

# Cyclic polyesters: 6. Preparation and characterization of two series of cyclic oligomers from solution ring-chain reactions of poly(ethylene terephthalate)

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Solution ring-chain reactions of poly(ethylene terephthalate) (PET) were carried out using a high boiling solvent, 1-methyl naphthalene and catalyst. At a dilution of 1/10 (w/w polymer/solvent) and catalyst concentration of 0.5% (w/w), a reaction with tetraisopropyl orthotitanate, gave cyclics at a yield of 3 wt%, with dibutyltin bis (2-ethyl-hexanoate) the yield was 11 wt%, and with zinc acetate it was 20 wt%. Increasing the dilution of the reaction to 1/30 (w/w polymer/solvent) using zinc acetate as catalyst, increased the yield of the cyclics to 30 wt%. The cyclics were analysed using PL-gel mixed-E gel permeation chromatographic columns, and by  $^1\text{H}$  nuclear magnetic resonance spectroscopy, fast atom bombardment mass spectrometry, and liquid chromatography tandem mass spectrometry. The cyclic compounds  $(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O})_x$ , where  $x = 3\text{--}13$ , 30–130 skeletal bonds), were identified together with a series of ring compounds  $(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O})_x\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$ , (where  $x = 2\text{--}7$ ) which were also found to be present. This latter series has not been previously reported. © 1997 Elsevier Science Ltd.

(Keywords: cyclic polyester; gel permeation chromatography; poly(ethylene terephthalate))

## INTRODUCTION

In an earlier investigation carried out in our laboratory over 25 years ago<sup>1</sup>, ring-chain equilibrium reactions were used to prepare cyclics of poly(ethylene terephthalate) (PET), which were analysed by gel permeation chromatography (g.p.c.) using columns packed with SX-1 Bio-beads. The molar cyclization equilibrium constants,  $K_x$  were measured and compared with theoretical values calculated using Jacobson and Stockmayer theory<sup>2</sup> together with the Flory and Williams<sup>3</sup> rotational isomeric state model of the linear polymer.

In previous studies reported in the chemical literature, extracts of samples of commercial PET were found to contain cyclic oligomers<sup>4–8</sup>. The detailed investigations of Goodman and Nesbitt<sup>6</sup> showed that the samples of extracted cyclics of commercial PET fibre and chip contained the ring compounds,  $(\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O})_x$  with  $x = 3\text{--}5$ , together with small amounts of a cyclic containing one ethylene glycol linkage,  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$  and one diethylene glycol linkage  $\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}$ . These glycol residues were believed to have been formed during the melt polymerization of PET<sup>9,10</sup>.

This paper describes how we have prepared cyclic oligomers of PET in good yields using solution ring-chain reactions at different levels of solvent dilution. Two series of cyclic oligomers, were identified in the products of the reactions. The preparative methods described here provide an effective route to substantial quantities of

cyclic oligomers of PET. These are required for future work in our laboratory.

## EXPERIMENTAL

### Materials

Samples of PET chip were supplied by ICI Materials, Wilton. 1-Methyl naphthalene, zinc acetate, and dibutyltin bis (2-ethyl-hexanoate) were supplied by Aldrich Co, tetraisopropyl orthotitanate by Fluka Chemika, chloroform by Fisons Chemicals, alumina (neutral, activated) by Jansen Chimica. All of the reagents were used as received.

### Solution ring-chain reactions

Commercial PET chip with a number-average molar mass,  $M_n = ca\ 2 \times 10^4$ , was dissolved in 1-methyl naphthalene at 513 K. The solution was refluxed for 24 h in the presence of a catalyst (0.5 wt% with respect to polymer). The catalysts used were tetraisopropyl orthotitanate, dibutyltin bis (2-ethyl-hexanoate) and zinc acetate, and each reaction was carried out at a polymer/solvent dilution ratio (by weight) of 1/10.

Further reactions were performed using zinc acetate as catalyst (0.5 wt%) at a polymer/solvent dilution ratio (by weight) of 1/20 and 1/30.

### Extraction of cyclics

The cyclic oligomers from all the solution ring-chain reactions were extracted using chloroform. The reflux mixture from the ring-chain reactions was cooled to

