Unsaturated polyesters based on terephthalic acid: 3. Characterization of poly(propylene terephthalate) prepolymer by gel permeation chromatography

A. W. Birley, J. V. Dawkins and D. Kyriacos†
Institute of Polymer Technology and Department of Chemistry, Loughborough University of Technology, Loughborough, Leicestershire LE11 3TU, UK
(Received 5 October 1979)

Oligomers in prepolymers prepared by the polyesterification of terephthalic acid (T) with excess 1,2-propylene glycol (P) have been separated by gel permeation chromatography (g.p.c.). The assignment of chromatogram peaks to oligomers according to the structure P $(TP)_n$ where n is the number of 1,2-propylene terephthalate repeating units has been confirmed by a g.p.c. examination of bis(2-hyroxypropyl) terephthalate and by a ^1H nuclear magnetic resonance (n.m.r.) spectroscopic study of fractions isolated from a preparative separation. The infrared g.p.c. detector response has been interpreted quantitatively in order to deduce the concentration of each oligomer from the area of its chromatogram peak. Mol fraction distributions as a function of n have been determined for the prepolymer samples. Number average molecular weights have been calculated for the terephthalate-based components of the prepolymer and for all components including excess propylene glycol. These g.p.c. molecular weights are in excellent agreement with values previously reported in a study of prepolymers by ^1H n.m.r. spectroscopy. G.p.c. studies on prepolymers after reactions with a carbodiimide and diazomethane suggest a very minor quantity of carboxyl terminated species in the prepolymer samples.

INTRODUCTION

Unsaturated polyesters based on terephthalate units are prepared by a two stage process, the first stage involving the reaction of all the terephthalic acid with excess 1,2-propylene glycol. The poly (1,2-propylene terephthalate) prepolymer which results 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 $n \geqslant 1$ is the number of propylene terephthalate repeating units. In Parts 1[1] and 2[2] we reported an examination of a range of prepolymer samples by ^1H (n.m.r.) which suggested that the average number of repeating units $\bar{n}$ was between 1.5 and 2.2. In this paper we describe the fractionation of the prepolymer by g.p.c. in order to identify the range of n values.

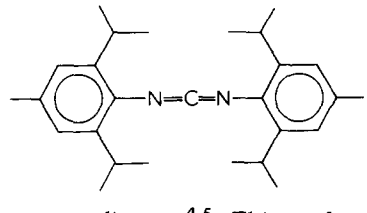
EXPERIMENTAL

Prepolymers

The synthesis of the T400A, T400B, T400C and T500 prepolymers, intermediates isolated after the first stage of the 'Impolex' unsaturated polyester process (ICI Ltd.), was described in Part 2. The preparation of $P(TP)_1$, bis(2-hydroxypropyl) terephthalate, was described in Part 1.

The acid number of a prepolymer was determined by a standard method[3]. Prepolymer (2 g) was accurately weighed into a 100 cm^3 conical flask and dissolved in 10 cm^3 neutral AR acetone. The solution was titrated against a solution of 0.182 N methanolic KOH using bromothymol blue indicator. The KOH solution was standardized with AR benzoic acid dissolved in ethanol using the same indicator as before.

Acidic species in the prepolymers were detected by reaction with a high molecular weight carbodiimide (Daltogard PR) which reacts rapidly and preferentially with a carboxylic



acid to give an *o*-acylisourea[4,5]. This product isomerized into an *N*-acylurea but may react with another free carboxyl group to give an acid anhydride and a urea derivative although this side reaction should be unimportant for a diaryl carbodiimide. A sample of prepolymer was accurately weighed into a 50 cm^3 round-bottomed flask. The stoichiometric quantity of I was calculated with the initial acid number of the prepolymer, and a 20% excess was then used. The reactants were dissolved in 20 cm^3 tetrahydrofuran and refluxed for various times. At the end of each time period the acid number was determined by titration with methanolic KOH and bromothymol blue indicator as before. The course of the reaction was followed by infrared spectroscopy. Films were cast from tetrahydrofuran onto sodium chloride discs. It was observed that the strong band at 2170 cm^{-1} resulting from the asymmetric stretching vibration of the carbodiimide group[6] gradually decreased in intensity, although the peak did not completely disappear because of the excess quantity of I.

† Present address: Upjohn Polymer B.V., S-Hertogenbosch, The Netherlands

0032-3861/80/060632-07$02.00

Other peaks in the spectrum of the carbodiimide were of less interest because they overlap with absorption bands in the prepolymer. The other prominent change in the spectrum of the prepolymer sample treated with the carbodiimide for 6 h was the presence of a strong band at 2290 cm^{-1} which falls in the absorption region of the isocyanate group; *N,N'* disubstituted ureas as well as anhydrides not having specific absorptions in this infrared region. In order to show the absence of a reaction between hydroxyl groups and the carbodiimide, 2.7 g propylene glycol and 0.234 g I were refluxed in 20 cm^3 tetrahydrofuran for 6 h. The presence of the strong asymmetric absorption at 2170 cm^{-1} suggested no reaction; reaction generally occurs at elevated temperatures when catalysed by a base. In order to show that the acidic species did not condense with the hydroxyl groups under the experimental conditions for the reaction with the carbodiimide, the prepolymer with I absent was refluxed for the longest time period (6 h). The acid number was determined and found to be unchanged.

