# A $^1$H and $^{13}$C n.m.r. study of the products from direct polyesterification of ethylene glycol and terephthalic acid

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Low molecular weight samples of poly(ethylene terephthalate), obtained by direct bulk polyesterification of terephthalic acid and ethylene glycol, were studied by $^1$H and $^{13}$C n.m.r. It was possible to determine degrees of conversions of acid and alcohol groups, distributions of free, monoesterified and diesterified terephthalic acid and ethylene glycol and to identify the dimer, trimer and tetramer. Side reactions were also studied.

## INTRODUCTION

Poly(ethylene terephthalate) (PET), obtained mainly from dimethyl terephthalate and ethylene glycol, contains well known side-products such as cyclic oligomer[1] and diesterified diethylene glycol (DEG)[2,3]. Until now, most quantitative studies have been achieved using classical chemical and/or physical techniques: DEG by hydrazinolysis followed by gas chromatography[2] or potentiometry[4]; cyclic oligomers by solvent extraction and chromatography[1], etc. There are no published n.m.r. studies on the microstructure of the low molecular weight PETs.

The present study deals with the examination by $^1$H and $^{13}$C n.m.r. of the low molecular weight PET samples obtained by direct bulk polyesterification of terephthalic acid and ethylene glycol at high temperature and without catalyst.

## EXPERIMENTAL

### Polyesterification

A paste (P) was obtained with pure terephthalic acid (T, 1 mol) and an excess of ethylene glycol (G, 1.1 mol) at 250°C under pressure. Polyesterification was then performed at 265°C with mechanical stirring. Three samples, S1, S2 and S3, were taken at 70, 110 and 150 min, respectively.

### Model compounds

The monoester of T (TG, 2-hydroxyethyl terephthalate) was synthesized using a method previously described[4]. The diester of T (GTG, bis-(2-hydroxyethyl) terephthalate) is a commercial product (Teijin). The cyclic hexamer (TG)$_3$ (or degree of polymerization = 6) was extracted from the powder using boiling dioxane.

### Acid end groups of PETs – quantitative determinations

Samples of PET were dissolved in anhydrous $N$-methyl pyrrolidone (NMP) and heated at 150°C. Acid end groups were determined by potentiometry using a solution of 0.05 mol l$^{-1}$ KOH in methanol.

### $^1$H and $^{13}$C n.m.r. spectrometry

N.m.r. spectra were recorded using a Caméca 350 FT spectrometer (350 and 88 MHz for $^1$H and $^{13}$C, respectively). PET samples were dissolved in DMSO-d$_6$ with hexamethyl disiloxane (HMDS) as internal reference ($\delta = 0$ ppm). The probe temperature was 140°C. Typical analysis conditions were as follows. $^1$H: pulse angle = 20°; acquisition time = 2.3 s for 16 k words; sweep width = 3520 Hz; number of scans = 20. $^{13}$C: pulse angle = 30°; acquisition time = 4.3 s for 32 k words; sweep width = 19 230 Hz; repetition time = 5.3 s; number of scans = 2000–3000.

The $^{13}$C analysis conditions allow quantitative determinations of the conversions by comparing CO-acid and CO-ester resonances. CO-acid groups have the longest $T_1$ value (7.6 s at 8.2 T), so according to the Ernst relation, with a repetition time of 5.3 s, even a pulse angle of 60° may be utilized.

## RESULTS AND DISCUSSION

Most known studies of side reactions in the synthesis of PET have been performed using chemical analysis and/or chromatography[2,3]. From our own experiments, the presence of DEG cannot be determined by $^1$H n.m.r. at 100 MHz. The $^1$H and $^{13}$C chemical shifts of G, T, DEG and those of some model compounds are reported in *Table 1*.

