Unsaturated polyesters based on terephthalic acid: 2. Quantitative characterization of prepolymers by proton magnetic resonance spectroscopy

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Integrated proton magnetic resonance spectra have been obtained for poly(propylene terephthalate) prepolymers prepared by the polyesterification of terephthalic acid with excess propylene glycol. From the peaks for the phenyl hydrogens and the methyl hydrogens, the molecular weight of the terephthalate-based components of the prepolymer is determined. The procedure may be extended to the determination of the molecular weight of all components, including excess propylene glycol. Methods for determining the concentration of excess propylene glycol and the quantity of propylene glycol lost during polyesterification are also presented.

INTRODUCTION

The molecular weight of a low polymer may be determined quantitatively from the integrated trace of a nuclear magnetic resonance (n.m.r.) spectrum[1–3]. For example the molecular weight of a *p*-octylnovolak resin, prepared from an excess of phenolic reagent, has been deduced from its spectrum using acetone or pyridine as solvent[4]. From the areas of the peaks for the methylene bridge protons and the aromatic protons, the number of structural units can be determined, from which the molecular weight may be calculated. Urman and coworkers[1] synthesized plasticizers by the transesterification of dibutyl adipate with different glycols and determined their molecular weights by comparing the area of the butoxyl end-group triplet with the proton area of a specific group present in one repeat unit. Fairly good agreement was found between the values obtained by n.m.r. and those determined by ebulliometry. The molecular weights of poly(ethylene glycol) and poly(propylene glycol) were determined by Page and Bresler[2] in terms of the shift that distinguishes the groups attached to the ether oxygen and those attached to the oxygen of the hydroxyl group. Very good resolution was obtained when pyridine heated with a small amount of HCl gas was used as the n.m.r. solvent. In addition to pyridine, the resolution of the near end-group multiplets can be improved in the presence of benzene and 1-chloro-naphthalene[5]. Superior, in that respect, is the effect of a shift reagent such as Eu(dpm)$_3$, tris(dipivalatomethanato) europium. This reagent has been used by Ho[3], to distinguish between the doublets of the end and internal methyl groups in poly(propylene glycol). The end methyls are shifted downfield from the interior methyls, and by comparing the areas of the corresponding absorption peaks, the number-average molecular weight has been calculated.

In part 1 (ref 6) the assignment of peaks in the proton magnetic resonance spectrum of poly(propylene terephthalate) was described. In this paper, the integrated traces of the spectra of several prepolymers are interpreted quantitatively in order to determine the molecular weight of the prepolymer, the quantity of unreacted propylene glycol, and the loss of propylene glycol during polyesterification.

EXPERIMENTAL

Prepolymers

The samples of poly(propylene terephthalate) which are intermediates in the 'Impolex' unsaturated polyester process operated by Imperial Chemical Industries Limited will be referred to as T400 and T500 prepolymers. The former are synthesized from 1 mol terephthalic acid and 2.2 mol propylene glycol, while 3.3 mol propylene glycol is used in the synthesis of the latter. The synthesis of the prepolymers by the ICI process involves two stages. First, both components are charged in the reactor and condensed under high temperature and pressure to give poly(propylene terephthalate) and water as by-product. The vigorous reaction conditions employed, as well as the subsequent water distillation step involved in the process, lead to the loss of some propylene glycol which should remain unreacted because of the non-stoichiometry of the feed. In order to compensate for these losses, additional propylene glycol is introduced into the reaction mixture and polycondensation is continued for a further period of time until the final acid value reaches a low figure as the extent of reaction approaches one. The resulting prepolymer is in the form of a transparent, viscous liquid, which yields an unsaturated polyester when condensed with maleic anhydride in the second stage.

