

20/1/91

Short Communication *262*

Identification of poly(ethylene terephthalate) cyclic oligomers by liquid chromatography-mass spectrometry

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ABSTRACT

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Plasmaspray liquid chromatography-mass spectrometry has been used to detect and identify cyclic oligomers, $(GT)_n$, in samples of poly(ethylene terephthalate). Operating the mass spectrometer at unusually high temperatures (370°C for the tip), the identity of the two main peaks, which were attributed to $(GT)_3$ and $(GT)_4$ on the basis of their UV absorption, could be confirmed by the m/z value of their molecular anions. The very poor results observed at lower temperatures exemplify the difficulty of vaporizing and ionizing these molecules.

INTRODUCTION

Poly(ethylene terephthalate) (PET) packaging materials may contain several monomers and low-molecular-weight polymers (oligomers) which are formed during the polymerization process. The use of PET as a food packaging material is expanding rapidly, especially for conventional or microwave heating and cooking, where PET is metallized with aluminium and bonded to a board surface to produce so-called 'active' packaging or 'susceptors'. Under these conditions temperatures over 200°C are reached, which may facilitate the migration of these chemicals into the packed food [1].

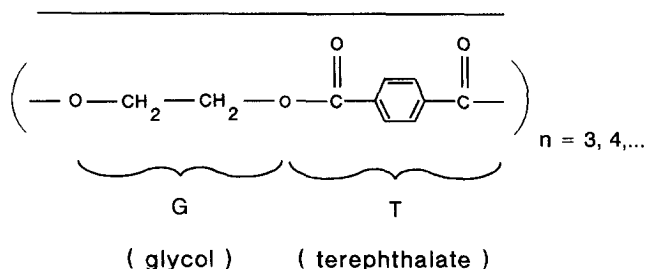


Fig. 1. General structure of the cyclic oligomers $(GT)_n$.

Quantitatively, the most important compounds are a homologous series of cyclic oligomers, $(\overline{GT})_n$ (Fig. 1), which have been isolated and characterized [2]. They can be easily separated by high-performance or thin-layer chromatography [3] but are difficult to synthesize. The migration of the oligomers has been analysed by determining dimethyl terephthalate by stable isotope dilution gas chromatography-mass spectrometry after hydrolysis to terephthalic acid and methylation, thus avoiding the need to ionize the oligomers themselves [1]. The formation of cyclic oligomers from PET has been studied by direct mass spectrometry either by heating the polymer in the ion source [4] or by pyrolysis [5]. However, a direct identification technique would be useful and liquid chromatography-mass spectrometry (LC-MS) should be the method of choice in spite of the difficulty of vaporizing and ionizing the molecules. In this study, LC-plasmaspray MS (LC-PSP-MS) was used to confirm the identity of the chromatographic peaks attributed to some of these compounds by providing information on their molecular weight.

EXPERIMENTAL

Extraction

A 300-mg amount of PET (obtained by delamination of a sample of Susceptor; Waddingtons Cartons, Leeds, UK) was dissolved in 30 ml of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) (Sigma, St. Louis, MO, USA)-dichloromethane (3:7). After precipitation of the polymer with 25 ml of acetone and centrifugation, the supernatant was evaporated and the pellet dissolved in 5 ml of N,N-dimethylacetamide (Eastman Chemical Products, Kingsport, TN, USA). Aliquots of 20 μ l of this solution were used for chromatographic separations.

Liquid chromatography

The LC system consisted of a Waters Assoc. (Milford, MA, USA) Model 600-MS pump, a U6K injector and a Nova-Pak C₁₈ column (15 cm \times 4.6 mm I.D.) packed with 4- μ m particles. The mobile phase was water-acetonitrile (2:1) adjusted to pH 3.5 with formic acid. The flow-rate was 2 ml/min.

Mass spectrometry

A Delsi Nermag (Argenteuil, France) Model R 10-10C quadrupole instrument was coupled to the LC system via a thermospray interface (Vestec, Houston, TX, USA) used in the plasmaspray (PSP) mode, *i.e.*, a discharge electrode (900 V, 10 kHz) was used to ionize the solutes and no salt was added to the mobile phase as in conventional thermospray operation.

The working temperatures were 370°C for the probe tip and 270°C for the ion-source block. A repeller electrode was set at -250 V. The mass spectrometer was operated in the negative-ion mode, scanning masses 100-800 u in 0.5 s. In some analyses, a UV detector (Spectroflow 773; Kratos, Manchester, UK) operated at 254 nm was used in place of the mass spectrometer.