### $^1$H n.m.r.

In sample P (*Figure 1a*), free T (aromatic singlet at

**Table 1** ¹H (350 MHz, figures not in parentheses) and ¹³C (88 MHz, figures in parentheses) chemical shifts of ethylene glycol (G), diethylene glycol (DEG), terephthalic acid (T), monoester of ethylene glycol terephthalic acid (TG), diester of ethylene glycol terephthalic acid (GTG), cyclic hexamer of ethylene glycol terephthalate ((TG)₃), polyethylene glycol terephthalate ((TG)ₙ) and polydiethylene glycol terephthalate ((TDEG)ₙ). Solvent, DMSO-d₆; temperature, 140°C; internal reference, HMDS ($\delta = 0$ ppm)



HO — CH₂ — CH₂ — OH  (G)

3.83   (61.66) 3.41

HO — CH₂ — CH₂ — O — CH₂ — CH₂ — OH  (DEG)

3.91   (59.31) 3.57   (70.63) 3.41

HOOC —⬡— COOH  (T)

11.6   (164.9) (133.1)   (127.54) 8.013

HOOC —⬡— COO — CH₂ — CH₂ — OH  (TG)

12.8   (164.63) (133.43) (127.5) 7.995   (132.2) (163.6)   (65.10) 4.30   (57.6) 3.705

HO — CH₂ — CH₂ —OOC —⬡— COO — CH₂ — CH₂ — OH  (GTG)

4.36   (57.66) 3.68   (65.20) 4.284   (163.56) (132.53) (127.5) 8.103

∼—OOC —⬡— COO — CH₂ — CH₂ — OOC —⬡— COO — ∼ (TG)₃
(cyclic hexamer)

(127.56) 7.961   (132.26) (163.1)   (61.11) 4.602

∼— OOC —⬡— COO — CH₂ — CH₂ — OOC —⬡— COO — ∼ (TG)ₙ
(linear polymer)

(127.62) 7.95   (132.33) (163.36)   (61.44) 4.63

∼— OOC —⬡— COO — CH₂ — CH₂ — O — CH₂ — CH₂ — OOC —⬡— COO∼(TDEG)ₙ

(127.38) 7.86   (132.09) (163.18)   (66.66) 4.37   (62.47) 3.78

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8 ppm) and free G (aliphatic methylene singlet at 3.4 ppm) are still present. In addition the free DEG (single wide methylene resonance at 3.5 ppm) and diesterified DEG (two wide methylene resonances at 3.8 and 4.4 ppm), identified using model compounds (*Table 1*), result from the dehydration of free G and monoesterified G (TG) respectively.

Free T only disappears in sample S1, but the proportion of diesterified DEG that increases notably in sample S1 (*Figure 1b*) seems to become stable at 5–6% in samples S2 and S3 (*Figure 2*). The cyclic hexamer ((TG)₃) cannot be detected because its methylenic and

aromatic resonances are hidden by the same ¹H resonances of the PET linear chains (*Table 1*). ¹H n.m.r. spectra permit the direct determinations of the T/G molar ratio (r) by comparison between the integral data of the aromatic (T) and methylenic (G + DEG) ¹H resonances. The calculated r value (1/1.15) does not differ from the theoretical value (1/1.1) within experimental error.