The work in part 1 was performed with a T400 prepolymer ready for further condensation with maleic anhydride, and we shall refer to it as prepolymer T400A to differentiate it from the prepolymers T400B and T400C which have been isolated prior to the addition of further propylene glycol at the end of the first stage. The proton magnetic resonance

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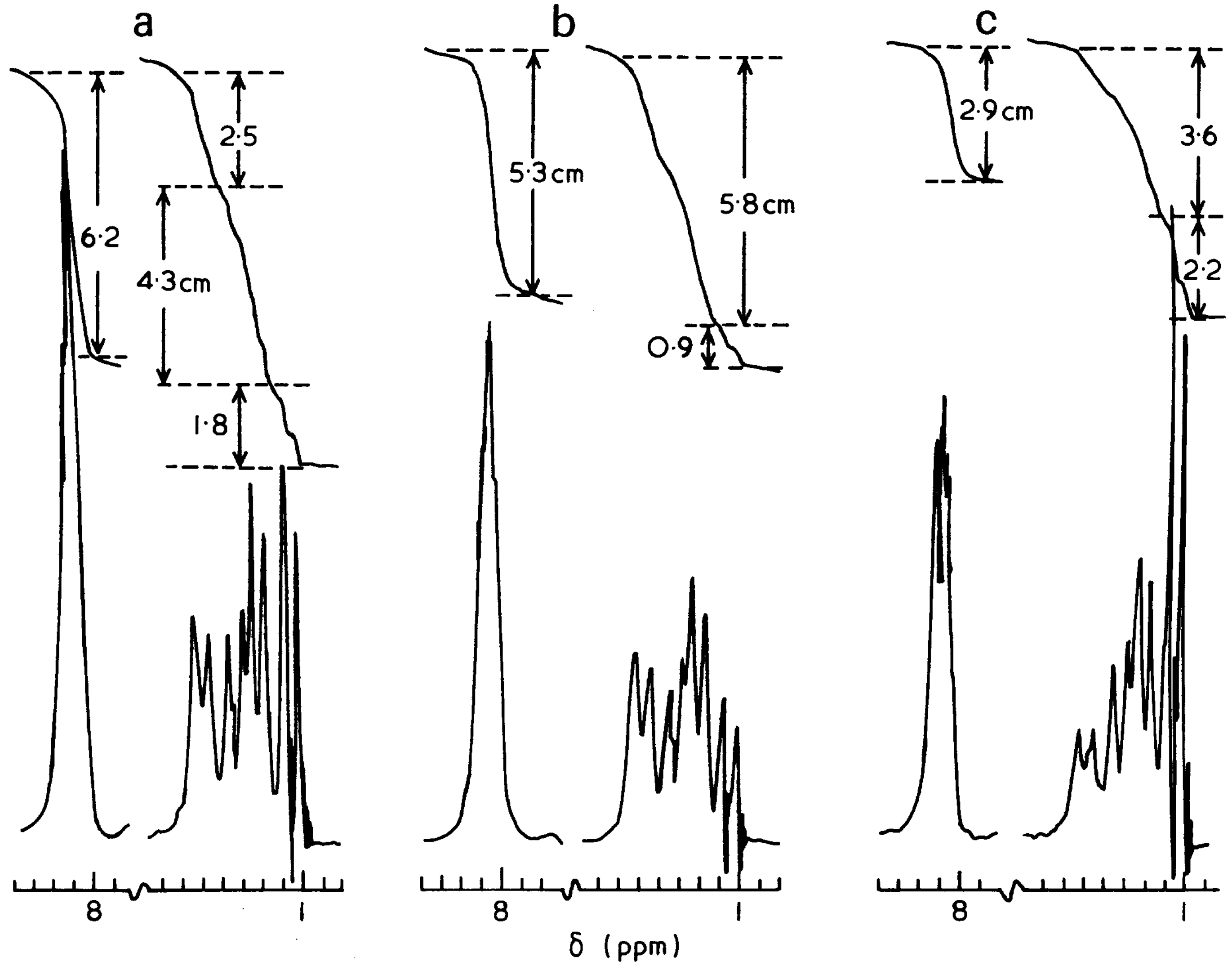

Figure 1 Proton magnetic resonance spectra of prepolymers. (a) T400B; (b) T400C; (c) T500

spectra of all these prepolymers at 90 MHz were obtained by preparing 30–40% solutions in dimethylsulphoxide (d_6). The spectrum for T400A is given in part 1 (*Figure 2, ref 6*) and the spectra for the other three prepolymers are shown in *Figure 1*.