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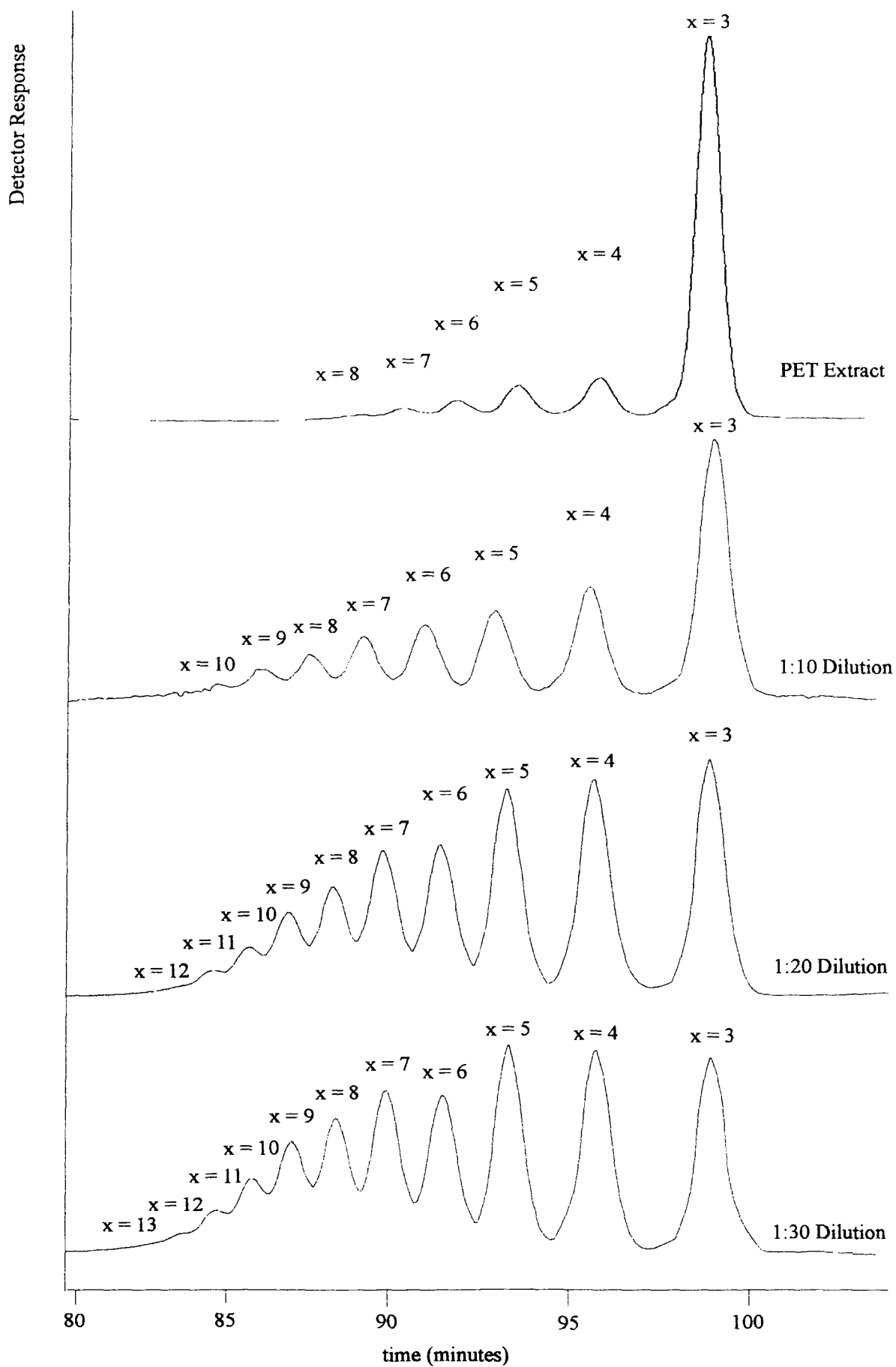


Figure 1 G.p.c. of cyclics  $(\text{CO.C}_6\text{H}_4.\text{CO.O.CH}_2.\text{CH}_2.\text{O})_x$ , where  $x = 3-8$ , from an extraction of chip with mixed xylene isomers, and solution ring chain reactions with zinc acetate as catalyst at polymer/solvent dilution ratios of 1/10, 1/20 and 1/30

room temperature, at which point the polymer reprecipitated. The mixture was poured into a beaker and stirred with twice its volume of chloroform for 1 h. Most of the polymer was then filtered off. The remaining mixed solvent solution was removed under vacuum. The chloroform was removed using a rotary evaporator and the 1-methyl naphthalene was removed by vacuum distillation (50°C, 0.1 mmHg). The crude extracts were purified by dissolving each extract in chloroform and adding alumina (10% w/w by extract) and then leaving the solution to stand for 2 h. The alumina was filtered off and the chloroform removed on a rotary evaporator. The extract was further dried under high vacuum (0.1 mmHg).

#### Gel permeation chromatography

The cyclic oligomers were analysed using a Knauer GPC instrument, equipped with four PL-gel 3  $\mu$ m mixed-E

