M, indicate the presence of F–PG–F diester:

HOOC   H   H   COOH
     \\   /   \\   /
      C = C   C = C
     /   \\   CH₃   /   \\
    H   COO—CH₂—CH—OOC   H

(F—PG—F)
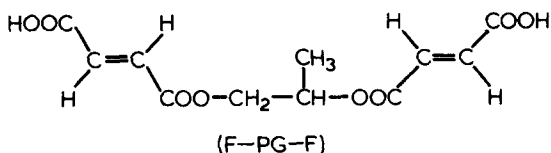
Some unresolved peaks between methine (66.6–70.0 ppm) and methylene group (66.8–67.1 ppm) are probably due to the mixed maleate/fumarate diesters (M–PG–F; two configurations). The absorptions arising from PG and related TDO were no longer present. The main components of the samples at 135°C are monoesters and diesters and probably some oligoesters with a low number of ester bonds.

As the temperature is increased to 180°C (samples Nos. 8 and 9), further *cis–trans* isomerization takes place and an oligomer chain begins to grow. At higher temperatures (up to 230°C), a significant increase of molecular mass occurs; most of the maleates are already converted to fumarates.

In the ¹³C n.m.r. spectrum of the final sample (No. 12 *Figure 2e*) there are only three main absorptions in the PG region arising from the main repeating unit in the poly(propylene glycol fumarate) chain: ∿∿F–PG–F∿∿. Small peaks assigned to FE1 and FE2 monoesters are the glycol end groups. Some unresolved signals on the upfield sides of ∿∿F–PG–F∿∿ methine and methylene peaks belong to the remaining maleates incorporated randomly in the polyester chain. There are also observable minor signals around the main methyl absorption which are due to the maleate units present (*Table 1*).

Additional information about the PG sequences can be obtained from the methyl absorption region in the ¹H n.m.r. spectra. However, the methylene doublets and methine multiplets of all possible configurations of maleates and fumarates overlap. In addition to the previously assigned PG methyl doublets (three due to maleate esters, one from PG and one from TDO), a series of four new doublets appear as the reaction temperature increased (sample No. 12, *Figure 3*). The intensity of those peaks was changing with increasing fumarate content and molecular mass. The most intensive absorption at 1.36 ppm arises from the main chain unit ∿∿F–PG–F∿∿, and the doublet centred at 1.33 ppm from the PG methyl group placed between fumarate and maleate units. Two high-field doublets correspond to the glycol end groups adjacent to fumarate unit (types FE1 and FE2).

¹³C n.m.r. spectra of maleic anhydride and related forms

The range of chemical shifts of the carbonyl groups of both maleates and fumarates is between 165.5 and 167.6 ppm. However, the olefinic absorptions are clearly separated into maleic and fumaric parts at 129.6–131.6 ppm and 133.4–134.9 ppm, respectively.

The corresponding peaks for MAn in acetone solution were observed at 165.8 and 137.7 ppm. Water evolved during the process gives MAc with peaks at 167.3 and 131.8 ppm.

The assignment of ME1 and ME2 peaks (sample No. 2) was based on the same arguments as for the PG groups. The carboxyl peak in a monoester is shifted upfield in comparison to the corresponding acid[10,14]. The olefinic part of the spectrum also displays four peaks. In addition to the shielding effects on the neighbouring carboxyl carbon, the upfield shift on olefinic carbons as well as on the second carbonyl is observed regardless of the configuration of glycol in both monoesters. All the corresponding chemical shifts are listed in *Table 4*.

In monoester ME1, where the PG methylene group is closer to the C-1 atom, the shielding effect on olefinic carbons C-2 and C-3 is almost equal. Sometimes a single peak for these two carbons is observed depending on the relative concentrations of monomers and esters. However, in monoester ME2, having a different configuration of the glycol unit, the steric effect of the

Figure 3 ¹H n.m.r. spectrum (expanded methyl region) of sample No.12

Table 4 ^{13}C chemical shifts (ppm from TMS) of olefinic and carboxyl groups[a]

