

polymer communications

Analysis of cyclic oligomers of poly(ethylene terephthalate) by liquid chromatography/mass spectrometry

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Cyclic oligomers $[\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}]_x$ (with $x = 3-8$) of poly(ethylene terephthalate) have been prepared by a polymer-supported reaction. They have been investigated by field desorption mass spectrometry and liquid chromatography/mass spectrometry. The particular stability of the cyclic trimer $x = 3$ is demonstrated by the results. © 1997 Elsevier Science Ltd.

(Keywords: cyclic oligomers; poly(ethylene terephthalate); mass spectrometry)

Introduction

Poly(ethylene terephthalate) (PET) with the repeat unit $[\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}]$ is a polymer with important commercial applications as synthetic fibres and plastics. Cooper and Semlyen^{1,2} reported the first successful gel permeation chromatographic analysis of the cyclic oligomers of PET $[\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}]_x$ with $x = 3-10$. They were obtained from ring-chain equilibration reactions.

In this communication, we report the field desorption mass spectra (f.d.-m.s.) and liquid chromatography/mass spectra (l.c.-m.s.) of individual cyclics of PET with $x = 3-8$ obtained by a polymer-supported reaction, which has already been described in detail for an aliphatic polyester system (poly(undecanoate))³⁻⁶. In addition, further structural information for the fragmentation of cyclic PET oligomers with $x = 3-6$ was obtained in a liquid chromatography/tandem mass spectrometry experiment (l.c.-m.s.-m.s.).

Experimental

Materials. Terephthalic acid mono 2-bromoethyl ester was reacted with the bicarbonate form of Amberlyst A-26 strong base anion exchange resin to give the polymer-supported carboxylate, as described in earlier papers³⁻⁶. The polymer-supported carboxylate was then heated in chloroform at reflux temperature for seven days. At the end of this period the resin beads were filtered off and washed with chloroform. The combined chloroform solutions were evaporated to dryness. The products obtained (polyester product yield 46%) were found by gel permeation chromatography and nuclear magnetic resonance spectrometry to be a mixture of cyclic oligomers and linear polymers. No attempt was made to purify the sample further, but the cyclic oligomers present were analysed by mass spectrometric methods as described here.

Spectrometric methods. Field desorption mass spectra (f.d.-m.s.) were obtained using a VG Analytical ZAB-2SE mass spectrometer of reverse geometry.

Liquid chromatography/mass spectra (l.c.-m.s. and l.c.-m.s.-m.s.) were obtained on a TSQ 7000 triple quadrupole mass spectrometer. The liquid chromatography conditions used were as follows:

- Column: Spherisorb S50DS2, 250 × 4.6 mm i.d.
- Column temperature: 40°C
- Mobile phase: A; acetonitrile, B; water
- Gradient:

Time (min)	%A	%B
0	40	60
15	100	0
20	100	0
21	40	60

- Injector volume: 5 µl
- Detector: u.v. at 240 nm
- Flow rate: 1.0 ml min⁻¹

Results and discussion

The products of the polymer-supported reaction were analysed by f.d.-m.s. The mass spectrum obtained (Figure 1) shows individual cyclic oligomers $[\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}]_x$ where $x = 3-8$, i.e. $M^+ = 576, 768, 960, 1152, 1345, 1537$ Da respectively. Each main spectral line is followed by two others corresponding to $(M + \text{Na})^+$ and $(M + \text{K})^+$.

The sample was then analysed by l.c.-m.s. Atmospheric pressure chemical ionization (APCI) in the presence of traces of ammonium ions was found to produce intense ammoniated molecular ions. Figure 2 shows the l.c.-m.s. spectrum with the individual mass chromatograms of the ammoniated cyclic PET oligomers from trimer to octamer with respect to the total ion chromatogram ($M + \text{NH}_4^+ = 594, 786, 978, 1171, 1363$ and 1555 Da).

