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Qualitative liquid chromatographic–atmospheric-pressure chemical-ionisation mass spectrometric analysis of polyethylene terephthalate oligomers

Karen A. Barnes, Andrew P. Damant, James R. Startin, Laurence Castle*

Ministry of Agriculture Fisheries and Food, CSL Food Science Laboratory, Norwich Research Park, Colney, Norwich NR4 7UQ, UK

Abstract

The oligomeric fraction of polyethylene terephthalate (PET) has been studied as it has the potential to migrate to foods and beverages packaged in virgin and recovered PET plastics. We have applied positive ion atmospheric-pressure chemical ionisation (APCI) to extracts of food-grade PET resin and beverage bottles. A reversed-phase HPLC system was connected directly to a VG Platform mass spectrometer. An acetonitrile–water–acetic acid gradient elution was performed. Low APCI probe temperatures (as appropriate for a polyethylene glycol calibrant) produced no significant ions from a PET cyclic trimer standard. A high probe temperature of 500–600°C gave a strong protonated molecular ion.

Characteristic spectra of the cyclic oligomers from the trimer to the heptamer were obtained. A second homologous series of substances 44 mass units higher than each PET oligomer eluted prior to each PET oligomer. The mass spectra indicated these to be oligomers with one monoethylene glycol unit replaced by a diethylene glycol unit. To our knowledge this is the first time that cyclic oligomers above the tetramer have been confirmed by LC–MS. The technique was considerably more sensitive than published thermospray methods and gave good spectra with sub-microgram quantities injected. This work demonstrates the advantages of APCI over thermospray as an MS technique for substances of this type.

1. Introduction

The plastic polyethylene terephthalate (PET) is widely used for food packaging. It has excellent heat stability allowing its use in microwave and conventional oven applications as films and containers. It also has good gas barrier properties and is widely used for carbonated drinks bottles. PET is a candidate material for plastics recovery and schemes for chemical and physical recovery along with straightforward re-use (refilling) are either in use to a limited extent or are under consideration [1,2].

One factor in assessing the suitability of PET in these applications is the question of chemical migration. PET is relatively free of additives and adventitious low-molecular mass impurities, and so has intrinsic low migration characteristics [3]. It is known to contain small amounts of low-molecular-mass oligomers [4]. APCI is a gas-phase ion-molecule reaction process which leads to the ionisation of analyte molecules under atmospheric pressure conditions. The process is analogous to chemical ionisation but the reactant

* Corresponding author.

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ions are produced from the effect of a corona discharge on a nebulised aerosol of solvent. Due to the atmospheric pressure conditions the high frequency of analyte/reactant ion collisions ensures a high sample ionisation efficiency. A "soft" ionisation results in predominantly protonated molecular ions $[M + H]^+$ in the positive-ion mode or deprotonated molecular ions $[M - H]^-$ in the negative-ion mode [5]. The purpose of this work was to develop a sensitive LC–APCI-MS method of analysis for these oligomers so that their chemical migration from virgin and recycled PET could be measured in the future.

2. Experimental

2.1. Materials

PET bottles (suitable for carbonated soft drinks), bottle pre-forms and PET resin were obtained from manufacturers during April 1994. A standard of PET cyclic trimer was prepared in house [3] and judged to be ca. 90% pure by ^1H NMR analysis.

2.2. Sample preparation

A portion (0.1 g) of polymer was dissolved in a mixture of dichloromethane and hexafluoro-2-propanol (7:3, v/v, 10 ml) and then acetone (8 ml) was added slowly to precipitate the high-molecular-mass polymer. The sample was filtered (pore size 4 μm), concentrated to almost dryness under a stream of nitrogen, and the residue dissolved in dimethylacetamide (2.0 ml).

2.3. Analysis by LC–APCI-MS

Liquid chromatography–atmospheric-pressure chemical-ionisation mass spectrometry (LC–APCI-MS) analysis was performed using a Lichrosorb RP8 (100 × 3 mm I.D.) column (Chrompack, Millharbour, UK) fitted with a 0.5-μm pre-column filter. The mobile phase was an acetonitrile–water–acetic acid linear gradient: solvent A, 15:85:0.25; solvent B, 85:15:0.25 (v/v). At time 0, 8, 16, 17, 30, 31 min the percentage solvent B was 4.3, 50, 60, 85, 85, 4.3, respectively.