	C-atom							
Form	1	1'	2	2'	3	3'	4	4'
MAc	167.31		131.80		131.80		167.31	
ME1	166.14	–	130.57	–	130.86	–	167.07	–
ME2	–	166.01	–	130.22	–	131.39	–	166.85
M–PG–M	165.86[b]	165.65[b]	130.55	129.87	130.74	131.38	166.83[b]	165.98[b]
FE1			134.03	–	134.56	–		
FE2			–	133.74	–	134.42		

[a] The figures are given to two decimal places with accuracy ±0.02 ppm (spectral width 200 Hz, digital resolution 0.10 Hz)
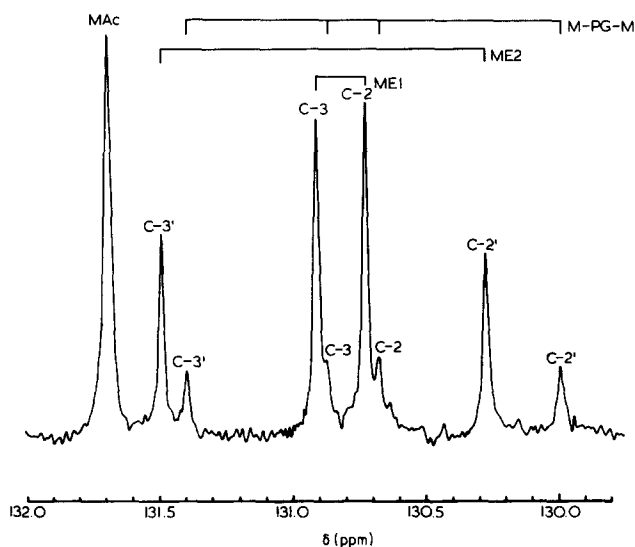[b] The assignments could be exchanged

Figure 4 Expanded olefinic region of [13]C n.m.r. spectrum of sample No.3

methyl group exhibits considerably different shifts on the olefinic carbons C-2' and C-3'.

The spectrum of sample No. 3 (*Figure 4*) shows four additional peaks in the olefinic region which are assigned to the diester M–PG–M. The absence of the glycol OH group in diester seems to enhance the influence of the glycol unit configuration on the chemical shifts of olefinic carbon[15]. There are also four peaks in the carbonyl region. The two peaks at higher fields are assigned tentatively to ester groups (atoms C-1 and C-1') and low-field peaks to acidic groups (atoms C-4 and C-4').

The sample with calcium chloride was used to assign the olefinic carbons of fumarate monoesters. It is reasonable to assume that the change in chemical shifts in fumarate is in the same direction as in the maleate monoesters. There is evidence that the substituent chemicals shift should not be affected by *cis–trans* isomerization[16]. Fritz and Sauter[14] proposed the opposite assignment for the fumarate monoester.

In the carbonyl part of the spectra of fumarates all the absorption peaks are found within 1.5 ppm. Therefore it was not possible to make an unambiguous assignment. When diesters of fumarate in the mixture with maleate diesters and monoesters are formed the assignment is very tedious. However, when the molecular mass is greater than 1000 and fumarate content about 90%, the main repeating unit of the polyester chain can be determined easily.