The conversions of alcohol groups ($C_a$) as well as the distributions of free (*G*, 3.4 ppm), monoesterified (–TG*, 3.7 and –T*G, 4.3 ppm) and diesterified (–T*G*T–, 4.6 ppm) Gs may be calculated easily using
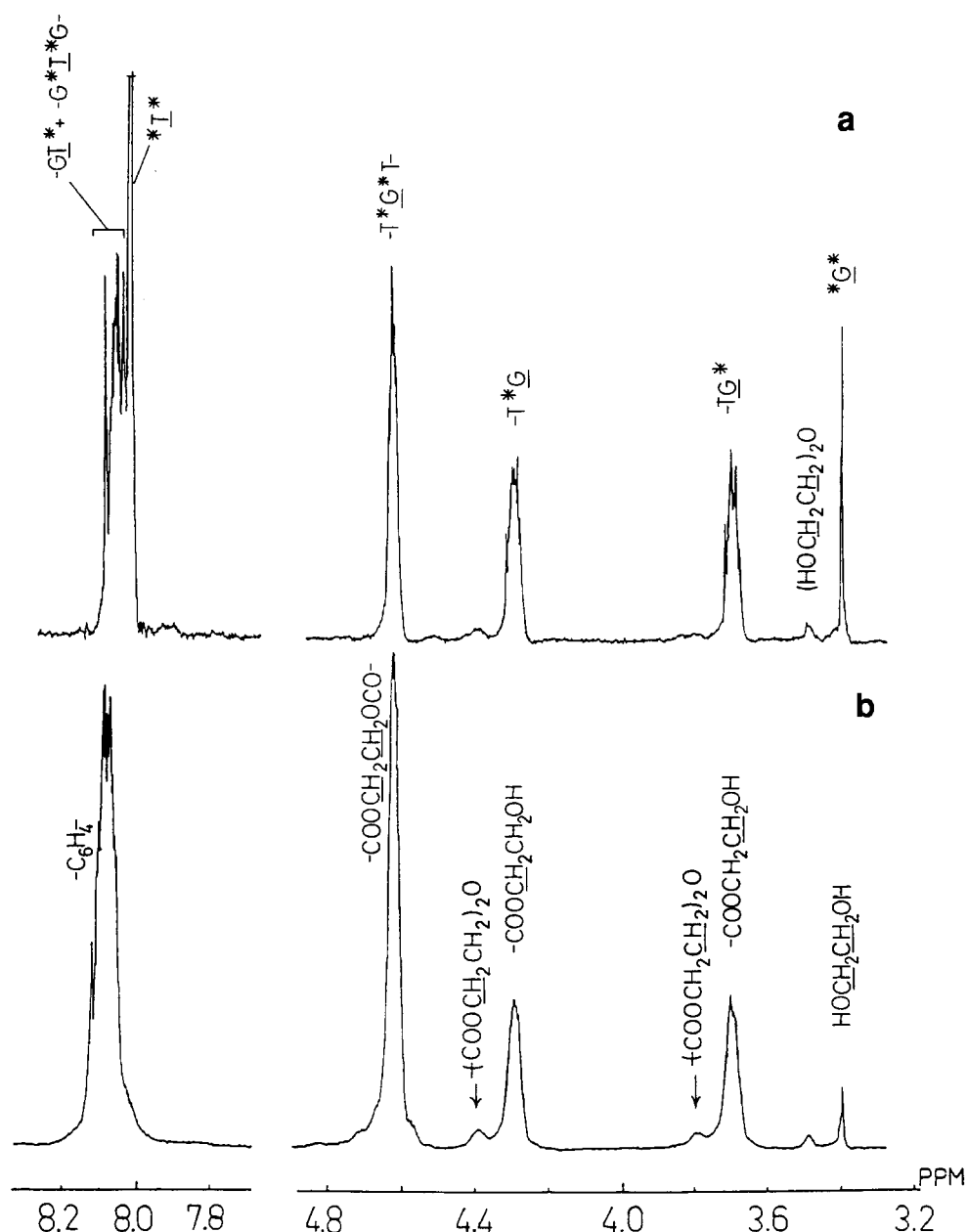
**Figure 1** ¹H (350 MHz) n.m.r. spectra of PET samples P (a) and S1 (b). (-TGT-), (-TG) and (G) = diesterified, monoesterified and free ethylene glycol, respectively; (-GTG-), (-GT) and (T) = diesterified, monoesterified and free terephthalic acid, respectively. Underlined letters and asterisks denote origins of the resonances. -GT* and -G*T*G- = aromatic protons of the T-acid end and T-diester unit, respectively. -T*G and TG* = methylene ester and methylene alcohol of G, respectively

methylenic proton resonances:

$$C_a = \frac{(-T^*G^*T-) + (1/2)[(-T^*G) + (-TG^*)]}{S} \quad (1)$$

$$\left.\begin{array}{l}(-TGT-)\% = 10^2 \times (-T^*G^*T-)/S \\ (-TG)\% = 10^2 \times [(-T^*G) + (-TG^*)]/S \\ (G)\% = 10^2 \times (^*G^*)/S\end{array}\right\} \quad (2)$$

$$S = (-T^*G^*T-) + (-T^*G) + (-TG^*) + (^*G^*)$$

Underlined letters and asterisks denote the origins of the methylene resonances (ester = -T*G, alcohol = *G* and -TG*). (-T*G*T), (-T*G), etc. are the relative integral intensities of the corresponding resonances in *Figures 1* and *2*. The conversions of T cannot be calculated from ¹H spectra because of the bad spectral

resolution of the aromatic resonances in the (8-8.2 ppm) region. All the calculated values are reported in *Table 2*.