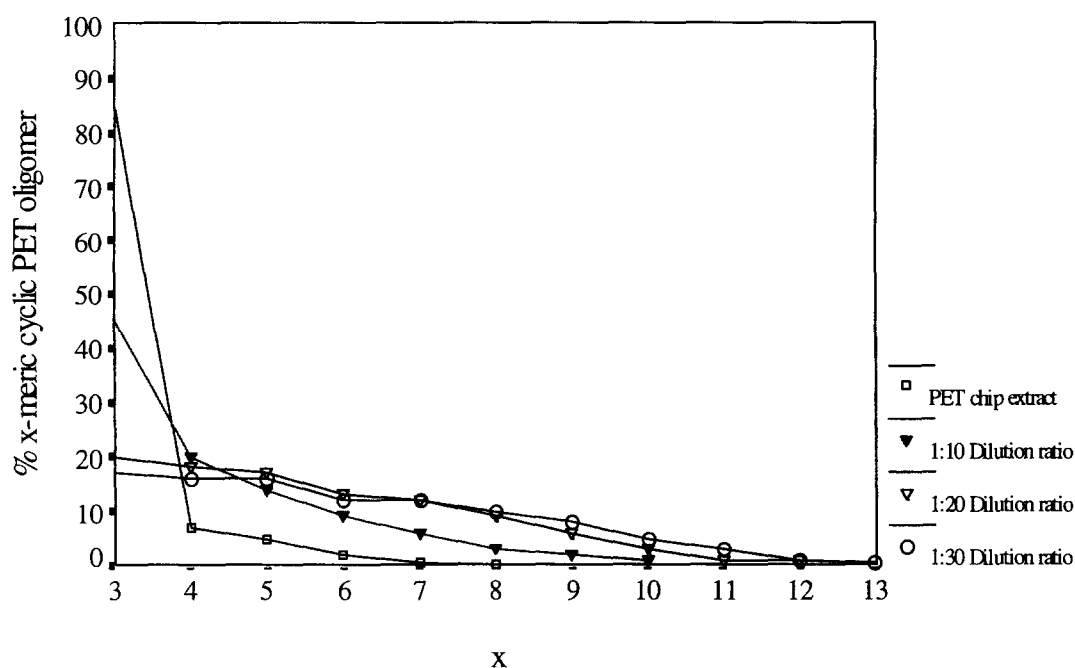
columns, supplied by Polymer Laboratories Ltd. The instrument was fitted with a Shimadzu RID-6A refractive index detector. Samples were analysed in chloroform solution at room temperature at a flow rate of 0.3 ml  $\text{min}^{-1}$ . The relative peak areas of each cyclic oligomer were estimated using Polymer Laboratories logical software.

#### Nuclear magnetic resonance spectroscopy

$^1\text{H}$  nuclear magnetic resonance (n.m.r.) spectra were obtained on a JOEL 270 MHz spectrometer, using deuterated chloroform as the solvent.

#### Fast atom bombardment mass spectrometry

Fast atom bombardment mass spectrometry (f.a.b.m.s.) of the cyclic oligomers were obtained using an autospec f.a.b.m.s. with caesium ions as the bombarding particles and 3-nitrobenzyl alcohol as the matrix.



**Figure 2** A plot showing the percentage of cyclic oligomers  $(\text{CO.C}_6\text{H}_4.\text{CO.O.CH}_2.\text{CH}_2.\text{O})_x$  in the cyclic extract from commercial PET chip compared to the cyclic oligomers from the solution ring-chain reactions with zinc acetate as catalyst at different dilutions ( $-\square-$ , PET extract from commercial chip;  $-\blacktriangledown-$ , solution ring-chain reaction at 1/10 dilution ratio;  $-\nabla-$ , solution ring-chain reaction at 1/20 dilution ratio;  $-\circ-$ , solution ring-chain reaction at 1/30 dilution)

**Table 1** Percentage amounts of each individual cyclic oligomer estimated by g.p.c. for the extract from a sample of commercial PET, compared to the cyclic oligomers formed in the solution ring-chain reactions at different dilution ratios

x	Percentage (%) individual cyclic oligomer of PET obtained			
	Commercial chip extract	Solution ring-chain reaction, 1/10 dilution ratio	Solution ring-chain reaction, 1/20 dilution ratio	Solution ring-chain reaction, 1/30 dilution ratio
3	85	45	20	17
4	7	20	18	16
5	5	14	17	16
6	2	9	13	12
7	>1	6	12	12
8	>1	3	9	10
9	-	2	6	8
10	-	>1	3	5
11	-	-	≈1	3
12	-	-	≈1	≈1
13	-	-	-	>1