On the assumption that the acidic species in the prepolymer may result from carboxyl groups, prepolymer was treated with diazomethane. A published procedure was employed for the preparation of the diazomethane[7]. Potassium hydroxide (6 g) dissolved in 10 cm^3 water, 35 cm^3 ethanol and 10 cm^3 ether was introduced into a round-bottomed flask equipped with a PTFE coated magnetic stirrer and heated to 343–348K. A solution of *p*-tolylsulphonylmethylnitrosamide (21.5 g) in 125 cm^3 ether was added regularly over a period of 15–20 min. When all the nitrosamide solution had been added, more ether was introduced at the previous rate until the distillate was colourless. The recovered ethereal solution was stored in a refrigerator. The solution of diazomethane (10 cm^3) was standardized by treating with an excess of an ethereal solution of benzoic acid at 273K and neutralizing the unreacted acid with a standard solution of KOH in methanol, with bromothymol blue indicator[8]. The stoichiometric quantity of diazomethane was calculated with the initial acid number of the prepolymer. The prepolymer (1.5427 g) dissolved in redistilled chloroform was treated with 1.7 cm^3 diazomethane solution at 273K. This solution was titrated with the standard alkali solution prepared before. Only a single drop of this solution was needed to turn the initial pale yellow colour of bromothymol blue into dark blue, indicating that esterification had proceeded to substantial completion.

Gel permeation chromatography

The preparative chromatographic system was constructed according to the techniques described by Mulder and Buytenhuys[9], except for the use of an infrared spectrometer as detector. Glass columns (100–110 cm in length and 1.00–1.25 cm in diameter) were used because separations were performed at very low pressures. The bottom end of the glass column was drawn until the inner diameter of the capillary formed matched the outer diameter of the connector tubing. Before the column was filled, a small wad of glasswool was pushed into the drawn end of the glass column above the connector, followed by a flat thin layer of sand in order to avoid irregularities in flow at the end of the separation and to support the gel itself. The column packings were polystyrene gels, Bio–Beads S–X1 (*MW* exclusion limit ~3500) and Bio–Beads S–X2 (*MW* exclusion limit ~2700) obtained from Bio–Rad Laboratories. G.p.c. solvents were analytical grade (Fisons, BDH, ICI) and were used without further purification.

A gel slurry was prepared by leaving the gel beads in contact with solvent for 24 h and then degassing with a water pump. Thick gel slurries in solvents such as tetrahydrofuran, dioxane and benzene were acceptable, whereas with chloroform in which the gel floats it was found that a more dilute slurry was preferable. Column packing was started by keeping the column outlet shut and filling the column to a quarter of its length with solvent. The gel slurry was poured with the aid of a glass rod into a funnel topping the column. In order to avoid gel splashing, the slurry was allowed to reach the solvent surface by sliding along the walls of the column. When the solvent reached a considerable height, the column outlet was opened and packing was continued under flow. During the packing operation the gel was not allowed to settle, otherwise a separating zone was formed when more gel was added. In addition the gel was topped with 15–20 cm of solvent except when the gel bed had reached the required height. The end fitting at the top of the column was a plunger constructed from steel according to the design of Mulder and Buytenhuys[9]. The plunger was placed on top of the gel bed and the horizontal ring of the plunger was turned in order to give a seal with the polyethylene ring between the plunger and the column wall. Stainless steel capillaries and serum needles (No. 1 or No. 0) of ~3 cm in length were used to interconnect the column, plunger, valve, solvent reservoir and detector with the intermediate of either PTFE or polyethylene flexible tubing. For example, a 2 cm capillary, half covered with plastic tubing, was inserted into the drawn end of the glass column to constitute the column outlet. Similarly, the plunger and its tubing were connected by means of a short steel capillary present in the plunger bore and by means of serum needles with Luer connections to a Hamilton three way valve which was connected in turn to the solvent reservoir. The gel was allowed to settle under the required working pressure. Very often a solvent gap developed between the plunger and the gel. This was alleviated by pushing the plunger down until it was again in contact with the gel surface. The flow rate in the range 15–25 $cm^3\ h^{-1}$ was controlled by a gravity feed by the height of the solvent reservoir. The average duration of a g.p.c. experiment was 5 h. The prepolymer in solution, typically 0.015 g in 0.5 cm^3 of solvent, was applied to the column through the three way valve under the effect of the solvent flowing through the column. After complete suction of the solution, the column was again connected to the reservoir by means of the valve. The whole 'injection' sequence lasted for ~4–5 min.

The outlet at the bottom of the column was connected with plastic tubing to a steel capillary inserted in the PTFE plug of a sodium chloride cell placed in a Perkin–Elmer 459 infrared spectrometer. The cell discs were separated by a PTFE spacer (0.07 mm). The outlet of the cell consisted of a PTFE plug equipped with a steel capillary connected to plastic tubing which fed the eluting solvent to a graduated cylinder. Solvents suitable for g.p.c. separations of prepolymers based on terephthalate units must have infrared absorption bands outside the regions 1715 cm^{-1} (carbonyl stretch) and 730 cm^{-1} (phenyl hydrogens out of plane bending). In addition, the solvent must completely dissolve the prepolymer and swell the polystyrene gel. The degree of swelling may be estimated from published data for the Mark–Houwink exponent for polystyrene in organic liquids, suggesting that chloroform, benzene, tetrahydrofuran and dioxane will all give a highly swollen gel. The first two solvents may be used for g.p.c. solutes having carbonyl groups. With tetrahydrofuran and dioxane the aromatic groups in a