¹³C n.m.r.

The best spectral resolution is obtained with PET dissolved in DMSO and examined at 140°C. The methylenic carbons (*Figure 3*) of free (*G*) and diesterified (-T*G*T-) Gs have the same chemical shifts (61 ppm), thus $C_a$ cannot be determined by ¹³C n.m.r. Free and diesterified DEG are also detected at 60 (shoulder), 62 and 66 ppm, respectively.

The carbonyl and quaternary aromatic carbon resonances of the very low molecular weight (*Figure 3*) P and S1 samples are very complex and their identifications required the examination of the dimer (GT) and trimer (GTG) model compounds (*Table 1*).
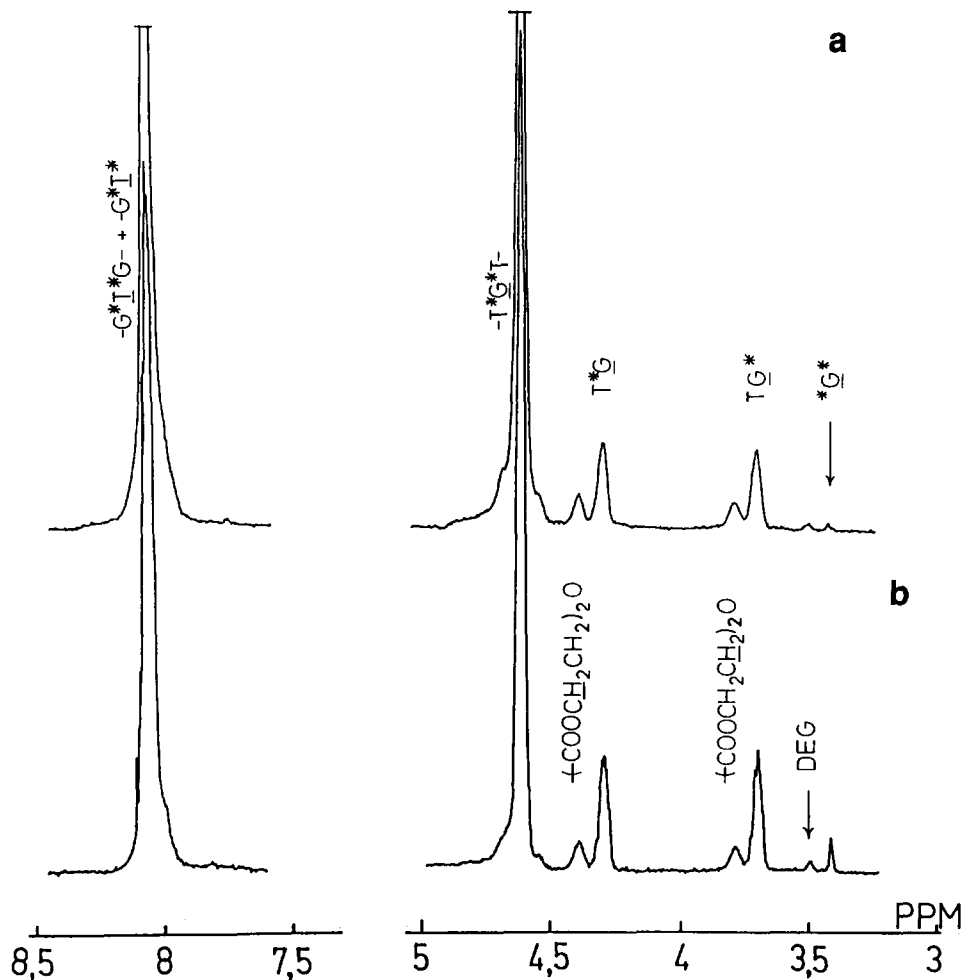
**Figure 2** ¹H (350 MHz) n.m.r. spectra of PET samples S3 (a) and S2 (b). Nomenclature as in *Figure 1*

