Unsaturated polyesters based on terephthalic acid: 1. Proton magnetic resonance spectrum of poly(propylene terephthalate) prepolymer

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Peaks in the proton magnetic resonance spectrum of the prepolymer prepared by the polyesterification of terephthalic acid with excess propylene glycol are assigned to the methyl, methylene and methine protons in propylene glycol units which may exist in four different environments. The assignments are confirmed by removing the excess propylene glycol from the prepolymer, by benzoylating the prepolymer, and by obtaining spectra for isopropanol, isopropyl benzoate, propylene glycol 1,2-dibenzoate, propylene glycol, and bis(2-hydroxypropyl) terephthalate.

INTRODUCTION

Unsaturated polyesters are conveniently prepared by mixing the saturated and unsaturated acids with a glycol in order to complete the polyesterification in one step[1]. Phthalic acid, or phthalic anhydride, and isophthalic acid have been widely used as the saturated acid[1,2]. Unsaturated polyesters based on terephthalate units have received much less attention, mainly because terephthalic acid has low reactivity and is not soluble under normal laboratory conditions in a one-step process.

A two-stage process was first developed to allow a smoother reaction for unsaturated polyesters based on isophthalic acid[3]. Cured resins produced from unsaturated polyesters prepared by the two-stage process may have markedly improved properties when compared with resins resulting from the one-step process, e.g. higher heat distortion temperature, flexural modulus, and impact strength[1,3]. A range of unsaturated polyester resins based on terephthalate units, marketed under the trade name 'Impolex', have been developed by Imperial Chemical Industries Limited[4]. A two-stage process is employed, so that all the terephthalic acid may react in the first stage with propylene glycol which forms a one phase system with the acid at elevated pressure and temperature. The poly(propylene terephthalate) prepolymer which results from this condensation may be represented by $P(TP)_n$, where P is a propylene glycol unit, either half-esterified or diesterified, T is a terephthalate unit, and n is the number of propylene terephthalate repeating units. The first-stage reaction is performed with an excess of propylene glycol, 2.2 or 3.3 mol propylene glycol to 1 mol acid, so that prepolymers containing T end-groups are considered to be absent. The second stage involving the reaction of the prepolymer with maleic anhydride to give the unsaturated polyester can be performed under normal laboratory conditions.

In this paper, we report an assignment of the peaks in the proton magnetic resonance spectrum of the poly(propylene terephthalate) prepolymer. This work forms part of a research programme to characterize by proton magnetic resonance spectroscopy and gel permeation chromatography the distribution of the various monomeric units along the polyester backbone in the products formed in stage 1 and stage 2. These quantitative studies will be reported separately.

EXPERIMENTAL

The poly(propylene terephthalate) sample was a T400 prepolymer intermediate isolated after the first stage of the 'Impolex' process operated by ICI Ltd. The proton magnetic resonance spectrum was obtained at room temperature with a Perkin–Elmer R-32 spectrometer operating at 90 MHz. The prepolymer was dissolved in deuterochloroform or dimethyl sulphoxide (d_6) (30–40% w/v).

The as-received T400 prepolymer contained excess propylene glycol. Distillation under reduced pressure was carried out initially at 120°C to remove the free propylene glycol from the prepolymer (bulk). The temperature was then raised to 190°C, to ensure that all volatile products which might be present (e.g. dipropylene glycol, b.p. 232°C/760 mmHg) were distilled off.

Bis(2-hydroxypropyl) terephthalate was prepared as follows. Propylene glycol (0.4 mol) and pyridine (10 cm^3) were mixed with diethyl ether (20 cm^3) to which terephthaloyl chloride (5 g, 0.02 mol) dissolved in diethyl ether

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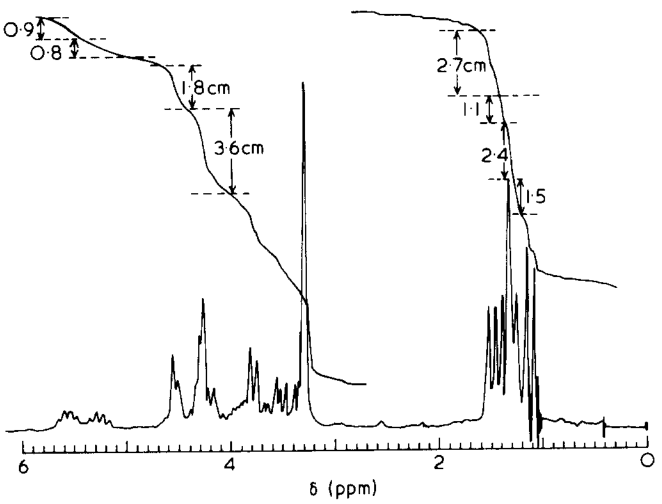