RESULTS

Molecular weight determination

It follows from part 1 that the constituents of the prepolymers may be represented by:

$$P(TP)_1, P(TP)_2, P(TP)_3 \ldots\ldots\ldots\ldots, P(TP)_n, \ldots\ldots\ldots\ldots$$

If each of these esters was analysed separately by n.m.r., then the integrated traces of the phenyl hydrogens and those of the methyl hydrogens, 4 and 3 respectively for each repeating unit, should be in the ratio:

$$\frac{4}{6}, \frac{8}{9}, \frac{12}{12}, \ldots\ldots\ldots\ldots\ldots\ldots, \frac{4n}{3n+3} \ldots\ldots \qquad (1)$$

and the general expression is:

$$\frac{4n}{3(n+1)} \qquad (2)$$

On the other hand, the molecular weight M of each of these esters may be expressed by the formula:

$$M = 282 + 206(n - 1) \qquad (3)$$

where 282 is the molecular weight of $P(TP)_1$ and 206 is the molecular weight of a propylene terephthalate repeating unit. Since the integrated trace of the n.m.r. spectrum of a prepolymer represents an average number of protons, then $\bar{n}$ will be taken as an average value for the species $P(TP)_{\bar{n}}$. The calculations will be illustrated with prepolymer T400B. A summary of all the results is given in *Table 1*. From the spectrum for prepolymer T400B in *Figure 1*, the areas beneath the peaks for the phenyl protons and the methyl protons can be estimated, omitting the methyl protons in propylene glycol. Therefore, from equation (2):

$$\frac{4\bar{n}}{3(\bar{n}+1)} = \frac{6.2}{6.8} \qquad (4)$$

giving $\bar{n} = 2.165$. From equation (3), the number-average molecular weight $\bar{M}_n$ of the prepolymer T400B is 522.

The $\bar{n}$ value above is used for the calculation of the number-average molecular weight of the terephthalate-containing units only. If propylene glycol is to be included, then its representative formula will be $P(TP)_0$ and in this particular case the subscript n defined above will take the

Table 1 Results for prepolymers

Prepolymer	$\bar{n}$	$\bar{M}_n{}^a$	$\bar{n}'$	$\bar{M}_n{}^b$	PG (n.m.r.) (%)	PG (g.c.) (%)	PG Loss (%)
T400A	1.833	454	1.011	284	12.0	9.5	9.6
T400B	2.165	522	1.179	319	10.87	8.86	16.0
T400C	2.175	524	1.457	376	6.7	5.0	23.4
T500	1.528	391	0.6	200	23.06	23.24	19.2

[a] Prepolymer containing terephthalate units only; [b] prepolymer and free propylene glycol

values 0, 1, 2, 3, . . . , n, . . . Equation (3) may still be used to calculate the molecular weight, since when $n = 0, M = 76$ which is the molecular weight of propylene glycol. Only the value of $\bar{n}$ will change to $\bar{n}'$, since the integrated trace of the whole methyl region will now be considered. giving, for prepolymer T400B in *Figure 1*:

$$\frac{4\bar{n}'}{3(\bar{n}'+1)} = \frac{6.2}{8.6} \tag{5}$$

Hence, $\bar{n}' = 1.179$, giving $\bar{M}_n = 319$ from equation (3).

The molecular weight of T400A prepolymer was also determined by the standard analytical method involving the acetylation of the hydroxyl groups with an excess of an acetylating reagent, followed by the titrimetric determination of the unreacted reagent[7]. The value of $\bar{M}_n$ was 329, which is rather higher than the value of 284 estimated by proton magnetic resonance spectroscopy (see *Table 1*).

Excess propylene glycol

The method in the previous section can be extended to the calculation of the quantity of free propylene glycol, since the latter has characteristic absorptions. If we assume that the prepolymer consists essentially of two species, namely propylene glycol and $P(TP)_{\bar{n}}$ of molar concentrations x and y respectively, then these should be in the ratio of the methyl protons of the constituents. Therefore, from *Figure 1* for prepolymer T400B, the ratio x/y is:

$$\frac{x}{y} = \frac{1.8/3}{6.8/3(\bar{n}+1)} = \frac{1.8(\bar{n}+1)}{6.8} \tag{6}$$