**Table 2** Characteristics of the four PET samples obtained by bulk polyesterification of terephthalic acid (1 mol) + ethylene glycol (1.1 mol) at 265°C. Quantitative determinations by ¹H and ¹³C n.m.r.

| | Sample | | | |
|---|---|---|---|---|
| Characteristic | P | S1 | S2 | S3 |
| $C_A{}^a$ | 0.575 | 0.865 | 0.935 | 0.975 |
| $C_a{}^b$ | 0.523 | 0.786 | 0.850 | 0.886 |
| $dP_n{}^c$ | 2.2 | 5.7 | 9.1 | 13.9 |
| G (mol%)$^b$ | | | | |
| Diester (-TGT-) | 37 | 55.5 | 70 | 77 |
| Monoester (-GT-) | 50.5 | 38.7 | 20.5 | 17.4 |
| Diol (G) | 8.7 | 1.8 | 3.5 | 0.1 |
| Diester (-TDEGT-) | 3.8 | 4.0 | 6.0 | 5.5 |
| T (mol%)$^a$ | | | | |
| Diester (-GTG-) | 47.5 | 77 | 87 | 95 |
| Monoester (-GT) | 17.5 | 13.2 | 8.4 | 3 |
| Diacid (T) | 29 | 2.8 | 0 | 0 |
| Anhydride (TT) | 6 | 7 | 4.6 | 2 |
| Acid end$^d$ | | | | |
| Potentiometry | 0.42 | 0.135 | 0.065 | 0.025 |
| ¹³C n.m.r. | 0.425 | 0.132 | 0.065 | 0.025 |

$^a$¹³C n.m.r. (equations (3) and (4))
$^b$¹H n.m.r. (equations (1) and (2))
$^c$Equation (7) or (8)
$^d$Fraction of remaining acid groups

Carbonyl resonances (163–165 ppm; *Figure 4a*, CO-acids (-GT*) and CO-esters (-G*T and -G*T*G-), resonate in two distinct regions: 164.5–165 ppm and 163.2–163.7 ppm, respectively. Even with an excess of G, acid chain ends were found in samples P, S1 and S2, probably because of the partial consumption of alcohol groups by dehydration giving free and diesterified DEG. The conversion of acid function $(C_A)$ and the distributions of free (T), monoesterified (-GT) and diesterified (-GTG-) Ts may be determined:

$$C_A = \sum_4^{10} \Big/ \Big( \sum_1^3 + \sum_4^{10} \Big) \tag{3}$$

$$
\left.
\begin{aligned}
T\% &= 10^2 \times (1)/2S \\
(-GT)\% &= 10^2 \times [(2) + (3)]/S \\
(-GTG-)\% &= 10^2 \times \sum_4^{10} - [(2) + (3)]/2S \\
S &= \sum_1^{10} \Big/ 2
\end{aligned}
\right\} \tag{4}
$$