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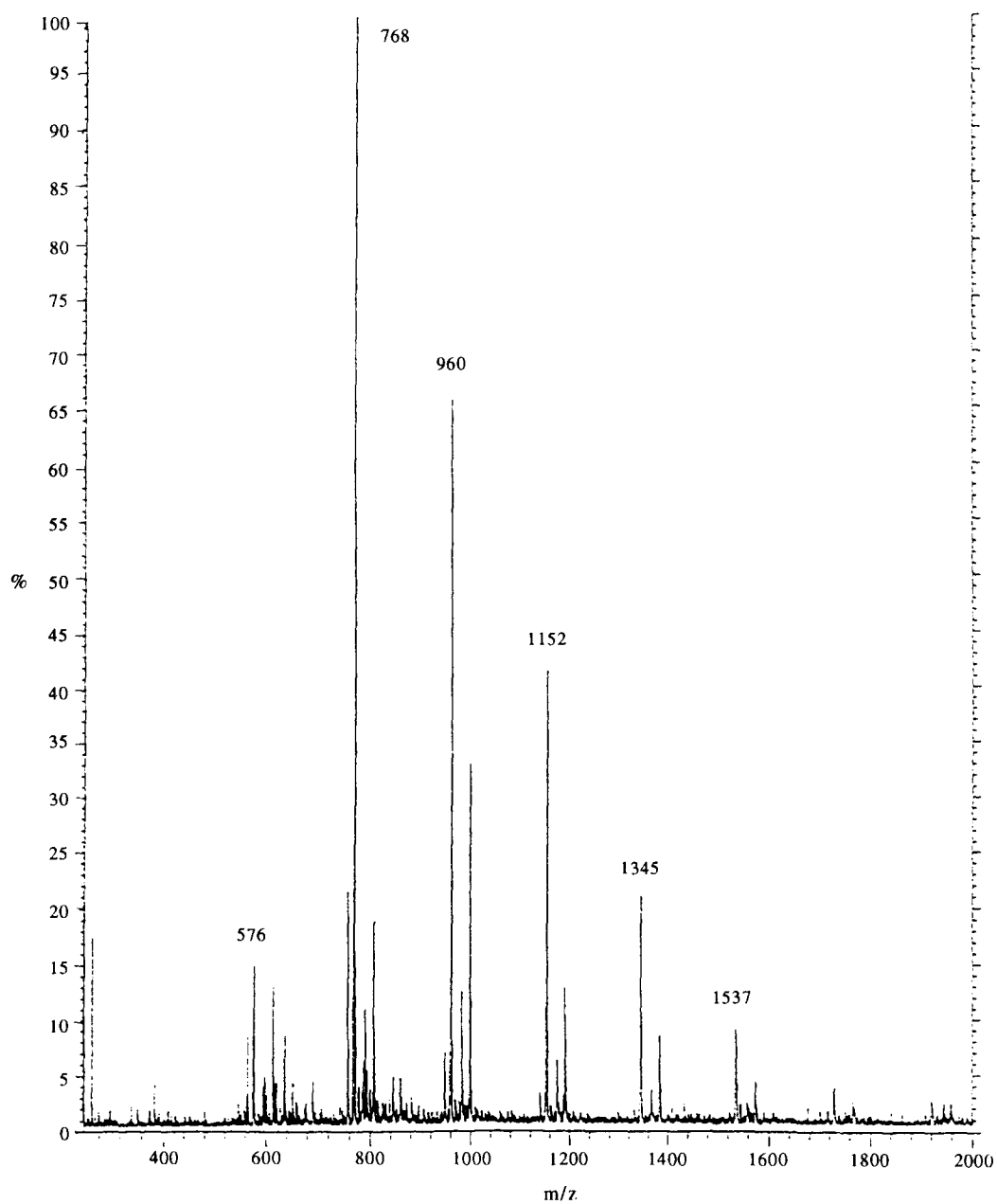


Figure 1 Field desorption mass spectrum of cyclic PET oligomers $[\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}]_x$ where $x = 3-8$