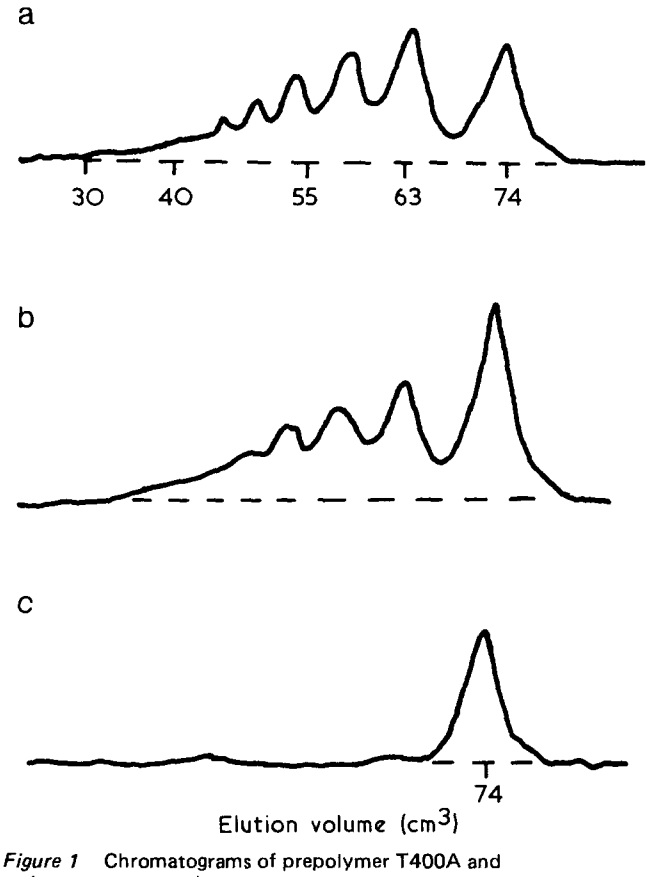


Figure 1 Chromatograms of prepolymer T400A and bis(2-hydroxypropyl) terephthalate in chloroform with infrared detection at 1715 cm^{-1}. (a) T400A; (b) T400A + $P(TP)_1$; (c) $P(TP)_1$

solute were monitored because despite the presence of inhibitors, solvent absorption in the infrared carbonyl region due to peroxide formation may arise with time.

During the separation of a prepolymer, the infrared spectrometer was fixed at a single wavelength where a specific group of the eluting component absorbed. The exact position of the absorption maximum was obtained from the spectrum of a dilute solution of the solute under examination. With the spectrometer wavelength fixed and solvent passing through the sample cell, the infrared pen was brought to its baseline (100% transmittance) by attenuating the reference beam either with an attenuator or with a NaCl reference cell containing pure solvent. Chromatograms were obtained on a JJ-type time response recorder which also amplified the infrared signal several times.

A twin column g.p.c. system was operated with columns in series subjected to downward flow. The first column was packed with Bio–Beads S–X2 and the second with Bio–Beads S–X1 in order to achieve a better separation of the high molecular weight chains from the short chain oligomers. This in conjunction with the length of the column system, the low flow rate and the minute quantity of sample separated should lead to reasonably well resolved chromatograms permitting a more accurate calculation of the areas under the peaks.

RESULTS AND DISCUSSION

Single column

The gel permeation chromatogram of prepolymer T400A is shown in *Figure 1*. Since the spectrometer was operated at 1715 cm^{-1}, propylene glycol will not be detected and will not be represented on the chromatogram. The g.p.c. separation mechanism leads to the highest molecular weight species appearing at 30 cm^3 and the lowest molecular weight component having a peak at 74 cm^3. The separation of prepolymer T400A was repeated with 0.003 g bis(2-hydroxypropyl) terephthalate added to the chloroform solution. The chromatogram for this mixture in *Figure 1* shows that the peak at 74 cm^3 has been enhanced. The chromatogram for bis(2-hydroxypropyl)terephthalate whose retention volume in *Figure 1* corresponded to the last peak in the chromatogram of prepolymer T400A, further confirms that the component eluting at 74 cm^3 may be assigned to $P(TP)_1$. In order to assign a structure to the component eluting at 63 cm^3 in *Figure 1*, a preparative separation of 0.15 g prepolymer in 2 cm^3 chloroform was performed. The eluting solvent containing the component giving rise to this peak in the chromatogram was isolated. The solution was concentrated and was reapplied to the column for further purification of the component from higher and lower molecular weight species. A part of the eluting solvent, assumed to contain the pure component, was isolated. After complete evaporation of the solvent, the clear liquid residue left was subjected to n.m.r. analysis, and the phenyl and methyl n.m.r. absorptions are shown in *Figure 2*. The observation that the ratio of their integrated traces is equal to 0.87 suggests that the component giving rise to the penultimate low molecular weight peak in the prepolymer chromatogram in *Figure 1* is $P(TP)_2$ which contains 8 phenyl hydrogens and 9 methyl hydrogens, the ratio of which is 0.89.

The acid value of prepolymer T400A was found to be 11. The significance of the acid value in terms of the number of free carboxyl groups present in 1 g of prepolymer may be