Figure 1 Proton magnetic resonance spectrum of T400 prepolymer in deuterochloroform

(20 cm^3) was added at room temperature. The addition was performed over a period of 2 h, after which the reaction mixture was stirred for a further 10 h at room temperature. Two layers appeared on standing. The bottom layer of propylene glycol contained a white dispersion which resulted in a white precipitate after separation of the ether and addition of ice cold water containing a small quantity of Na_2CO_3. The precipitate was vacuum dried and then recrystallized from water (pH 8). The larger part dissolved in hot water while the remainder formed a heavy oily layer. The clear aqueous solution was filtered, and on subsequent cooling a crystalline compound precipitated. The latter was recrystallized from boiling water to give a compound melting at 131°C. The molecular weight of bis(2-hydroxypropyl) terephthalate was confirmed by mass spectrometry and gel permeation chromatography[5]. The proton magnetic resonance spectrum was obtained with dimethyl sulphoxide (d_6) as solvent (30–40% w/v) to which deuterochloroform was added in order to dissolve the tetramethylsilane internal standard.

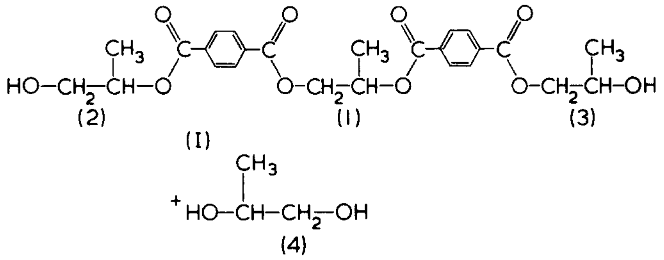
Benzoylation of propylene glycol, isopropanol and the T400 prepolymer was performed as follows. Propylene glycol (0.13 mol) was mixed with pyridine (25 cm^3) and benzoyl chloride (0.3 mol) was added dropwise, at room temperature, under continuous stirring. After complete addition, the solution was left to stand overnight. Separation of the product involved dissolution of the reaction mixture in chloroform, followed by washings with dilute sodium bicarbonate solution and water. After drying over anhydrous sodium sulphate, propylene glycol 1,2-dibenzoate was isolated by distillation under reduced pressure, b.p. 232°C/12 mmHg. A similar procedure was applied to synthesize isopropyl benzoate from isopropanol and benzoyl chloride, and the product was isolated by distillation, b.p. 218°C/760 mmHg. The benzoylation of the prepolymer itself was carried out in a chloroform solution in the absence of pyridine. The addition of benzoyl chloride was carried out at 40–50°C with continuous stirring, and then the mixture was refluxed for a further 1 h. Only the solvent was distilled off, and the spectrum of the benzoylated prepolymer was recorded in the presence of traces of benzoyl chloride whose absorption did not interfere with those of the prepolymer paraffinic segment. Proton magnetic resonance spectra for these benzoylated compounds were obtained by the procedure described above with the same instrumental conditions.

RESULTS AND DISCUSSION

A proton magnetic resonance spectrum of the poly(propylene terephthalate) prepolymer is shown in *Figure 1*. The spectrum can be subdivided into three distinct regions, which, expressed in terms of δ values from the tetramethylsilane internal standard, are:

(i) 1.0–1.6 ppm
(ii) 3.1–5.8 ppm
(iii) a singlet at 8.01 ppm

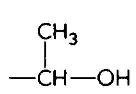
In order to assign the absorptions occurring in these regions to hydrogen atoms belonging to specific groups, the polymer will be represented by the following structural model the different segments of which will be numbered:



It is well known that the methyls of such a spin system will absorb radiofrequency at high fields, i.e. in the 1.0–1.6 ppm region, the methylene and methine groups in region (ii), while the phenyl groups absorb in the lowest field region. The hydroxyl groups are expected to give rise to singlets in the 3.00–5.00 ppm region. In the following discussion, the absorptions of each group will be treated separately.