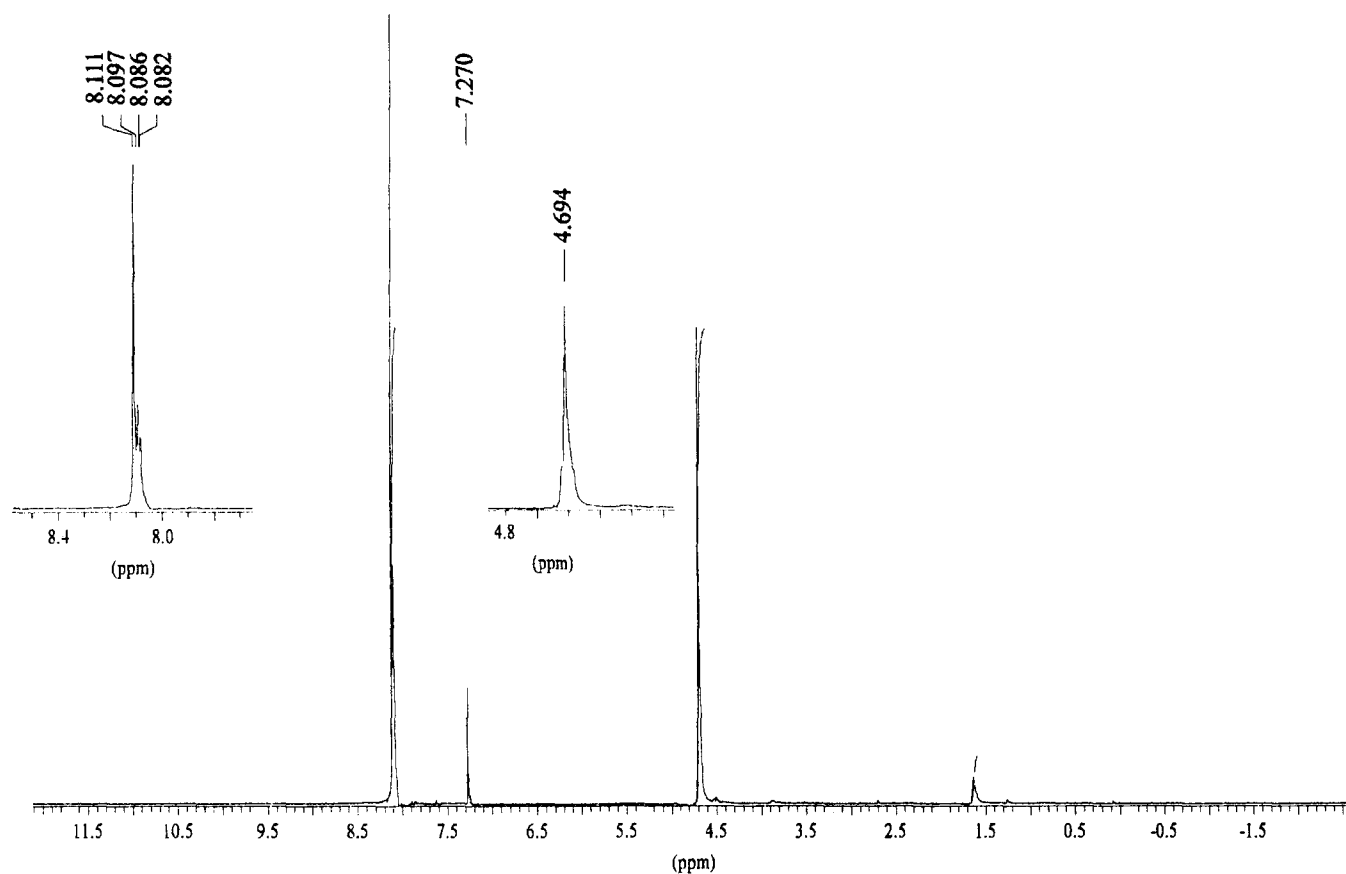


Figure 3 <sup>1</sup>H n.m.r. spectra of cyclic oligomers of PET from a solution ring-chain reaction at a polymer/solvent dilution ratio of 1/10, with zinc acetate as catalyst