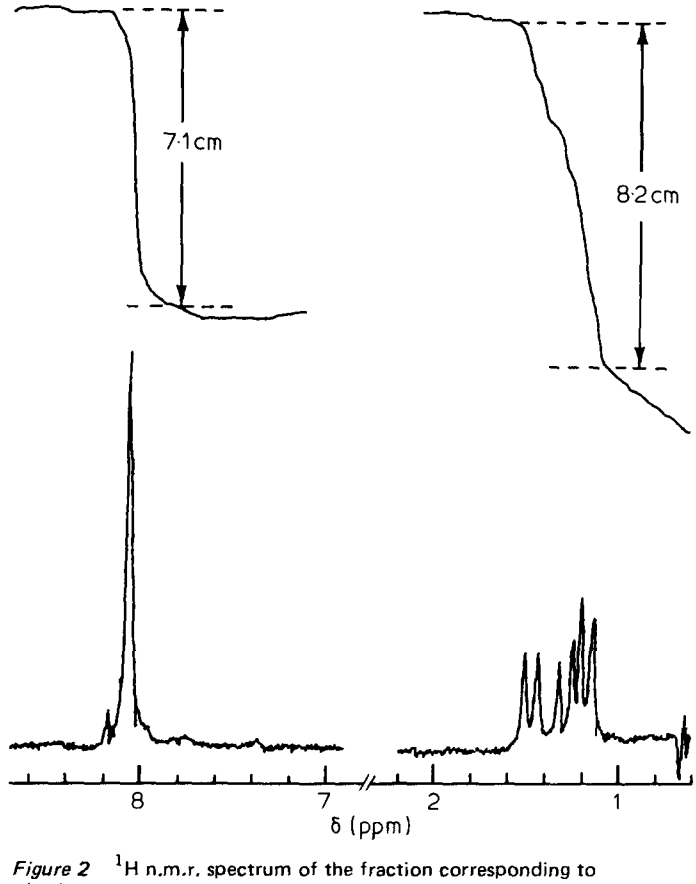


Figure 2 ^1H n.m.r. spectrum of the fraction corresponding to $P(TP)_2$

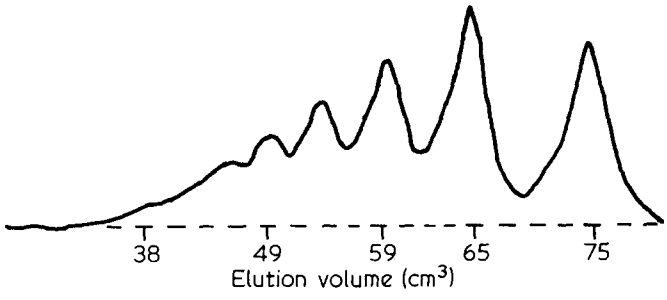


Figure 3 Chromatogram of prepolymer T400A in tetrahydrofuran with infrared detection at 730 cm^{-1}

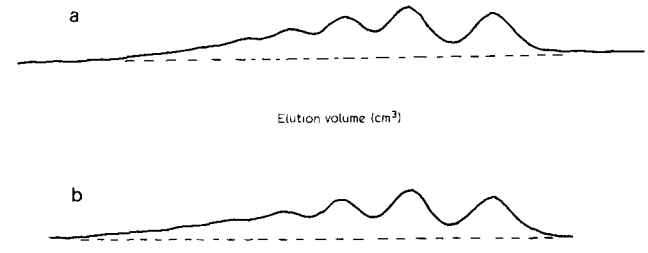


Figure 4 Chromatograms of prepolymer T400A. (a) T400A in benzene with infrared detection at 1715 cm^{-1}; (b) T400A in dioxane with infrared detection at 730 cm^{-1}

estimated since the acid number of the original feed of 166 g terephthalic acid and 167 g propylene glycol may be calculated theoretically. It follows that 3.3% of the carboxyl groups remain unreacted. If all this acidity resulted from monohydroxypropyl terephthalate PT, then prepolymer T400A would contain 4.4% by weight PT. In view of these low concentrations and the assignments of the peaks to $P(TP)_1$, and $P(TP)_2$, we may suggest that the peaks in the chromatogram in *Figure 1* may be assigned to

$$P(TP)_1, P(TP)_2, P(TP)_3, \ldots P(TP)_n \qquad (1)$$

provided that the contribution of carboxyl terminated components to the chromatogram is trivial. This representation has been used in the interpretation of the n.m.r. spectra of the prepolymers in Parts 1 and 2.

The chromatogram pattern shown in *Figure 1* for prepolymer T400A in chloroform was also obtained for g.p.c. separations with tetrahydrofuran (*Figure 3*) and with benzene and dioxane (*Figure 4*). For all solvents good resolution of oligomers $P(TP)_1$, $P(TP)_2$, $P(TP)_3$, and $P(TP)_4$ was obtained. Extensive overlap between the peaks for the higher oligomers is always observed. It may be concluded that the type of solvent and the wavenumber absorption in the infrared detection do not grossly influence the chromatogram pattern. This suggests that any interactions between solute, solvent and gel which might be dependent on solvent do not change the chromatogram pattern. If hydrogen bonding was a factor in determining solute size, then intramolecular hydrogen bonding within an oligomer might result in a non-polar solvent such as benzene, whereas the prepolymer may be non-hydrogen bonded or hydrogen bonded to solvent molecules in a polar solvent such as tetrahydrofuran.

It was found that the reaction between the carboxyl groups in the prepolymer and I reduced the acid value of the prepolymer from 11.0 to 1.5 after 6 h. Furthermore, the carbodiimide did not react with the free hydroxyl groups. G.p.c. curves for the prepolymer T400A in tetrahydrofuran before and after treatment with I for 6 h are shown in *Figure 5*.