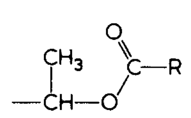
Methyl absorptions

Because of their vicinity to methine groups, the methyls of the prepolymer, as well as those of the glycol, are expected to give rise to doublets in the high field region of the spectrum. Since more than one doublet appears in this region, it is evident that the methyls are present in different magnetic environments. It is assumed at this stage that the inductive–I effects exercised by the hydroxyl and the ester groups on their neighbouring methyl groups are responsible for the different chemical shifts of the doublets. At first glance, two types of electronically different methyls can be distinguished:



$$-\overset{CH_3}{\overset{|}{C}}H-OH$$

(β to hydroxyl group)



$$-\overset{CH_3}{\overset{|}{C}}H-O-\overset{O}{\overset{\|}{C}}-R$$

(β to ester group)

Consequently, the stronger–I effect of the ester group[6] will result in a lower field absorption of the neighbouring methyl compared to the methyl beta to the hydroxyl group. In support of this claim, the following evidence is provided. The stronger deshielding effect of the ester group is shown by the methyl doublets in the spectra for isopropanol and the derived benzoate in *Table 1*. Accordingly, the spectrum of the polymer should show only two doublets in the high field region; however, this is not the case. It is apparent in *Figure 1* that this region comprises:

(a) a doublet at 1.09–1.09–1.16 ppm
(b) a triplet (like) at 1.25, 1.32, 1.40 ppm
(c) a doublet at 1.45–1.53 ppm

Table 1 Absorptions in spectra of model compounds

Compound	Methyl doublet (ppm)	Methylene doublet (ppm)	Centre of methine multiplet (ppm)
Isopropanol	1.15–1.23	–	4.00
Isopropyl benzoate	1.32–1.40	–	5.30
Propylene glycol 1,2-dibenzoate	1.44–1.51	4.49–4.54	5.56
Propylene glycol	1.10–1.20	3.46–3.52	3.80

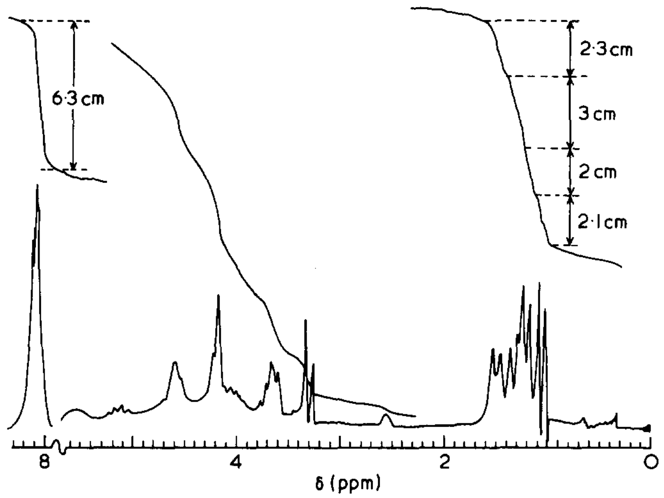
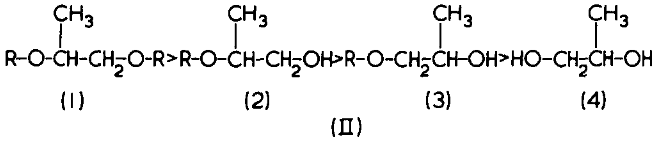


Figure 2 Proton magnetic resonance spectrum of T400 prepolymer in dimethyl sulphoxide (d_6)

The triplet will be regarded as being composed of two doublets, since the same spectrum taken from a dimethyl sulphoxide (d_6) solution shows four methyl doublets, see *Figure 2*. It follows that four magnetically different methyls are present in this region.