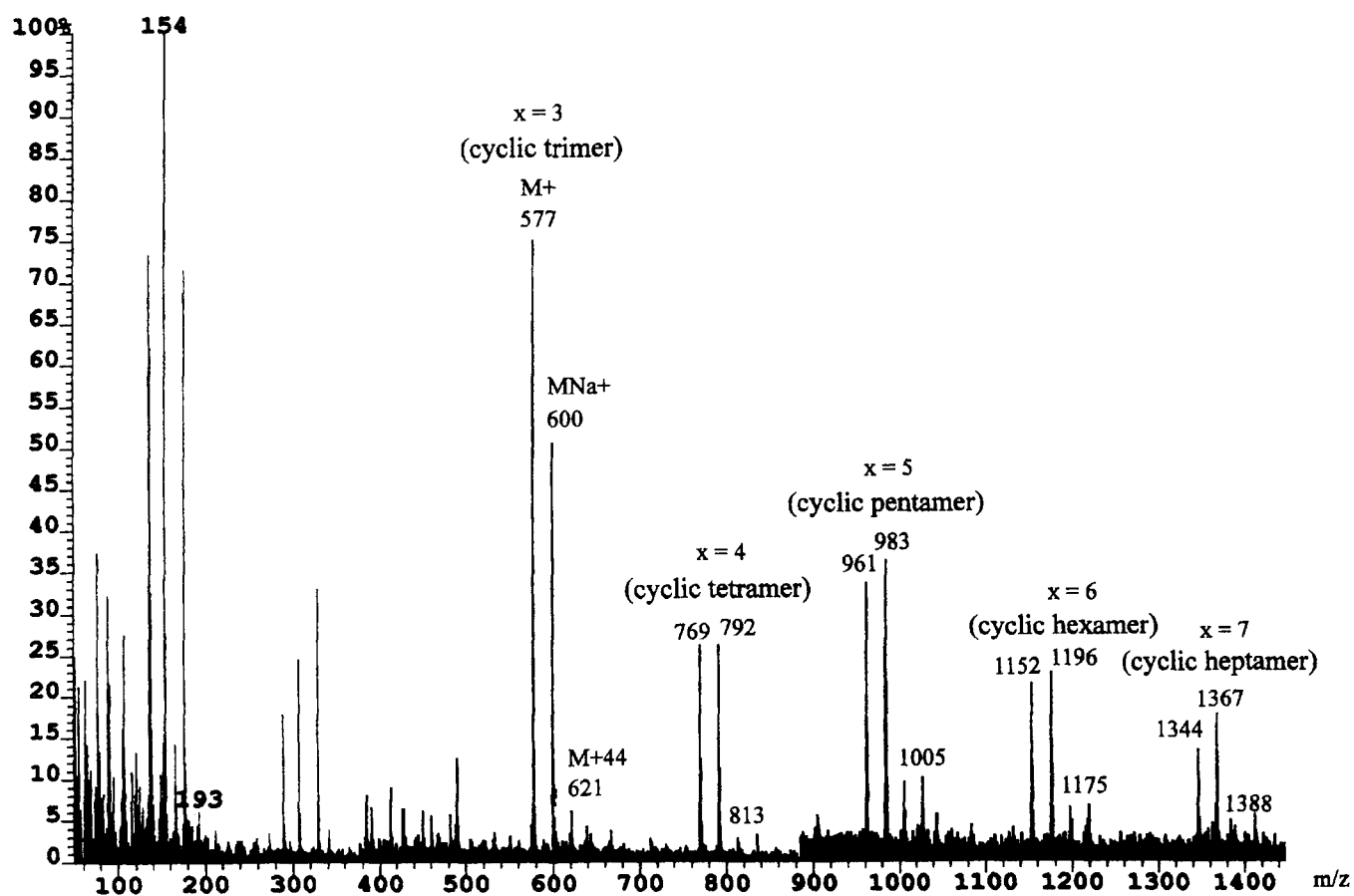


Figure 4 F.a.b.m.s. of cyclic oligomers of PET from a solution ring-chain reaction at a polymer/solvent dilution ratio of 1/10, with zinc acetate as catalyst

*Liquid chromatography tandem mass spectrometry*

The cyclic oligomers were analysed using a Finnigan MAT TSQ 7000 triple quadrupole mass spectrometer. Atmospheric pressure chemical ionization (APCI) in the presence of traces of ammonium ions was used. Further fragmentation was achieved using 30 eV argon in a collision cell.

## RESULTS AND DISCUSSION

*Ring-chain reactions with catalyst*

The extracts from the reactions carried out with the catalysts, tetraisopropyl orthotitanate, dibutyltin bis (2-ethyl-hexanoate) and zinc acetate at 1/10 polymer/solvent dilution ratio were analysed by g.p.c., f.a.b.m.s. and  $^1\text{H}$  n.m.r. spectroscopy.

The yield of cyclic extract was calculated with respect to the total amount of polymer chip used initially in the reaction. The yields of the cyclic extract  $(\text{CO.C}_6\text{H}_4.\text{CO.O.CH}_2.\text{CH}_2.\text{O})_x$  (where  $x = 3-10$ ), were 3 wt% for tetraisopropyl orthotitanate, 11 wt% for dibutyltin bis (2-ethyl-hexanoate) and 20 wt% for zinc acetate. The distribution of products was found to be the same for all the catalysts used. The rings from  $x = 3$  to  $x = 10$  were completely resolved by g.p.c. analysis using the mixed E-columns. A typical chromatogram of a cyclic extract, from the ring chain reaction using zinc acetate as catalyst is shown in *Figure 1*.

The extraction procedure used here, utilizes the solubility difference between cyclic oligomers and linear oligomers of PET. It is well known that cyclic oligomers of PET are fully soluble in chloroform, whereas linear PET is insoluble in this solvent. Therefore the g.p.c. traces show no linear material. All this is in contrast to other more soluble aliphatic polyesters presently being investigated in our laboratory (see, for example ref. 9). The crude PET extract may contain a very small quantity of linear material, but any such material would be removed by using alumina columns. The linear material is adsorbed onto the alumina through the hydroxyl terminated functionality on the linear PET.

From our previous investigation<sup>1</sup>, it was shown that ring-chain equilibrium was attained in the melt after  $\sim 12$  h. In this investigation using solvents the reaction time for the ring-chain reactions was chosen to be 24 h and equilibrium was not reached on this time scale.

Tetraisopropyl orthotitanate, which has been shown in other investigations<sup>11,12</sup> to work well for cyclic aliphatic polyesters, here gave the lowest cyclic oligomer yield for PET. Tin catalysts have been used with success in the polymerization of cyclic aromatic polyester oligomers<sup>13</sup>, but dibutyltin bis (2-ethyl-hexanoate) did not produce as high a yield as the zinc acetate catalyst. Hence the solution ring-chain reactions at higher dilutions were carried out with the latter catalyst.