It is evident in *Figure 5* that the chromatogram pattern at 730 cm^{-1} and the elution volumes of the peaks of the prepolymer components are not changed by the reaction with carbodiimide. We may conclude that the assignment of the peaks according to (1) is valid. A chain having a terminal carboxyl group will increase its molecular weight by 390 if the reaction with I yields an acyl urea, which is a sufficiently large increase to displace a peak from its original position on the chromatogram of the untreated prepolymer towards low elution volumes. Such an alteration of the chromatogram is not observed. The only change after the reaction with carbodiimide is the appearance of a small peak at high elution volume corresponding to a low molecular weight peak which cannot be attributed to a carbodiimide adduct since the molecular weight of $P(TP)_1$ is 282, unless this adduct, say just from PT, is retarded by solute–gel interactions which do not occur for $P(TP)_n$. An alternative proposal is that the peak corresponds to a reaction by-product. It will be recalled that the prepolymer treated with carbodiimide had a strong infrared absorption at 2290 cm^{-1} which is expected to be in the reaction product. Therefore, a g.p.c. separation of this product was performed with the infrared detector fixed at 2290 cm^{-1}, giving the chromatogram shown in

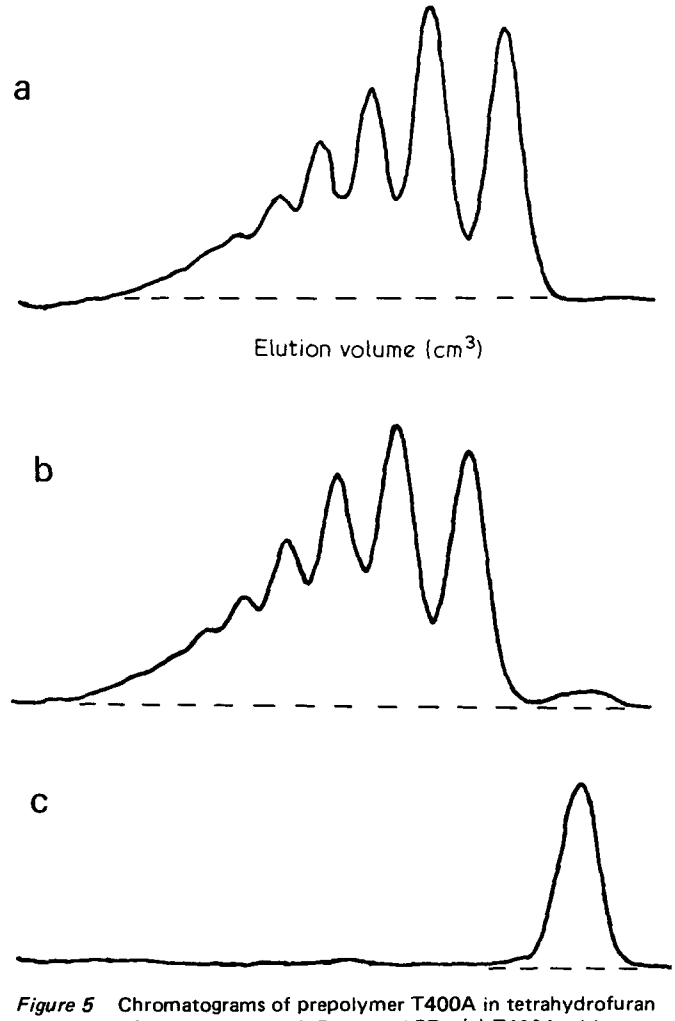


Figure 5 Chromatograms of prepolymer T400A in tetrahydrofuran before and after treatment with Daltogard PR. (a) T400A with infrared detection at 730 cm^{-1}; (b) T400A treated with I with infrared detection at 730 cm^{-1}; (c) T400A treated with I with infrared detection at 2290 cm^{-1}

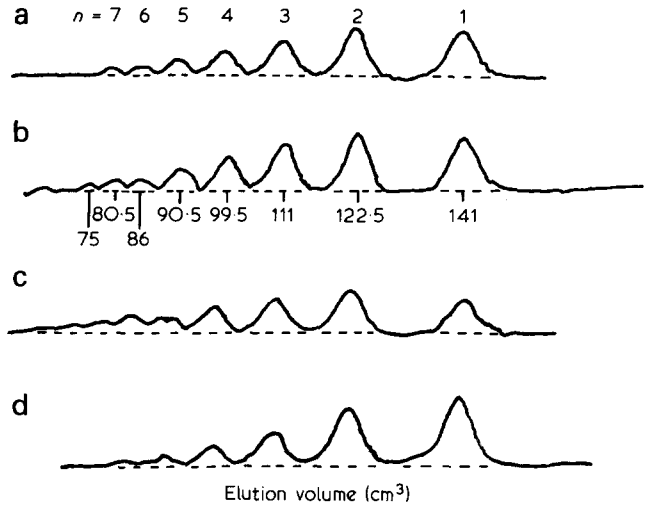


Figure 6 Chromatograms of prepolymers in chloroform with infrared detection at 1715 cm^{-1}. (a) T400A; (b) T400B; (c) T400C; (d) T500

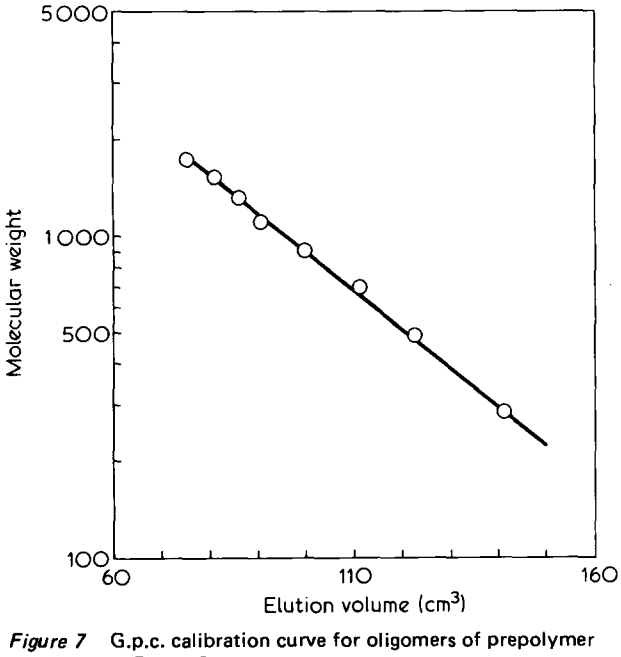


Figure 7 G.p.c. calibration curve for oligomers of prepolymer T400B from *Figure 6*

Figure 5. The small peak at the high elution volume represents all the species giving rise to the strong infrared absorption at 2290 cm^{-1}. These observations may be rationalized by the suggestion that the *o*-acylisourea formed is involved in a side reaction with a carboxylic acid to give an isocyanate (absorbing at 2290 cm^{-1}), an anhydride and an amine.