The parameter y can be calculated from the integral trace of the phenyl hydrogens, the population of which is $4\bar{n}$. For prepolymer T400B in *Figure 1*:

$$y = 6.2/4\bar{n} \tag{7}$$

The value of $\bar{n}$ was found above to be 2.165 so that we calculate $y = 0.716$ mol and $x = 0.6$ mol. Consequently, the wt % of propylene glycol (PG) in the prepolymer is:

$$\mathrm{PG} = \frac{0.6 \times 76 \times 100}{0.6 \times 76 + 0.716 \times 522} = 10.87\% \tag{8}$$

The same result can be obtained from $\bar{n}' = 1.179$. The parameter y is replaced by z to express the molar concentration of the prepolymer plus the propylene glycol; the corresponding integrated trace will therefore be 6.8 + 1.8 = 8.6 cm. Hence:

$$\frac{x}{z} = \frac{1.8}{8.6}(1.179 + 1) \tag{9}$$

Since all the phenyl integral is regarded as corresponding to a single component of molecular weight = 319, then:

$$z = 6.2/4\bar{n}' = 1.315 \tag{10}$$

Consequently, $x = 0.6$ as before. The wt % of propylene glycol is given by:

$$\mathrm{PG} = \frac{0.6 \times 76 \times 100}{1.315 \times 319} = 10.87\% \tag{11}$$

The values of x and y may also be used in the determination of the number average molecular weight of the prepolymer by means of the equation:

$$\bar{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i} \tag{12}$$

where N_i is the number of mol of the component with molecular weight M_i. For the mixture of prepolymer and propylene glycol equation (12) becomes:

$$\bar{M}_n = \frac{0.6 \times 76 + 0.716 \times 522}{0.6 + 0.716} = 319 \tag{13}$$

which is in agreement with the value derived previously.

The unreacted propylene glycol in the prepolymers was determined independently by quantitative gas chromatography (g.c.). The internal standardization method was applied[8], with *m*-cresol as internal standard. A comparison of these values with the values from proton magnetic resonance spectroscopy is given in *Table 1*.

Loss of propylene glycol during polyesterification

It has been found that $\bar{n} = 2.165$. Therefore, 1 mol $P(TP)_{\bar{n}}$ consists of 2.165 mol terephthalic acid and 2.165 + 1 = 3.165 mol propylene glycol. It has also been found that the molar concentration y of $P(TP)_{\bar{n}}$ is 0.716. It follows that the actual concentration of terephthalic acid is 0.716 x 2.165 = 1.550 mol. The molar concentration of esterified propylene glycol is 0.716 x 3.165 = 2.266 mol. Since the molar concentration, x, of free propylene glycol is 0.6 then the total concentration of propylene glycol units (reacted and free) in the reaction product is 2.266 + 0.6 = 2.866 mol. Since a T400B prepolymer is synthesized from 1 mol terephthalic acid and 2.2 mol propylene glycol, then the theoretical quantity N of propylene glycol corresponding to 1.550 mol terephthalic acid, assuming no propylene glycol loss during the reaction, is:

$$\frac{N}{2.2} = \frac{1.550}{1} \tag{14}$$

so that N is 3.41 mol. From this value and the value of

2.866 mol, the quantity of propylene glycol lost during the polyesterification is 16.0%.

The same result can be obtained from $P(TP)_{\bar{n}'}$, where $\bar{n}' = 1.179$ so that 1 mol $P(TP)_{\bar{n}'}$ is associated with 1.179 mol terephthalic acid and 2.179 mol propylene glycol. As before, the theoretical quantity N of propylene glycol should be:

$$\frac{N}{2.2} = \frac{1.179}{1} \qquad (15)$$

so that N is 2.59 mol. From the actual and theoretical values of propylene glycol, the quantity of propylene glycol lost during the polyesterification is 16.0%.

CONCLUSIONS

These results demonstrate that proton magnetic resonance spectroscopy is extremely useful in characterizing quantitatively the species present in the poly(propylene terephthalate) prepolymer formed in the first stage of the two-stage process for preparing unsaturated polyesters. These spectroscopic measurements may be employed to monitor the reproducibility of the first polyesterification stage. The calculation of the hydroxyl group content from the molar concentrations of poly(propylene terephthalate) and excess propylene glycol is of particular relevance to the addition of the stoichiometric concentration of the unsaturated acid component in the second polyesterification stage.

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