*Ring-chain reactions at higher dilutions*

As expected, solution ring-chain reactions of higher dilution were found to increase the yield of the cyclic oligomers in the extract. For dilutions of 1/10, 1/20 and 1/30 (w/w polymer/solvent) the yield of cyclic product (by weight of total polymer chip used initially) was found to be 20, 25 and 30 wt% respectively. Furthermore the amount of each individual cyclic oligomer, was found to be relatively greater than those obtained using

conventional procedures for extracting oligomers from PET samples using low boiling solvents<sup>4-8</sup>. In our investigation we extracted cyclic oligomers of PET at a yield of 1 wt%, from a commercial sample of chip using mixed xylene isomers.

*Figure 1* shows the g.p.c. trace of cyclic oligomers of PET extracted from chip with mixed xylene isomers, together with the g.p.c. traces from the solution ring-chain reactions at 1/10, 1/20, and 1/30 polymer/solvent dilution ratio, where values of  $x$  can be observed from  $x = 3$  to  $x = 10$  for the 1/10 dilution ratio, and  $x = 3$  to  $x = 13$  for the 1/30 dilution ratio.

*Figure 2* shows the percentage amounts of each individual cyclic component (estimated by g.p.c.) for cyclics extracted from commercial chip using mixed xylene isomers, compared to the cyclics obtained from the ring-chain reactions at dilution ratios of 1/10, 1/20 and 1/30. Conventional procedures for extracting cyclic oligomers using low boiling solvents produces mainly cyclic trimer ( $\sim 85\%$  in our investigation), and only smaller amounts of the higher cyclic oligomers.

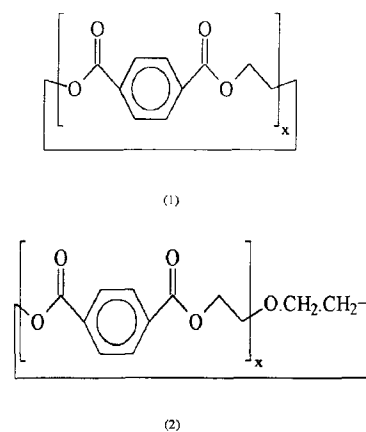
*Table 1* shows the percentage values of each individual cyclic oligomer estimated by g.p.c. from the cyclics obtained from the extraction of commercial PET chip, compared to the cyclics formed in the solution ring chain reactions at different dilutions. The values quoted are only estimates calculated by the relative peak areas from the g.p.c. traces using Polymer Laboratories logical software. For the higher oligomers ( $x = 6, 7, 8, \dots$ ) these estimates will be less accurate as the peaks slightly coalesce.

*Nuclear magnetic resonance spectroscopy*

$^1\text{H}$  n.m.r. spectroscopy (*Figure 3*) shows two singlets,  $\delta = 8.111$  ppm (aromatic H) and  $\delta = 4.694$  ppm ( $\text{O.CH}_2.\text{CH}_2.\text{O}$  in a cyclic PET ring unit) characteristic of cyclic PET. The series of peaks at  $\delta = 8.082$ , 8.086, and 8.097 ppm are due to some residual 1-methyl naphthalene from the reaction mixture. The peak at  $\delta = 7.270$  ppm is due to chloroform.

*Fast atom bombardment mass spectrometry and liquid chromatography tandem mass spectrometry*

The cyclic oligomer extract was investigated by f.a.b.m.s. This method has been used previously to identify cyclic oligomers<sup>14,15</sup>. Liquid chromatography has been reported to have been used with thermospray mass spectrometry<sup>16</sup>



**Figure 5** The structures of the two series of cyclic oligomers formed in the solution ring-chain reactions

and plasm spray mass spectroscopy<sup>17</sup> to analyse oligomers in PET, including cyclic species. The f.a.b.m.s. (Figure 4) shows a regular series of spectral lines corresponding to exact multiplets of the repeat unit (1) (Figure 5)  $(\text{CO.C}_6\text{H}_4\text{.CO.O.CH}_2\text{.CH}_2\text{.O})_x$  (formula weight = 192.04) where  $x = 3-7$ . A further series of spectral lines corresponding to  $(\text{M} + \text{Na})^+$  is also present. Furthermore a series of spectra lines corresponding to the repeat unit (2) (Figure 5)  $(\text{CO.C}_6\text{H}_4\text{.CO.O.CH}_2\text{.CH}_2\text{.O})_x\text{CH}_2\text{.CH}_2\text{.O}$ , where  $x = 3-7$ , is believed to be due to the cyclic PET

repeat unit containing one diethylene glycol residue. Some of these ring compounds have been identified previously in cyclic extracts from PET<sup>6,16</sup>.