where (1), (2) ... are the relative intensities of peaks 1, 2, ... respectively and $\sum_m^n$ is the sum of the relative intensities of the peaks numbered from $m$ to $n$. All the calculated values are reported in *Table 2*.
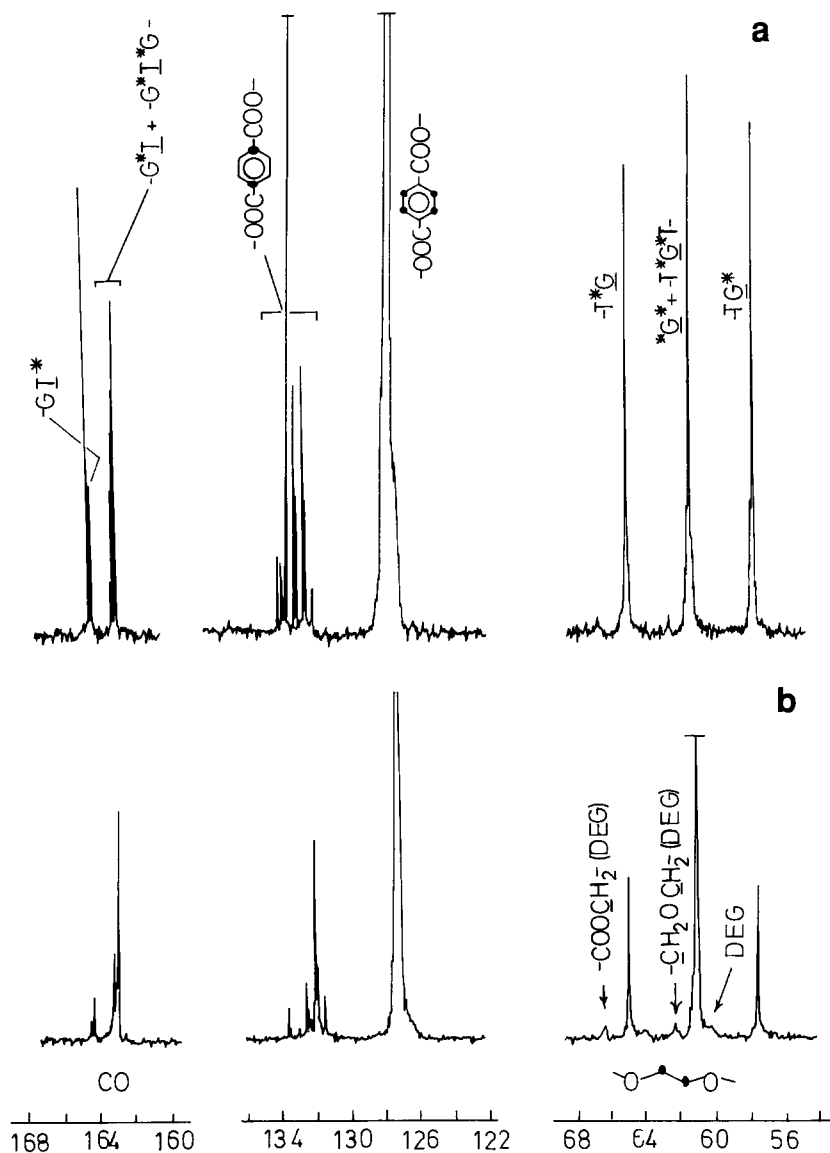
Figure 3  $^{13}$C (88 MHz) n.m.r. spectra of PET samples P (a) and S1 (b). Nomenclature as in *Figure 1*

Acid end groups may also be calculated from free (T%) and monoesterified (-GT%) Ts:

$$COOH = (T\%) + (1/2)(-GT\%) \qquad (5)$$

The values obtained are in good agreement with those given by potentiometry.

For the CO-esters (163.2–163.7 ppm), it is noteworthy that their resonances are shifted towards high fields with increasing degree of polymerization. The CO-esters of GT and GTG resonate at 163.7 (*Figure 4*, peak 5) and 163.6 ppm (peak 6), respectively, while those of high molecular weight PET are found at 163.34 ppm (peak 10). From the preceding observations, peak 7 (163.5 ppm) should be assigned to the GTGT tetramer because of the intensity ratio (7)/(8) ∼2/1 (2 and 1 CO-ester groups for the internal and external T units, respectively).
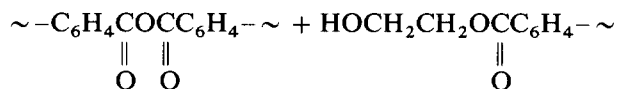
Quaternary aromatic resonances (131.5–134 ppm) (*Figure 4b*)—quaternary aromatic carbons bearing acid and ester carbonyls also resonate in two distinct regions: 133–134 ppm and 131.5–133 ppm, respectively. But peaks 11 (133.7 ppm) and 19 (131.75 ppm) should belong to the quaternary aromatic carbons of the same

T unit linked to an anhydride group and an ester group, respectively. Effectively these two peaks were actually found in the spectrum of the compound obtained by heating the mixture (T + TG) at 180° for 48 h. Peaks 11 and 19 allow determination of anhydride groups:

$$\text{anhydride (mol\%)} = 10^2 \times (1/2)[(11) + (19)]/\sum_{11}^{19}$$

$$(6)$$

where (11) and (19) are the relative intensities of peaks 11 and 19 and $\sum_{11}^{19}$ is the sum of the relative intensities of the peaks number from 11 to 19.