In both the carboxylic and olefinic part of the [13]C n.m.r. spectrum of the polyester chain (sample No. 12, *Figure 5*), four clearly resolved peaks are obtained. They reflect the statistical distribution of different PG unit configurations in the main chain. The fumarate unit can be placed between two symmetrical and one asymmetrical PG configuration:
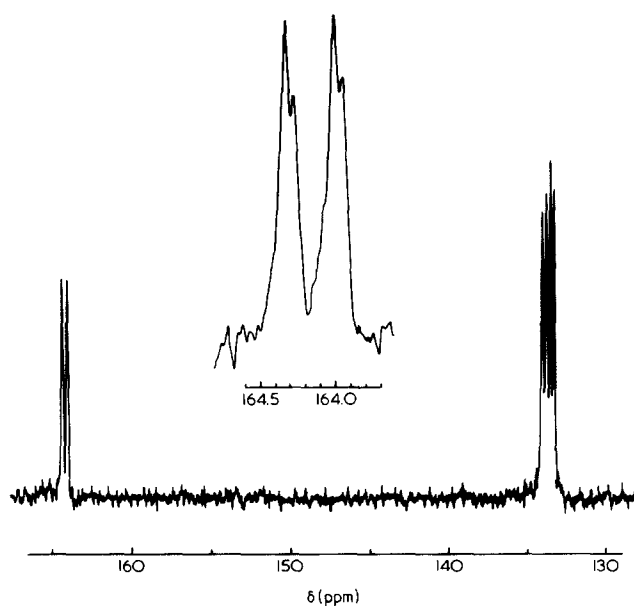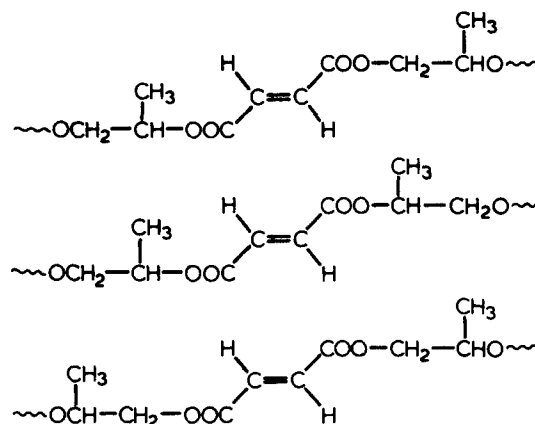

Figure 5 Expanded olefinic and carbonyl region of [13]C n.m.r. spectrum of sample No.12

Each symmetrical arrangement gives rise to a single peak, while the asymmetrical configuration results in two peaks. Since the intensities of the four peaks are approximately equal it appears that the number of symmetrical and asymmetrical arrangements of the polyester sequences is nearly identical. The carbonyl part of the spectrum shows very similar features which can be explained in the same way. However, the smaller differences in chemical shifts are due to the lower sensitivity of carbonyl carbon to the PG configuration.

If the spectrum is recorded in a narrow region (500 Hz, digital resolution 0.50 Hz) four additional peaks in the olefinic part due to the fumarate end groups are revealed (type FE1 and FE2).

The analysis clearly demonstrates the sensitivity of the ^{13}C n.m.r. spectra in the determination of the main chain structure depending on different configurations of monomer units. Moreover, the residual end groups can be efficiently detected.

ACKNOWLEDGEMENTS

REFERENCES

1   Vancsó-Szmercsányi, I., Maros-Grégor, K. and Makay-Bödi, E. *J. Polym. Sci.* 1961, **53**, 241
2   Vancsó-Szmercsányi, I., Maros, L. K. and Zahran, A. A. *J. Appl. Polym. Sci.* 1966, **10**, 513
3   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
4   Percival, D. F. and Stevens, M. P. *Anal. Chem.* 1964, **36**, 1574
5   Urman, Ya. G., Khramova, T. S., Avdeeva, G. M., Sedov, L. N. and Slonim, I. Ya. *Vysokomol. Soedin. A* 1972, **14**, 2597
6   Sauer, W., Kuzay, P., Kimmer, W. and Jahn, H. *Plaste Kautsch.* 1976, **23**, 331
7   Khramova, T. S., Urman, Ya. G., Avdeeva, G. M., Sedov, L. N. and Slonim, I. Ya. *Vysokomol. Soedin. A* 1973, **15**, 148
8   Urman, Ya. G., Alekseeva, S. G. and Slonim, I. Ya. *Vysokomol. Soedin. A* 1977, **19**, 299
9   Randall, J. C. 'Polymer Sequence Determination', Academic Press, New York, 1977
10   Stothers, J. B. 'Carbon-13 NMR Spectroscopy', Academic Press, New York, 1972
11   Pihlaja, K. and Nurmi, T. *Finn. Chem. Lett.* 1977, 141
12   Vancsó-Szmercsányi, I., Makay, E. and Maros, K. *Polimery* 1966, **11**, 355
13   Birley, A. W., Kyriacos, D. and Dawkins, J. V. *Polymer* 1978, **19**, 1290
14   Fritz, H. and Sauter, H. *J. Magn. Res.* 1975, **18**, 527
15   Andreis, M., Meić, Z. and Veksli, Z. unpublished results
16   Meić, Z. and Vikić-Topić, D. unpublished results