Liquid chromatography tandem mass spectrometry (l.c.-m.s.-m.s.) confirms the two series of cyclic oligomers in the extract from the solution ring-chain reaction. Figure 6 shows a series of peaks corresponding to cyclic oligomers of PET,  $(\text{CO.C}_6\text{H}_4\text{.CO.O.CH}_2\text{.CH}_2\text{.O})_x$  where  $x = 3-9$ . In addition to the series of peaks corresponding to cyclic oligomers of PET, a further series of peaks was

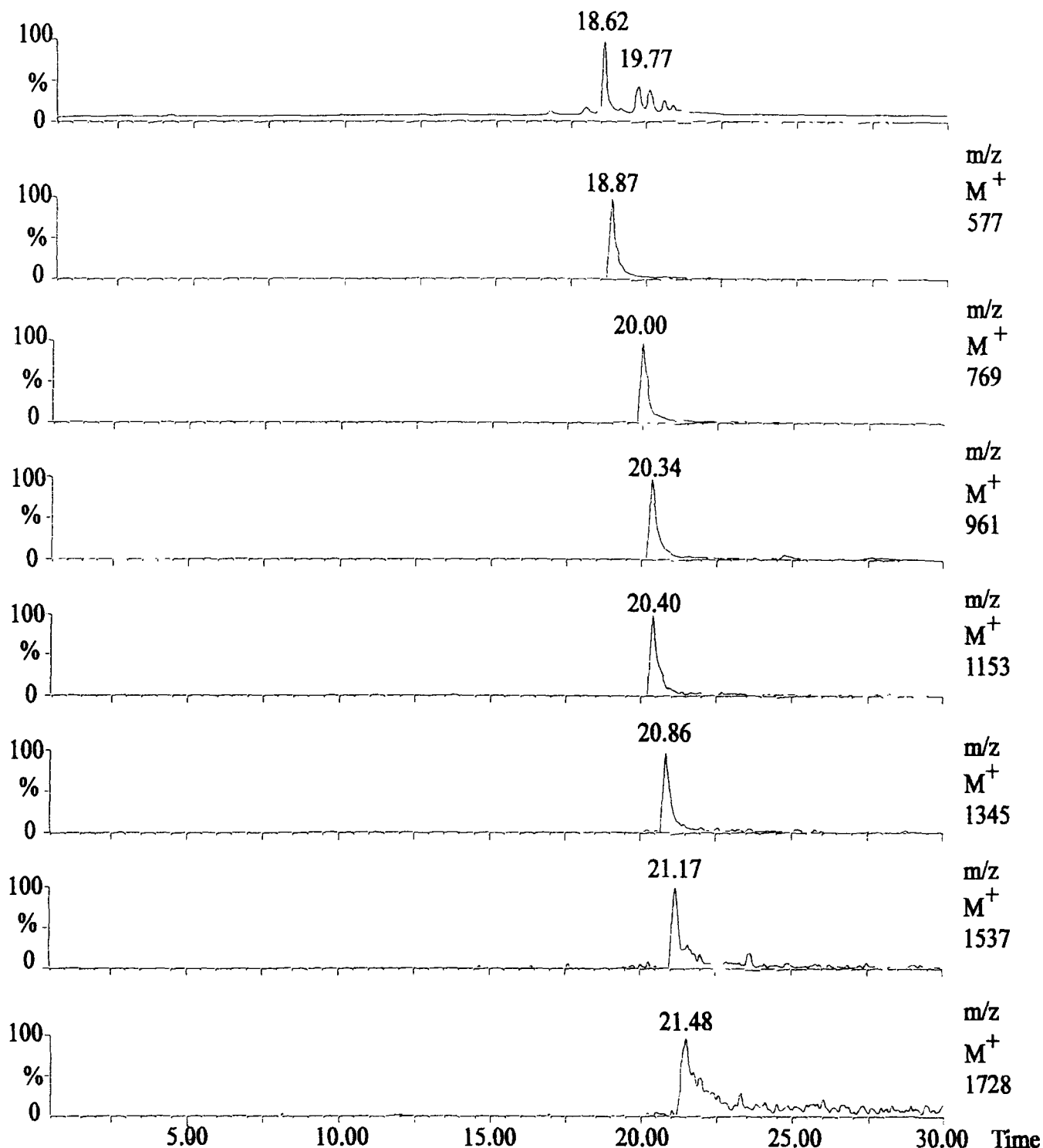


Figure 6 Liquid chromatogram of cyclic oligomers of PET from a solution ring-chain reaction at a polymer/solvent dilution ratio of 1/10, with zinc acetate as catalyst. The corresponding  $m/z$  values were determined using tandem mass spectrometry (see text)