If the combined inductive effects of the hydroxyl and ester groups on the methyl are considered, then logically the four methyls, in order of decreasing inductive influence are:

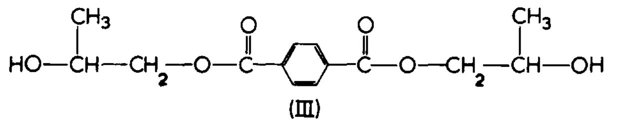


$$\underset{(1)}{\mathrm{R{-}O{-}\overset{CH_3}{\overset{|}{C}}H{-}CH_2{-}O{-}R}} > \underset{(2)}{\mathrm{R{-}O{-}\overset{CH_3}{\overset{|}{C}}H{-}CH_2{-}OH}} > \underset{(3)}{\mathrm{R{-}O{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}H{-}OH}} > \underset{(4)}{\mathrm{HO{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}H{-}OH}}$$

(II)

Complete benzoylation of the prepolymer should convert all those segments bearing free hydroxyl groups, i.e. (2), (3) and (4) to the form of (1), and the result should be a single doublet giving the exact chemical shift of the methyl group of segment (1). The spectrum of the benzoylated prepolymer in *Figure 3* shows one doublet only, at 1.43–1.50 ppm, which when transposed to the spectrum of the prepolymer in *Figure 1* corresponds to the lowest field doublet at 1.46–1.53 ppm. As further proof, the only high field doublet of propylene glycol 1,2-dibenzoate (see *Table 1*) occurs in the same region. These observations lead to the conclusion that the doublet at 1.46–1.53 ppm is due to the methyl of segment (1).

Removal of the unreacted propylene glycol from the T400 prepolymer by vacuum distillation leaves behind a glassy mass, the spectrum of which is shown in *Figure 4*. It is evident that the doublet at 1.09–1.16 ppm of *Figure 1* is absent. In addition, examination of the spectrum of the distillate confirms that it consists of pure propylene glycol. Therefore, the highest field doublet is due to the methyl group of propylene glycol, see *Table 1*. Furthermore, when the propylene glycol free prepolymer has its spectrum taken in the presence of the shift reagent, Eu(fod)$_3$, europium 1,1,1,2,2,3,3,-heptafluoro-7,7-dimethyl-4,6-octanedione, three distinct sets of doublets appear, thus clarifying the nature of the triplet in *Figure 1*. In addition bis(2-hydroxypropyl) terephthalate:



(III)

the methyl groups of which are of type (3), gives a doublet at 1.18–1.25 ppm, see *Figure 5*, which corresponds exactly to the doublet next to the propylene glycol doublet in *Figure 2*.

On the basis of these three assignments it becomes obvious that the electronegativity trend cited above holds. Therefore, the doublet at 1.3–1.36 ppm in *Figure 2* will be assigned to the methyl of segment (2).

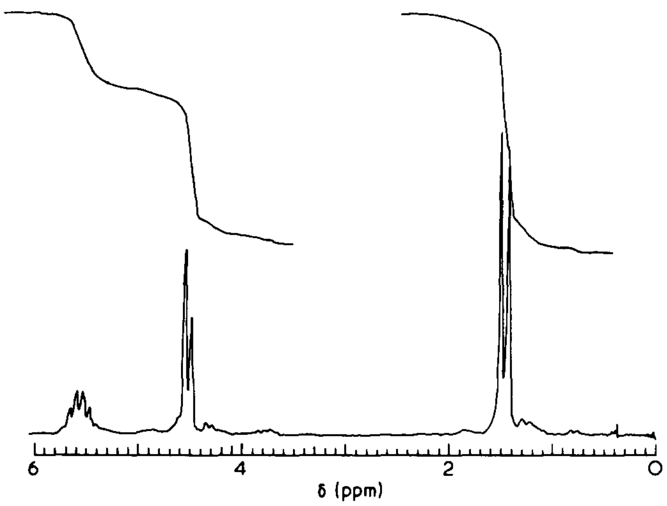


Figure 3 Proton magnetic resonance spectrum of benzoylated T400 prepolymer in deuterochloroform

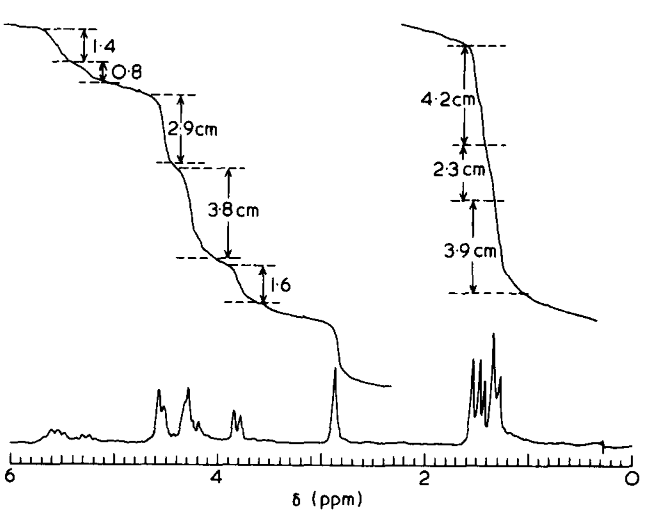


Figure 4 Proton magnetic resonance spectrum of prepolymer free of excess propylene glycol