RESULTS AND DISCUSSION

The UV trace obtained under the separation conditions used (Fig. 2A) is in full agreement with those usually obtained with this type of sample. By comparison with

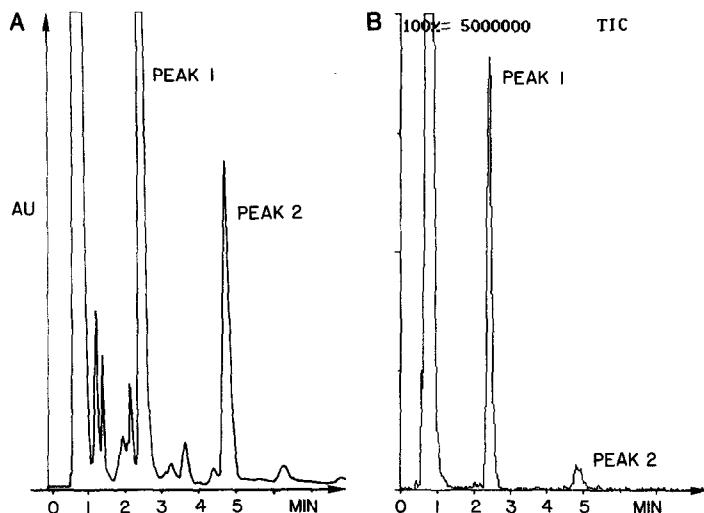


Fig. 2. (A) UV trace (254 nm) of a PET extract sample. (B) LC-PSP-MS TIC recording of the same sample under the same conditions (see text). Peaks 1 and 2 were identified by their retention times.

the published literature, peaks 1 and 2 can be tentatively attributed to $(\overline{GT})_3$ and $(\overline{GT})_4$, respectively. Fig. 2B shows the reconstructed total ion current (TIC) trace of an aliquot of the same sample.

The mass spectra for peaks 1 and 2 are shown in Fig. 3. In each spectrum, only one main ion is observable, probably the molecular anion. In fact their m/z values, 576 and 768, respectively, correspond to the molecular weight of each oligomer and the chromatographic peaks can be attributed to $(\overline{GT})_3$ and $(\overline{GT})_4$ with high probability.

The full UV trace of the sample (not shown) shows a series of at least five compounds. They all have identical UV absorption spectra, indicating high structural similarity and that they probably belong to the series $(\overline{GT})_n$ where $n=3-7$. At the time these experiments were done, the calibrated mass range of the mass spectrometer did not allow the detection of masses higher than 800. In spite of this, the tip and source temperatures necessary to observe oligomers higher than $n=4$ would have been very difficult to reach.

The probe tip temperature used here was 370°C , which is unusually high for LC-thermospray MS operation. At a lower temperature of 290°C , which is already in the upper range of those commonly used, the analysis was much worse. This is shown in Fig. 4, which presents the TLC trace and the m/z 576 and 768 ion current recordings. There, the presence of peak 2 can only be guessed and the shape of the peaks and the abundance of the fragments are really unsatisfactory. Evidently, this type of cyclic molecule with no polar function is difficult to vaporize and ionize. In fact, preliminary experiments showed that by using conventional thermospray conditions (no discharge and 0.1 M ammonium acetate added to the mobile phase) no signal corresponding to the oligomers could be observed.