Several proposals may be advanced for the absence of g.p.c. peaks due to acidic components such as PT. The simplest assumption is that the concentration of the carboxyl terminated components is far too low for these species to be detected by our infrared detection system. An alternative view is an irreversible interaction between the gel and the carboxyl groups. A further possibility is that the acidic species are intramolecularly bonded to all the other species and therefore do not give rise to any specific chromatogram peak. This explanation does not appear to be tenable because the same interaction could have taken place between the hydroxyl ended components. Furthermore, the similar chromatogram patterns for the g.p.c. solvents in *Figures 1, 3* and *4* suggest that such interactions do not have a marked influence on the g.p.c. separation. The suggestion that no g.p.c. peak for PT is observed because the position of its carbonyl absorption is different from that of $P(TP)_n$ may be disproved by the experiment that no peak for PT occurs when the phenyl absorption at 730 cm^{-1} is monitored. Dimethyl terephthalate and terephthalic acid both have an out of plane bending vibration of the phenyl hydrogens exactly at 730 cm^{-1}.

Twin column system

In order to improve the resolution of oligomers with $n > 4$, the twin column system was used with chloroform as g.p.c. solvent and with the infrared detector monitoring at 1715 cm^{-1}. It is evident in *Figure 6* that the resolution of the high molecular weight components in prepolymer T400A is far better than that shown in *Figure 1* for the single column. Chromatograms for T400B, T400C and T500 prepolymers are also shown in *Figure 6*. From the assignment of the peaks in *Figure 6* a molecular weight calibration may be constructed for the twin column system, and a linear relation is demonstrated in *Figure 7* for prepolymer T400B.

The g.p.c. results for the carbodiimide treated prepolymer were not definitive, and it was suggested that carboxyl terminated oligomers were not detected because of their low concentration or that such oligomers were physically bonded to the surface of the gel in the g.p.c. column. Since prepolymer T400B had the highest acid number of 16 (see *Table 1*), an attempt was made to detect carboxyl terminated oligomers in prepolymer T400B with the twin column system. Elution volumes for peaks corresponding to oligomers such as PT and $(PT)_2$ may be predicted from the calibration curve in *Figure 7*. Thus, the elution volume for PT (*MW* = 224) is predicted to be ~ 150 cm^3, but an examination of the chromatogram for prepolymer T400B in *Figure 6* suggests the absence of a peak at this elution volume. A chromatogram for prepolymer T400B after treatment with diazomethane is presented in *Figure 8*. In order to enhance the intensity of the peaks arising from acidic (now esterified)

Table 1 Results for prepolymers

Prepolymer	Acid number	Prepolymer containing terephthalate units only: $\bar{M}_n$ (g.p.c.)[a]	$\bar{M}_n$ (n.m.r.)[b]	PG (%, w/w)	Prepolymer and free propylene glycol: $\bar{M}_n$[c]	$\bar{M}_n$[b]
T400A	11	453	454	11.1	292	284
T400B	16	474	522	10.9	302	319
T400C	13	508	524	6.7	368	376
T500	9.6	400	391	23.1	202	200

a Equation (7)
b Part 2
c Equation (9)

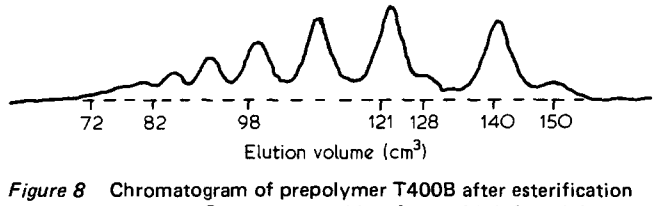


Figure 8 Chromatogram of prepolymer T400B after esterification with diazomethane. G.p.c. solvent chloroform with infrared detector at 1715 cm^{-1}

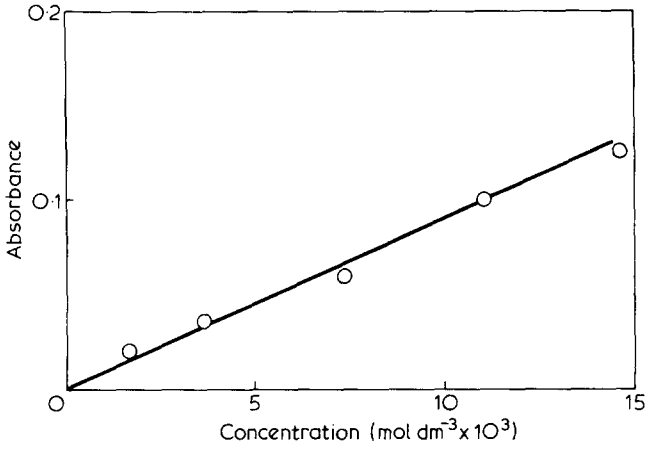


Figure 9 Experimental dependence of infrared absorbance for the carbonyl band at 1715 cm^{-1} on the concentration of bis(2-hydroxypropyl) terephthalate in chloroform