In the four samples examined, in contrast to the increase in DEG to 6 mol% (*Table 2*), the concentration of anhydride was found to reach its highest value of about 6–7 mol% in S1 and then decrease to 2–3 mol% in S3. Anhydride groups should react with alcohol ends giving back acid and ester functions as already suggested[1] but not demonstrated.

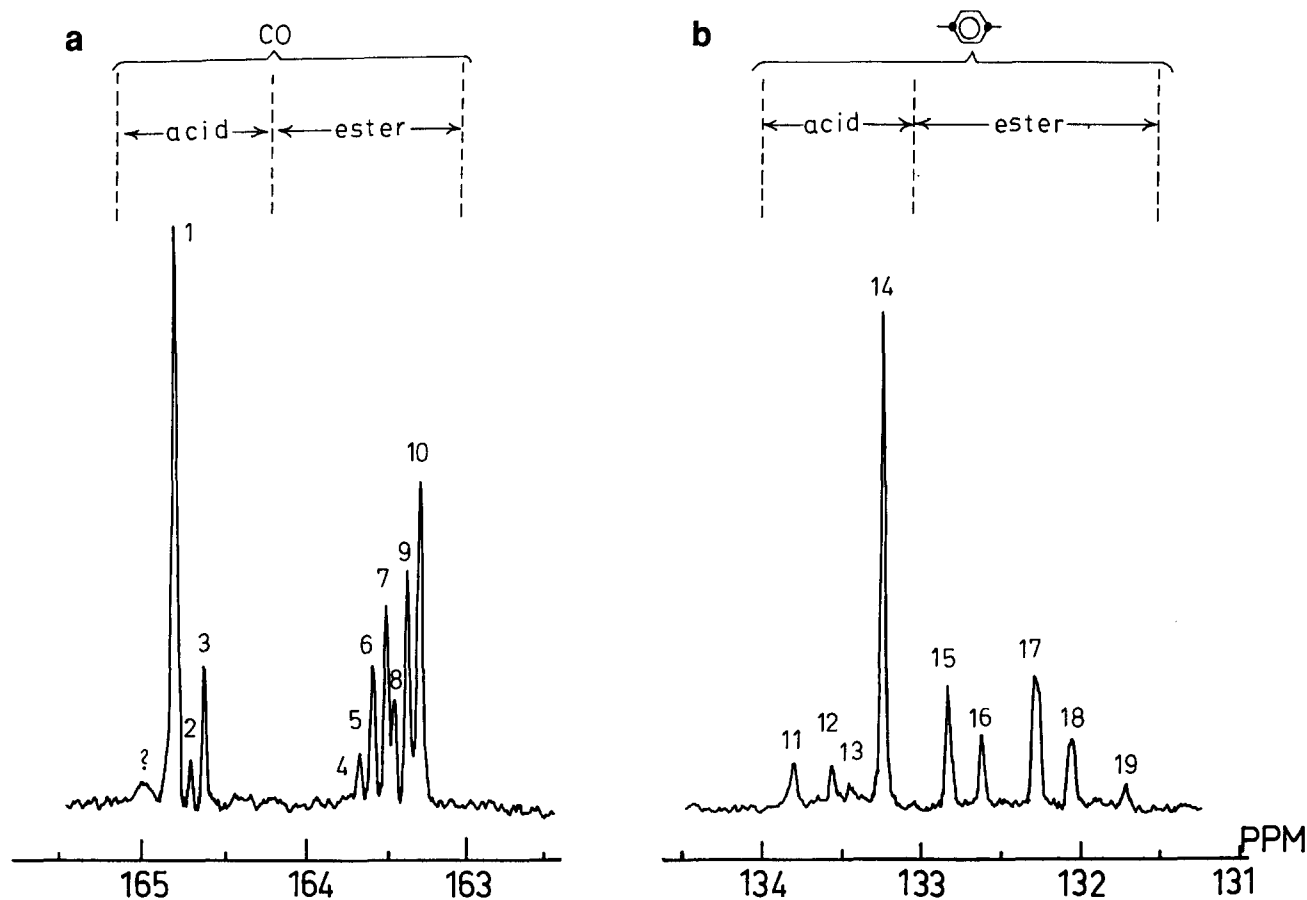$$\sim\!-C_6H_4COCC_6H_4\!-\!\sim + HOCH_2CH_2OCC_6H_4\!-\!\sim$$