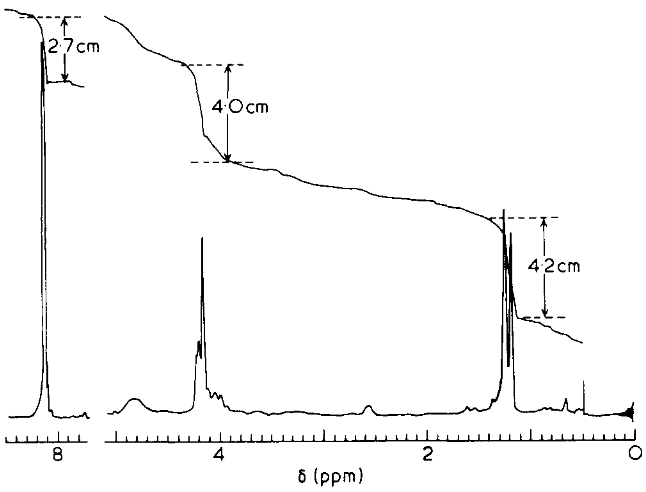


Figure 5 Proton magnetic resonance spectrum of bis(2-hydroxypropyl) terephthalate

Methylene absorptions

The CH_2 groups of the prepolymer should give rise to doublets because of their proximity to methine groups. If we compare the spectrum of the propylene glycol free prepolymer in *Figure 4* with the spectrum of the benzoylated derivative in *Figure 3*, and with the methylene doublet in benzoylated propylene glycol (see *Table 1*), it is clear that the methylene doublet of segment (1), in the sequence cited above, occurs at 4.52–4.57 ppm. In addition, the corresponding integrated trace, 1.8 cm in *Figure 1*, is equal to 2/3 of that of the methyl doublet of (1), 2.7 cm, confirming that both groups belong to the same segment. The methylene group of bis(2-hydroxypropyl) terephthalate results in a doublet at 4.15 ppm in *Figure 5* which corresponds to the doublet at 4.25 ppm in *Figure 1*. The shift (0.1 ppm) is due to a solvent effect, since the spectrum in *Figure 2* shows the same doublet at 4.18 ppm. Therefore, the latter will be assigned to the methylene group of segment (3). In fact, the integrated trace of this doublet, overlapping with a –CH multiplet and therefore corresponding to three hydrogen atoms, see *Figure 4*, is approximately equal to the integrated trace of the methyl doublet of the same segment. The only doublet to interpret now, is the one occurring at 3.78–3.84 ppm in *Figure 4*. The only possibility is that it is caused by the methylene group of segment (2) since it has an integrated trace which corresponds to the neighbouring methyl group. The methylene doublet of free propylene glycol can be identified unambiguously by superimposing the spectrum of pure propylene glycol on the spectrum of the prepolymer.

The relative position of each doublet again favours the combined inductive effects of the ester and the hydroxyl group on the chemical shifts of the methylene groups. The order of decreasing inductive influence is:

$$\underset{(1)}{ROCH_2\text{-}\overset{CH_3}{\overset{|}{C}}H\text{-}OR} > \underset{(3)}{R\text{-}OCH_2\text{-}\overset{CH_3}{\overset{|}{C}}H\text{-}OH} > \underset{(2)}{RO\overset{CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}OH} > \underset{(4)}{HO\overset{CH_3}{\overset{|}{C}}H\text{-}CH_2OH}$$

(IV)