components, a higher solute concentration and detector amplification factor were employed compared with the chromatographic conditions operating for the previous separations giving the chromatograms in *Figure 6*. The chromatogram pattern for prepolymer T400B in *Figure 6* is again observed in *Figure 8* with the addition of two further peaks, one appearing at 150 cm^3 which corresponds to a low molecular weight component identified from the calibration curve in *Figure 7* as the methyl ester of PT (MW = 238). The second peak at 128 cm^3 may be assigned with the same calibration curve to the methyl ester of $(PT)_2$ (MW = 430). These results demonstrate that low concentrations of the acidic components can be detected by g.p.c. provided the prepolymer samples are fully esterified before the g.p.c. separation. Therefore, the most probable explanation for the absence of peaks arising from acidic components in chromatograms of prepolymers not esterified with diazomethane, is a physical interaction between the carboxyl groups and the gel surface.

Molecular weight distribution

The absorbance from an infrared detector at 1715 cm^{-1} is directly proportional to the number of carbonyl groups present in the solution. This was confirmed for dilute solutions of bis(2-hydroxypropyl) terephthalate in chloroform in cells with a path length of 0.07 mm placed directly into the infrared spectrometer. The linear plot of absorbance *versus* solute concentration is shown in *Figure 9*. Provided low solute concentrations are employed in g.p.c., it has been shown that an infrared detector output in terms of transmittance gives areas under chromatogram peaks which are also directly proportional to solute concentration[10]. In order to determine accurately the concentrations of the oligomers represented by (1) from the chromatograms in *Figure 6*, the relation between oligomer concentration, the number of absorbing groups in each oligomer and peak area must be considered.

We consider first a solution of $P(TP)_1$ which contains two carbonyl groups. If the Beer–Lambert law is stated in terms of the carbonyl concentration, then the absorbance A_1 is given by:

$$A_1 = 2\epsilon_\lambda l c_1 \tag{2}$$

where ϵ_λ is the extinction coefficient of a single carbonyl group, l is the cell path length (which is a constant), and c_1 is the concentration (mol) of $P(TP)_1$. The next oligomer to consider is $P(TP)_2$ which contains four carbonyl groups. A solution of $P(TP)_2$ gives an absorbance A_2 which is related to the concentration c_2 (mol) of this oligomer by:

$$A_2 = 4\epsilon_\lambda l c_2 \tag{3}$$

It is therefore evident that provided the value of ϵ_λ is the same for all carbonyl groups the absorbance A_n for each oligomer having a concentration c_n (mol) is given by the general expression:

$$A_n = 2n\epsilon_\lambda l c_n \tag{4}$$

For a chromatogram showing a mixture of oligomers as in *Figure 6*, the area S under a peak corresponding to one oligomer is represented by the sum of the deflections, each deflection being the result of an independent infrared experiment for species i having a concentration c_i[10]. The value of S is proportional to the total concentration of that oligomer given by Σc_i. It follows from equation (4) that the area under the peak corresponding to each oligomer is given by:

$$S_n = 2nk\Sigma c_i \tag{5}$$

where k is the product of ϵ_λ and l. Hence, the concentration (mol) of each oligomer is obtained with the general expression

$$\Sigma c_i = S_n/2nk \tag{6}$$

which involves dividing the area under the g.p.c. peak corresponding to each oligomer by the number of carbonyl groups present in that oligomer.

If we assume that all oligomers present are represented according to (1) with $n \geqslant 1$ and that the g.p.c. separation is not perturbed by interaction effects between solute, solvent and gel, then the number average molecular weight $\bar{M}_n$ (g.p.c.) may be calculated for each prepolymer from the expression:

$$\bar{M}_n \text{ (g.p.c.)} = \frac{\Sigma(S_n/n)M_n}{\Sigma(S_n/n)} \tag{7}$$

where M_n is the molecular weight of an oligomer. Equations (6) and (7) enable values of $\bar{M}_n$ (g.p.c.) to be calculated from the chromatograms in *Figure 6*. Full details of the mol fractions of each oligomer for all the prepolymers are tabulated elsewhere[11]. In *Table 1* the data for $\bar{M}_n$ (g.p.c.) are in good agreement with the values which were obtained by ^{1}H n.m.r. as described previously in Part 2. The loss of the minor quantities of PT and $(PT)_2$ in g.p.c. separations does not appear to have introduced large errors in the calculation of $\bar{M}_n$ (g.p.c.).

Equation (7) is based on oligomers containing terephthalate units. However, the prepolymer samples all contain free propylene glycol (PG) which does not give a peak in the chromatograms because the detector employed infrared absorptions at 1715 cm^{-1} (carbonyl) and 730 cm^{-1} (phenyl). The concentration of free propylene glycol PG (%, w/w) has been determined by ^{1}H n.m.r. in Part 2, and values are presented again in *Table 1*. The complete composition of each prepolymer may be evaluated as follows. We shall assume that the sum of the mol fractions of the terephthalate based components is normalized to unity, i.e. $\Sigma(S_n/n) = 1.0$, which