Figure 4   $^{13}$C (88 MHz) n.m.r. spectrum of PET sample P. Expansion showing (a) CO and (b) quaternary aromatic resonances

Table 3   PET oligomers. Assignments of the carbonyl and quaternary aromatic carbon resonances (see *Figure 4*): T, terephthalic acid; G, ethylene glycol; underlined letter(s), origin(s) of the resonance(s); dP, degree of polymerization

| Peak number | | δ (ppm) | Assignment | dP |
|---|---|---|---|---|
| Carbonyl | | | | |
| Acid | 1 | 164.86 | free T | 1 |
| | 2 | 164.72 | GT$^b$ | 2 |
| | 3 | 164.67 | -GTGT | ≥4 |
| Ester | 4 | 163.8 | -TT-$^c$ | – |
| | 5 | 163.7 | GT | 2 |
| | 6 | 163.62 | GTG | 3 |
| | 7 | 163.55 | GTGT(?) | 4 |
| | 8 | 163.5 | GTGT(?) | 4 |
| | 9 | 163.42 | | |
| | 10 | 163.34$^a$ | -GTG- | ≥5 |
| Quaternary aromatic | | | | |
| Acid | 11 | 133.77 | -TT- | – |
| | 12 | 133.5 | -GTGT- | ≥4 |
| | 13 | 133.4 | GT$^b$ | 2 |
| | 14 | 133.2 | free T | 1 |
| Ester | 15 | 132.82 | GTGT | 4 |
| | 16 | 132.61 | GTG | 3 |
| | 17 | 132.28$^a$ | -(GT)$_n$- | ≥5 |
| | 18 | 132.02 | GT$^b$ | 2 |
| | 19 | 131.75 | -TT- | – |

$^a$Chemical shifts of high molecular weight PET
$^b$Identifications using oligomer models (see *Table 1*)
$^c$Anhydride

$$\sim\!-C_6H_4COOH + \sim\!-C_6H_4\overset{\parallel}{\underset{O}{C}}OCH_2CH_2O\overset{\parallel}{\underset{O}{C}}C_6H_4-\sim$$
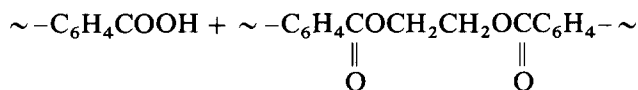
The proposed assignments for all the $^{13}$C resonances of the carbonyl and quaternary aromatic carbons are reported in *Table 3*.

*Number average degrees of polymerization ($dP_n$)*

With the conversions of acid groups ($C_A$) and the molar ratio $r = T/G = 1/1.1$ that may be verified for each sample ($r = C_a/C_A$), the $dP_n$ values calculated using equation (7)[5] (or the derived equation (8)) are reported in *Table 3*.

$$dP_n = (1 + r)/(1 + r - 2rC_A) \tag{7}$$

$$dP_n = (C_A + C_a)/[C_A(1 - 2C_a) + C_a] \tag{8}$$

These $dP_n$ values are only approximate because of the side reactions – mostly dehydrations and cyclizations – giving cyclic oligomers, ether and anhydride groups.

CONCLUSION

Low molecular weight PETs obtained from the direct bulk polyesterification of terephthalic acid and ethylene glycol have been studied by $^1$H and $^{13}$C n.m.r. Complementary $^1$H and $^{13}$C information made it possible

to determine the degrees of conversions of acid and alcohol groups, the distributions of free, monoesterified and diesterified terephthalic acid and ethylene glycol as well as to identify the dimer, trimer and tetramer. Concerning the side reactions, ether and anhydride groups resulting from dehydrations were quantitatively determined but the well known cyclic hexamer could not be identified by n.m.r. techniques.

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