Methine absorptions

Since the methines in the structural model I have neighbouring methyl and methylene groups, the methine group is expected to give rise to a sextet. The methine group in segment (1) is assigned to the multiplet centred at 5.58 ppm in *Figure 1*. This assignment follows from the spectra for benzoylated prepolymer in *Figure 3* and from the multiplet for propylene glycol 1,2 dibenzoate (see *Table 1*) which is centred in the same region. In addition, the integrated trace of this absorption, 1.4 cm in *Figure 4*, is approximately equal to the integrated trace of the methylene absorption (2.9 cm) and the methyl group doublet (4.2 cm) of the same segment after taking into consideration the relative populations of hydrogen atoms. The methine group of bis(2-hydroxypropyl)terephthalate in *Figure 5* absorbs at 4.00 ppm and the multiplet partly overlaps with the neighbouring methylene doublet at 4.15 ppm. The same pattern exists in the spectrum of the prepolymer at 4.00 ppm in *Figure 2* and is assigned to the methine of segment (3). The only multiplet left in *Figure 4* is the one at 5.27 ppm which will be assigned to the methine of segment (2). Its integrated trace, 0.8 cm, is 1/2 the integral of the neighbouring $-CH_2$ group (1.6 cm) at 3.8 ppm and approximately equal to 1/3 of the integral of the methyl group doublet of the same segment (3.9 cm). By superimposing this spectrum with the spectrum of pure propylene glycol, it is found that the –CH multiplet of the latter overlaps with the doublet of the methylene group of segment (2).

Phenyl absorptions

The phenyl hydrogen absorption of bis(2-hydroxypropyl) terephthalate in *Figure 5* occurs at 8.11 ppm and gives rise to a sharp and well-defined peak accounting for the magnetic equivalence of the four hydrogens of the terephthalate ring. Fine splitting of the phenyl absorption is observed in the spectrum of the prepolymer in *Figure 2*, which is attributed to the different dispositions of the diesterified segments at either side of the terephthalate ring, giving slight loss in magnetic equivalence of the phenyl hydrogens caused by the position of the electron repelling methyl group with respect to the ester oxygen. Some evidence for this explanation is obtained from a mixture of bis(1-hydroxypropyl), bis(2-hydroxypropyl) and (1,2′ bishydroxypropyl) terephthalates which gives a phenyl absorption spectrum showing fine splitting[5].

Hydroxyl absorptions

The hydroxyl hydrogen absorption in the prepolymer occurs at 3.29 ppm. in *Figure 1*. However, its location was found to vary in the 3–4 ppm range, as confirmed by obtaining spectra of the prepolymer containing additional quantities of propylene glycol and bis(2-hydroxypropyl) terephthalate.

Bis(2-hydroxypropyl)terephthalate

In view of the use of the spectrum in *Figure 5* in interpreting the spectrum of the prepolymer, the elucidation of structure III from *Figure 5* will be described. The ratio of phenyl, to methyl plus methylene, to methyl hydrogens in *Figure 5* follows approximately the stoichiometric sequence 4:6:6 of bis(hydroxypropyl) terephthalate.

The doublet at 1.18–1.25 ppm in *Figure 5* indicates the presence of a methyl group neighbouring a methine group. Since, as cited previously, the methyl groups of isopropanol absorb at higher fields than the methyl groups of isopropyl benzoate, then only one methyl doublet is expected for a molecule with the same segments linked to the terephthalate ring. The methine group in the neighbourhood of a methylene and methyl group gives rise to a sextet overlapping with the methylene doublet at 4–4.3 ppm in *Figure 5*. The methine multiplet of propylene glycol, see *Table 1*, occurs at 3.8 ppm in $CDCl_3$, while its methylene hydrogens absorb at higher field (3.45 ppm). The methine sextets of isopropanol and isopropyl benzoate in *Table 1* show the effect of the more electronegative ester group in increasing the chemical shift expressed in delta values from tetramethylsilane. In addition, the fact that both methine and methylene absorptions overlap at around 4 ppm in *Figure 5* indicates that while the methine is almost magnetically equivalent to that of propylene glycol and isopropanol, the methylene doublets (4.15 ppm) appear at lower fields than those of propylene glycol, indicating that the group in their vicinity is more electronegative than the –OH. The only other alternative is the presence of an ester group and it follows therefore that the terephthalate has the structure III.

CONCLUSIONS

The representation of the prepolymer formed by reacting terephthalic acid with excess propylene glycol, by the $P(TP)_n$ structure is justified by the qualitative interpretation of the proton magnetic resonance spectrum. The assignment of peaks in the spectrum according to the structural model I shows that oligomeric species with $n > 1.0$ are present in the prepolymer. The identification of the range of n values will be discussed in a subsequent paper.

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