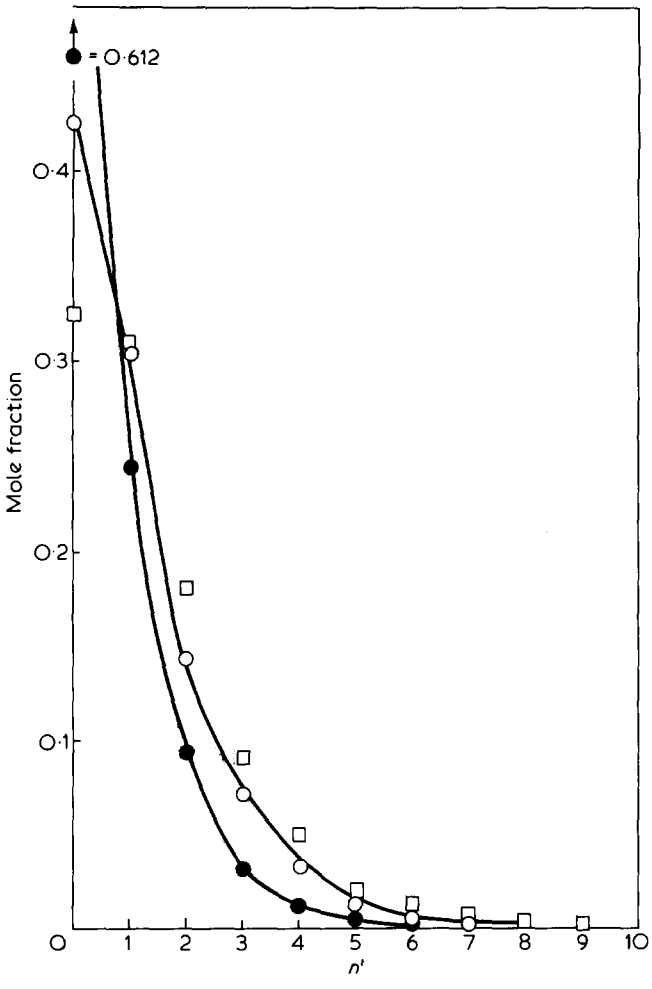


Figure 10 Mol fraction distributions of components in prepolymers. ○, T400A; ——, T400B; □, T400C; ●–●–●, T500

corresponds to a weight (g) of terephthalate based components given by $\bar{M}_n$ (g.p.c.) in *Table 1*. Then, the concentration x(mol) of free propylene glycol in a prepolymer is given by

$$x = \frac{\mathrm{PG}\bar{M}_n(\mathrm{g.p.c.})}{76(100-\mathrm{PG})} \tag{8}$$

Mol fractions may then be evaluated for all components in a prepolymer, so that $n' \geqslant 0$ includes propylene glycol. The results for the four prepolymers are shown in *Figure 10*. From these mol fractions, values of $\bar{M}_n$ for the whole prepolymer may be calculated with:

$$\bar{M}_n = \frac{\Sigma N_{n'} M_{n'}}{\Sigma N_{n'}} \tag{9}$$

where $N_{n'}$ is the mol fraction of each component having molecular weight $M_{n'}$ in a prepolymer. The results are presented in *Table 1* and compare favourably with values determined by ^{1}H n.m.r. in Part 2. The curves in *Figure 10* show the behaviour typical of condensation polymers prepared by step-reaction polymerization. The distribution contains a high proportion (mol) of unreacted propylene glycol and the fraction of each terephthalate-based oligomer is substantially lower, with the mol fraction decreasing as the number of propylene terephthalate repeating units is increased. It was not possible to calculate a single theoretical distribution for the polyesterification because of non-stoichiometry and incomplete reaction as discussed by Flory[12]. It is evident in *Figure 10* that prepolymer T500 which was synthesized with 3.3 mol of propylene glycol has a significantly different distribution from those for the other three prepolymers which were prepared with 2.2 mol of propylene glycol (see Part 2).

CONCLUSIONS

The g.p.c. technique gives excellent resolution of the oligomer components in the prepolymers and confirms the representation of the prepolymer structure by P(TP)$_n$ as proposed from ^{1}H n.m.r. studies in Parts 1 and 2. Assignment of peaks in the chromatogram demonstrates that significant concentrations of terephthalate-based oligomers with n from 1 up to 6, 7, 8 or 9 are present. The infrared g.p.c. detector provides a way of estimating quantitatively the concentration of each oligomer from peak areas in the chromatogram. The mol fraction distributions of the prepolymers clearly show that $\bar{n} > 1.0$. Values of number average molecular weight determined from these g.p.c. distributions are in excellent agreement with values determined by ^{1}H n.m.r. in Parts 1 and 2. Although the presence of low molecular weight components terminated by carboxyl groups in a prepolymer may be demonstrated, their concentration is almost trivial, and consequently the qualitative and quantitative interpretations of the chromatograms in terms of the structure P(TP)$_n$ are not affected.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. H. W. B. Reed for his interest in this work and the Petrochemicals Division of Imperial Chemical Industries Limited for a research grant.

REFERENCES

1 Birley, A. W., Kyriacos, D. and Dawkins, J. V. *Polymer* 1978 **19**, 1290
2 Birley, A. W., Dawkins, J. V. and Kyriacos, D. *Polymer* 1978, **19**, 1433
3 BS 3532: 1962, Appendix H, p 13
4 Khorana, H. G. *Chem. Rev.* 1953, **53**, 145
5 Smith, P. 'The Chemistry of Open Chain Organic Nitrogen Compounds', Benjamin, New York, 1965, Vol 1, p 250
6 Awram, M. and Mateescu, G. D. 'Infrared Spectroscopy', Wiley–Interscience, New York, 1970
7 *Org. Synth. Coll. Vol.* 1963, **4**, 250
8 *Org. Synth. Coll. Vol.* 1943, **2**, 165
9 Mulder, J. L. and Buytenhuys, F. A. *J. Chromatogr.* 1970, **51**, 477
10 Birley, A. W., Dawkins, J. V. and Kyriacos, D. *Polymer* 1978, **19**, 350
11 Kyriacos, D. *Ph. D. Thesis*, Loughborough University of Technology, UK 1977
12 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953