Mass spectra of these oligomers have been obtained by heating PET in the ion

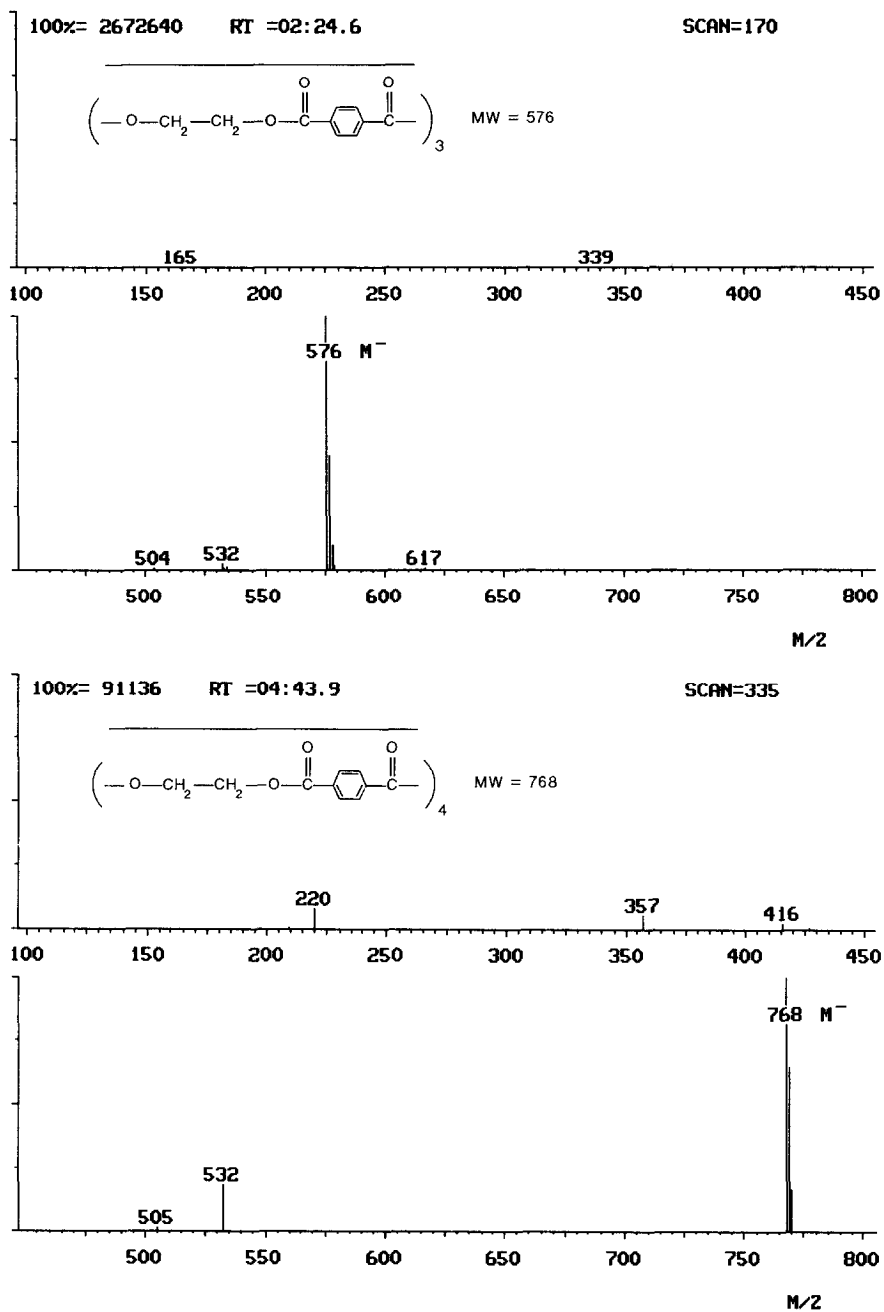


Fig. 3. Mass spectra for peaks 1 and 2 and probable structure of the main fragments. RT = Retention time in min:s; MW = molecular weight.

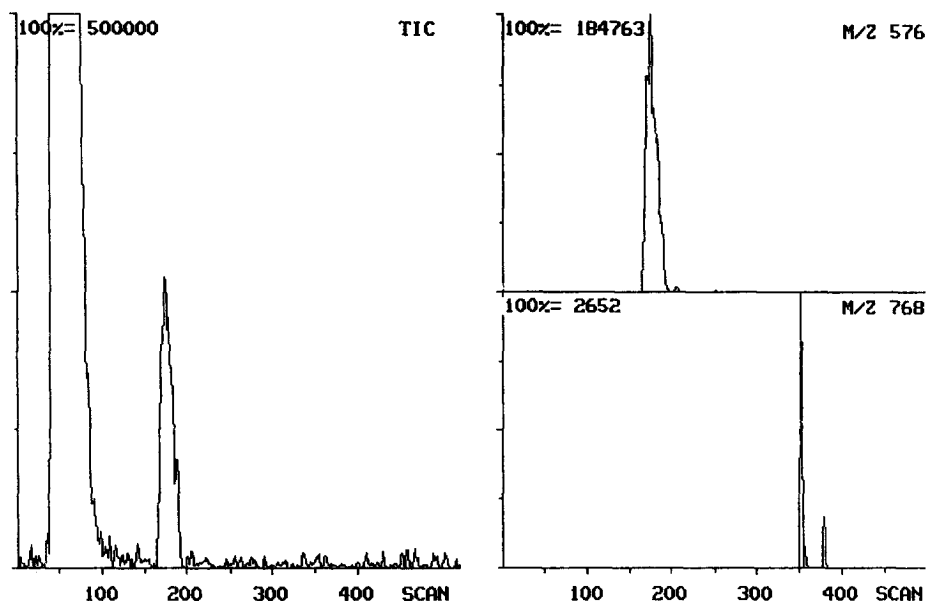


Fig. 4. LC-PSP-MS TIC and m/z 576 and 768 recordings of the same sample at a tip temperature of 290°C. Note the poor shape of the peaks and the very low abundance of m/z 768.

source [4] or in a pyrolysis probe [5]. The aim of these studies was to investigate the formation of oligomers by thermal degradation and temperatures up to 400°C were used. The electron impact mass spectrum of $(\overline{GT})_3$ contains an intense fragment ion at m/z 533 [4] and the negative-ion chemical ionization mass spectrum of a mixture of the cyclic oligomers contains intense ions at m/z 768, 576 and 532 [5], thus providing further support that peaks 1 and 2 in our study do correspond to $(\overline{GT})_3$ and $(\overline{GT})_4$.

ACKNOWLEDGEMENTS

The author acknowledges the contribution of J. Ruiz to the chromatographic separations and his skillful technical assistance and also the help of E. Castella.

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