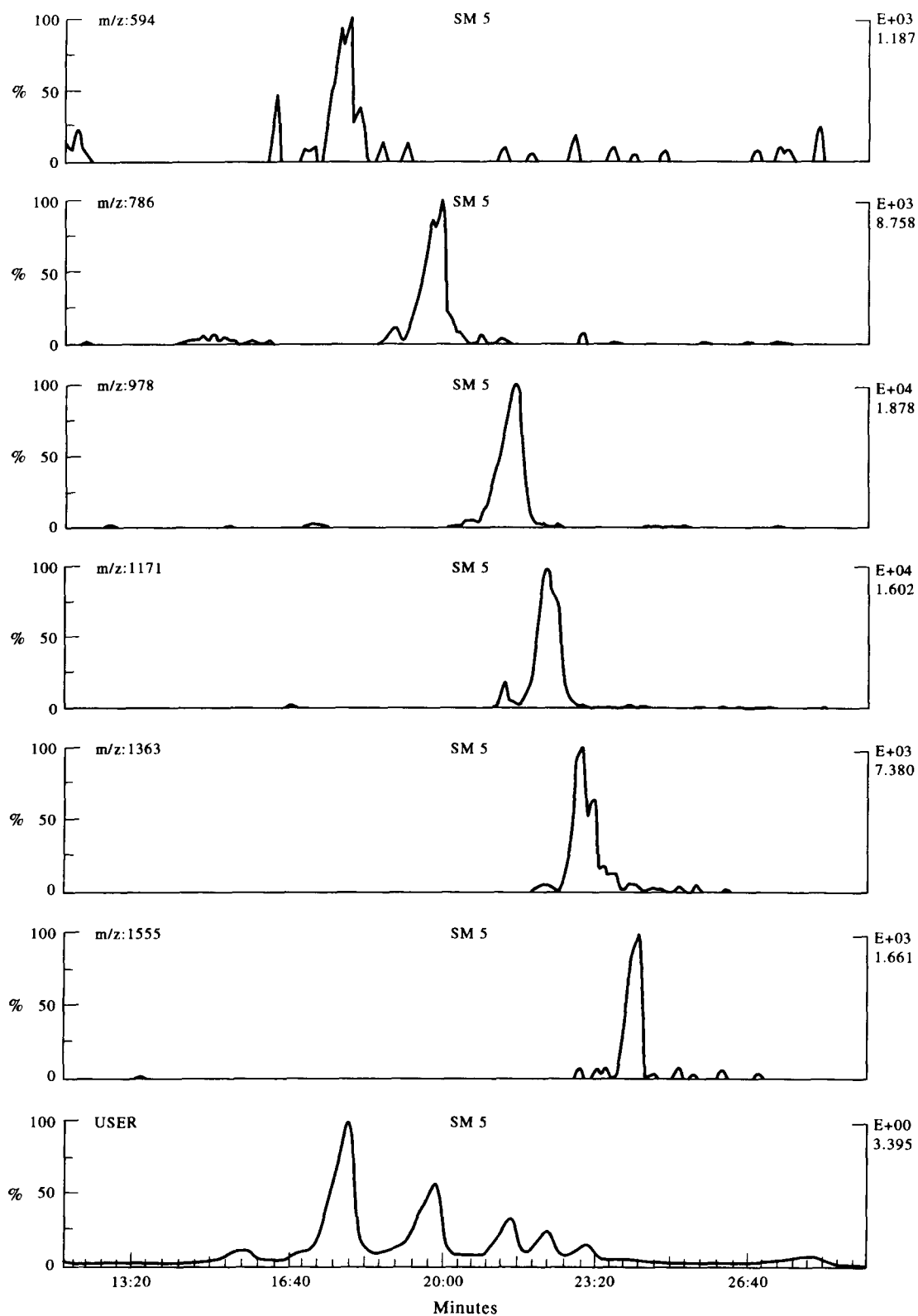


Figure 2 Liquid chromatography/mass spectrum of ammoniated cyclic PET oligomers $[\text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O}]_x$ where $x = 3-8$