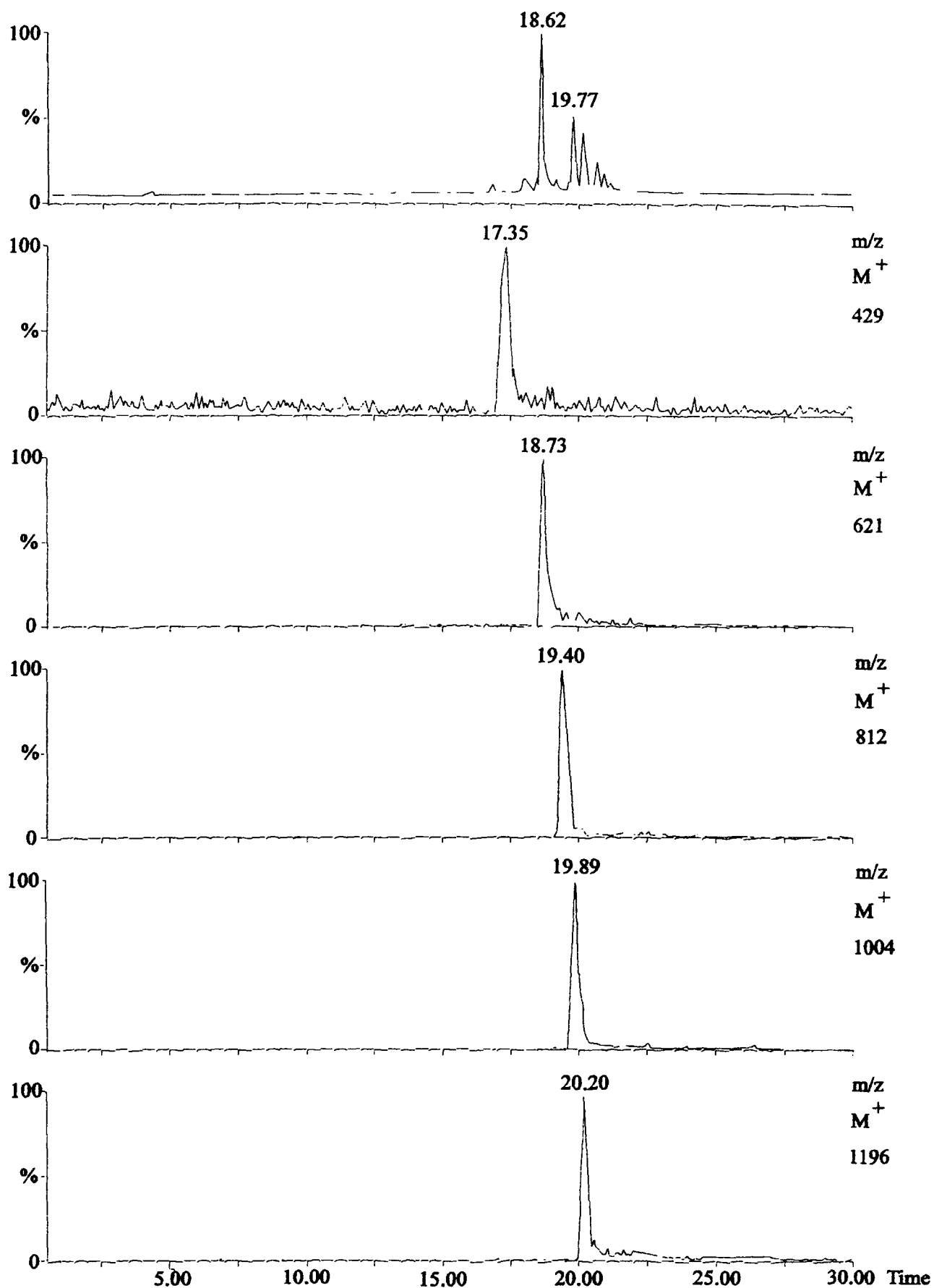


Figure 7 Liquid chromatogram of cyclic oligomers from PET including the ethylene glycol residue  $(\text{CO.C}_6\text{H}_4\text{CO.O.CH}_2\text{CH}_2\text{O})_x\text{O.CH}_2\text{CH}_2$ , from a solution ring-chain reaction at a polymer/solvent dilution ratio of 1/10, with zinc acetate as catalyst. The corresponding  $m/z$  values were determined using tandem mass spectrometry (see text)

observed (Figure 7). These corresponded to cyclic oligomers of PET containing ethylene glycol residues,  $(\text{CO.C}_6\text{H}_4.\text{CO.O.CH}_2.\text{CH}_2.\text{O})_x\text{CH}_2.\text{CH}_2.\text{O}$ , where  $x = 2-6$ . These cyclics have not been previously reported.

The molar masses of the two series of cyclic oligomers ( $M^+$ ) were determined by tandem mass spectrometry.

#### Conclusions

In this investigation we have described how the use of zinc acetate as a catalyst is effective in the formation of cyclic oligomers of PET. Furthermore by increasing the solvent dilution ratio, the solution ring-chain reaction favours the formation of the larger cyclic oligomers in good yield. In addition to the cyclic oligomers of PET, another series of cyclics has been identified.

Further investigations of cyclic oligomers of PET and other polyesters are in progress in our laboratory.

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