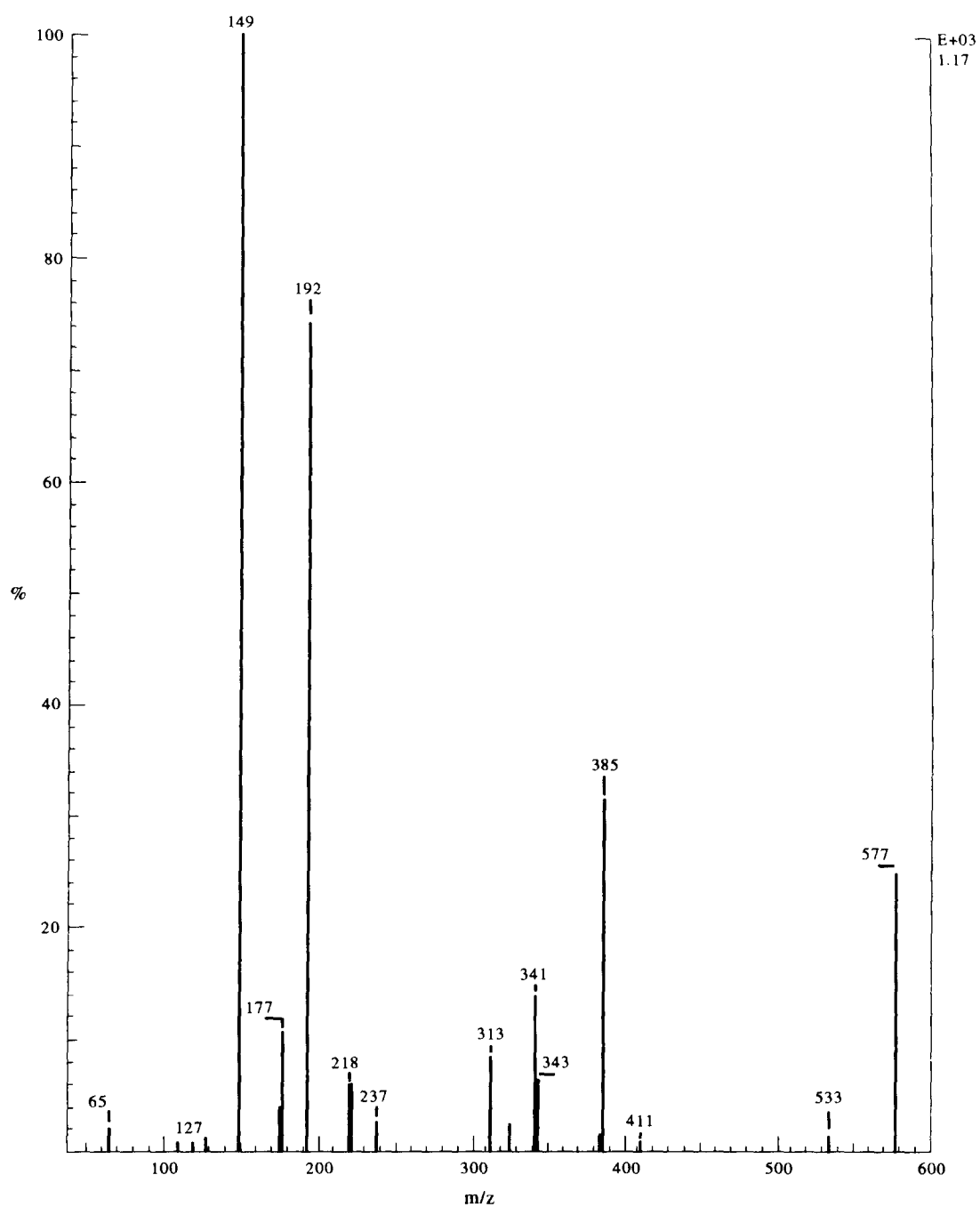


Figure 3 Mass spectrum of cyclic PET trimer

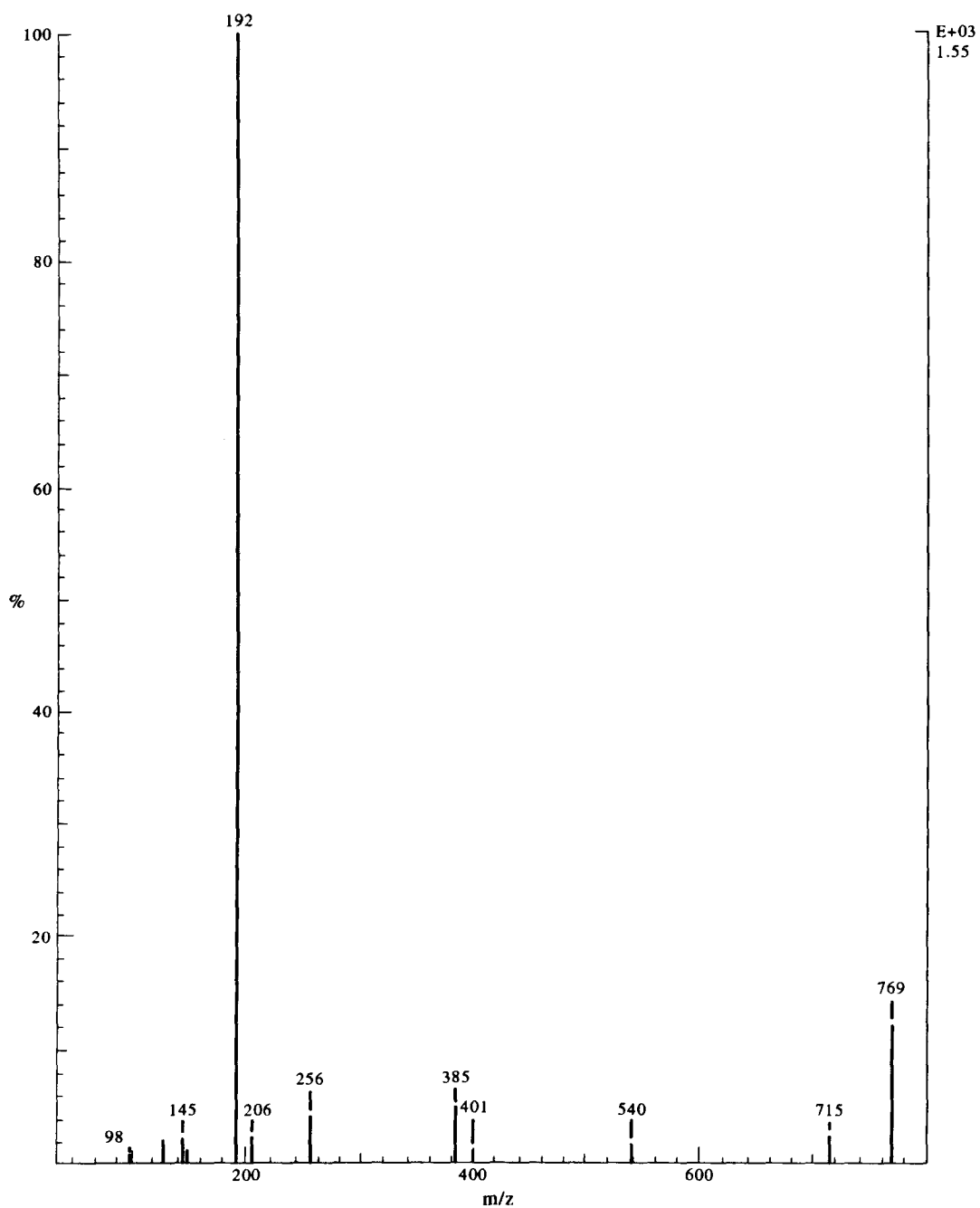


Figure 4 Mass spectrum of cyclic PET tetramer

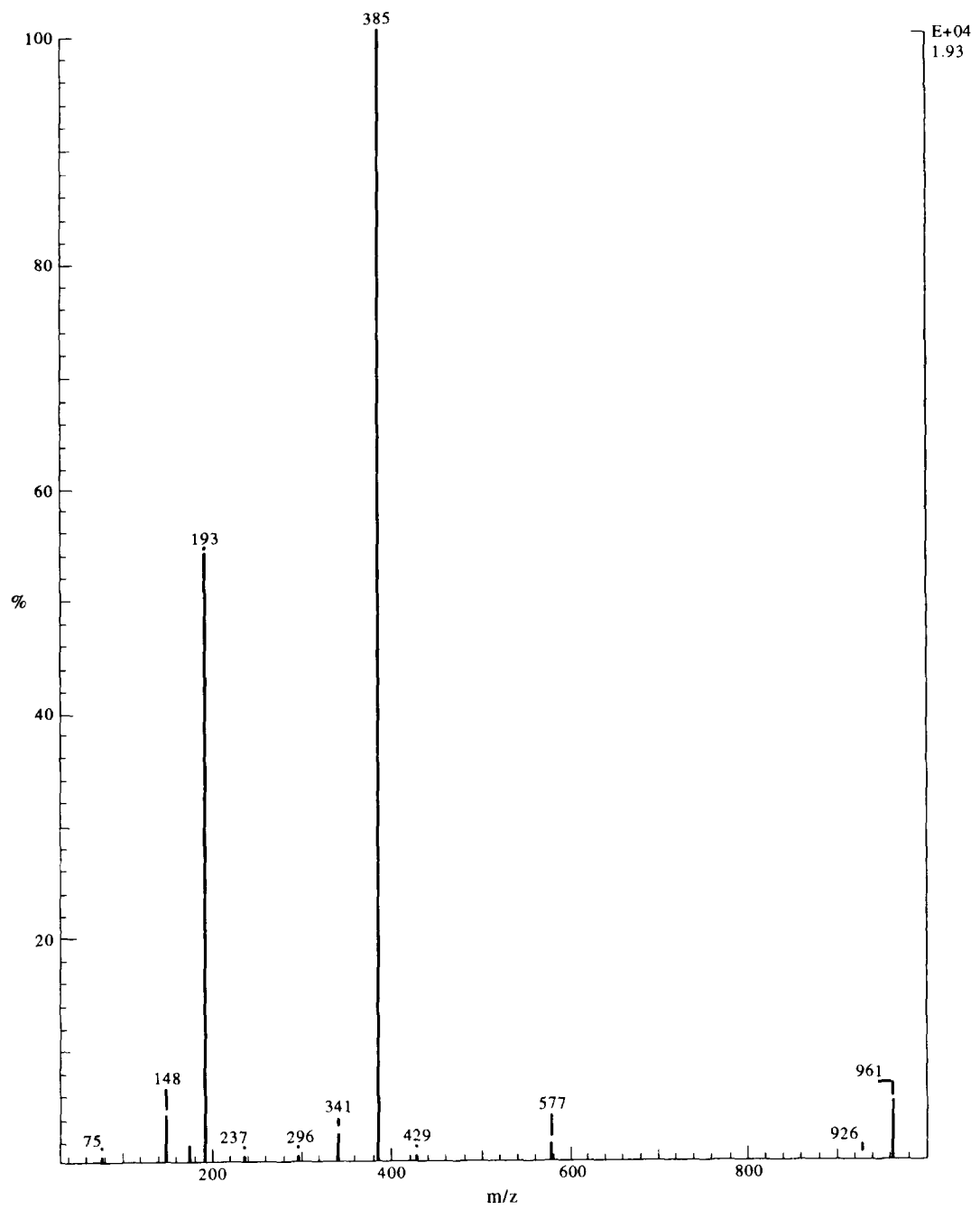


Figure 5 Mass spectrum of cyclic PET pentamer

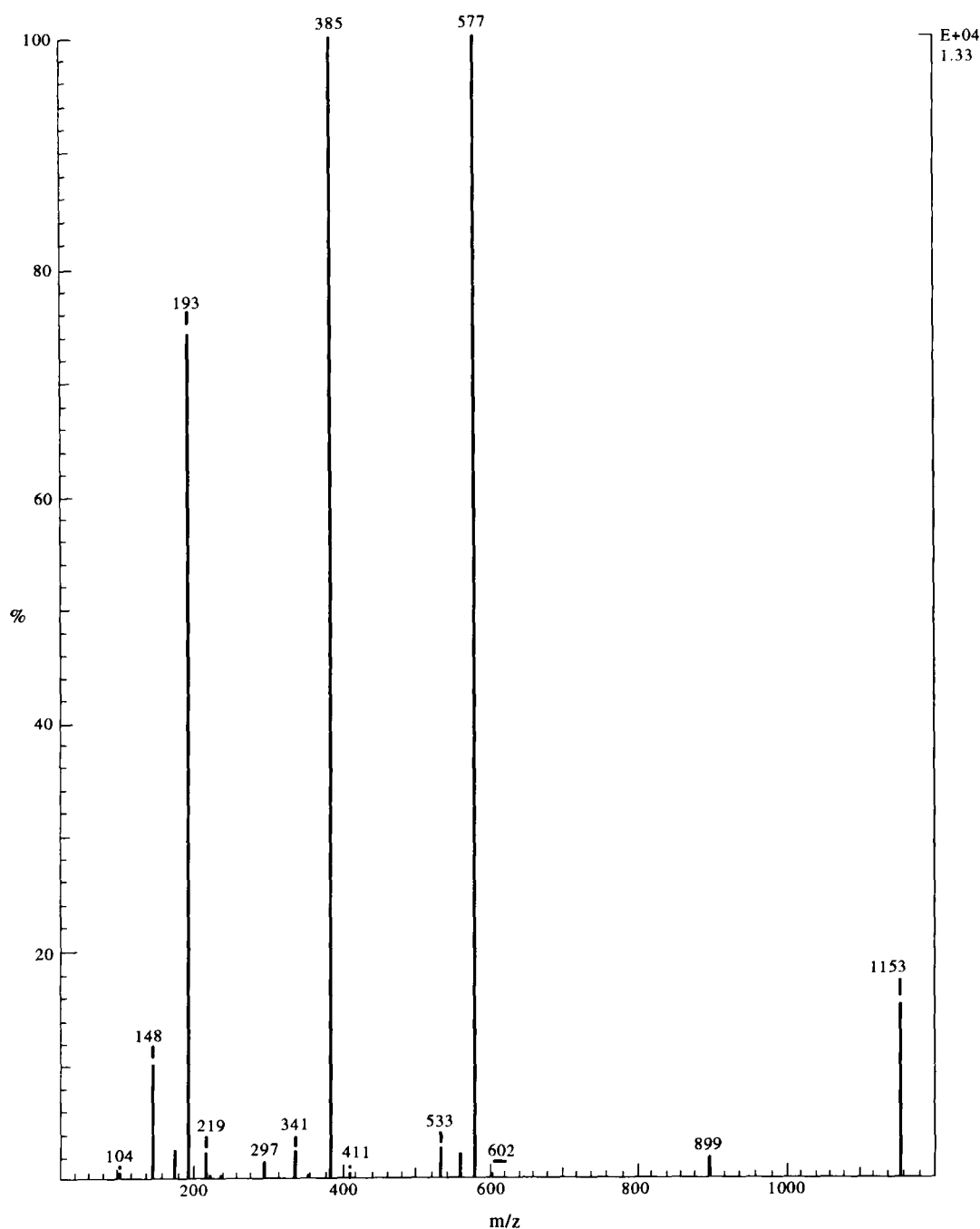


Figure 6 Mass spectrum of cyclic PET hexamer

To obtain additional structural information, the ammoniated cyclic PET oligomers with $x = 3-6$ were fragmented by 30 eV argon in the collision cell of the triple quadrupole, thus yielding m.s.-m.s. spectra. The resulting product ion spectra of cyclic PET trimer, tetramer, pentamer and hexamer are shown in Figures 3-6. A point to note is that a major loss of 576 Da is seen in the spectra of the tetramer and higher oligomers (i.e., 769 Da-192 Da, 961 Da-385 Da, 1153 Da-577 Da). This fragmentation is consistent with the loss of a neutral cyclic trimer species, suggesting a mechanism whereby a cyclic oligomer ion first ring-opens and then undergoes cyclodepolymerization by 'back-biting'.⁷ It provides further evidence for the particular stability of the cyclic PET trimer.⁸ Further investigations of cyclic oligomers and polymers of PET and other polyesters are in progress.

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