The mobile phase was delivered at 0.6 ml/min by a Spectra-Physics SP8800-020 tertiary pump (San-Jose, CA, USA). Injections (50 μl) were made using a Gilson 231XL autosampler (Villiers-le-Bel, France) fitted with a 200 μl Rheodyne loop. A Spectroflow 757 UV detector set at 254 nm (Kratos, Manchester, UK) was connected in series between the HPLC system and the mass spectrometer. The time axis of the UV analog trace was adjusted to allow for the delay between the two detectors in series.

The VG Platform "Classic" benchtop mass spectrometer (Fisons Instruments, Manchester, UK) was operated in the positive-ion atmospheric-pressure chemical-ionisation mode. The instrument was initially tuned on the mobile phase background ions. Tuning was then optimised on a PET cyclic timer standard (2 mg/ml in acetonitrile) injected directly via a 500 μl Rheodyne loop. Typical tuning parameters were as follows: corona 3.22 kV, high voltage lens 0 kV, extraction 20 V, focus 25 V, source temperature 120°C, APCI probe temperature 600°C, low mass resolution 14.3, high mass resolution 14.9, ion energy 0.9 V, ion energy ramp 0 and multiplier 650. The instrument was calibrated over a mass range 50–1800 using a mixture of polyethylene glycol (PEG) 300, 600, 1000 and 1540, at a scan time of 5 s.

3. Results

3.1. Optimisation of LC–APCI-MS conditions

Initial calibration and tuning of the VG Platform was carried out at low APCI probe temperatures most suited to the PEG calibrant. At these low temperatures, flow injection of the PET trimer standard produced no significant ions and this prevented optimisation of the instrument. A change of mobile phase to methanol gave a sufficiently strong protonated molecular ion for tuning purposes, as a result of which it was discovered that a probe temperature in the range 500–600°C gave maximum sensitivity. A

temperature at the high end of this range i.e. at 600°C was selected. A return to the original mobile phase (acetonitrile–water–acetic acid) also gave a strong protonated molecular ion at this high probe temperature. The temperature profile for the PET trimer is shown in Fig. 1.

3.2. Chromatograms

Figs. 2 and 3 show the UV and total-ion chromatogram (TIC) obtained for a PET extract. The UV trace showed the characteristic profile reported earlier [6,7] for the cyclic trimer followed by decreasing amounts of the tetramer through to the octamer. Comparison of Figs. 2 and 3 show the TIC trace to be considerably inferior to the detection by UV. In contrast, Fig. 4 shows the reconstructed ion chromatograms for the protonated molecular ions of the PET cyclic trimer, tetramer, pentamer, hexamer and heptamer where the oligomers can be clearly observed. It was noted that each cyclic oligomer was preceded by a second, smaller peak giving rise to a second series of oligomers of 44 mass units higher than the first. This series is also shown in Fig. 4. Diode-array analysis showed that all the peaks had a very similar absorption spectrum indicating a common chromophore (data not shown).

3.3. Mass Spectra

Spectra for the PET cyclic trimer through to the heptamer are shown in Fig. 5. Spectra for the corresponding LC peaks for the second oligomer series are shown in Fig. 6. Fig. 5 shows clearly the expected series of cyclic PET oligomers and Fig. 6 shows the homologous series at 44 mass units higher. Ions at m/z 193 and 385 can be seen in many of the spectra and these are attributed to the protonated PET base unit (the $n = 1$ "monomer") and dimer, respectively.

4. Discussion

4.1. PET cyclic oligomer series

As a polyester of terephthalic acid (TPA) and monoethylene glycol (MEG), the main oligomer fraction extracted from food grade PET is expected to be the series $[TPA]_m[MEG]_n$. The cyclic oligomers (where $m = n$) predominate [7]. There are two commercially important routes to

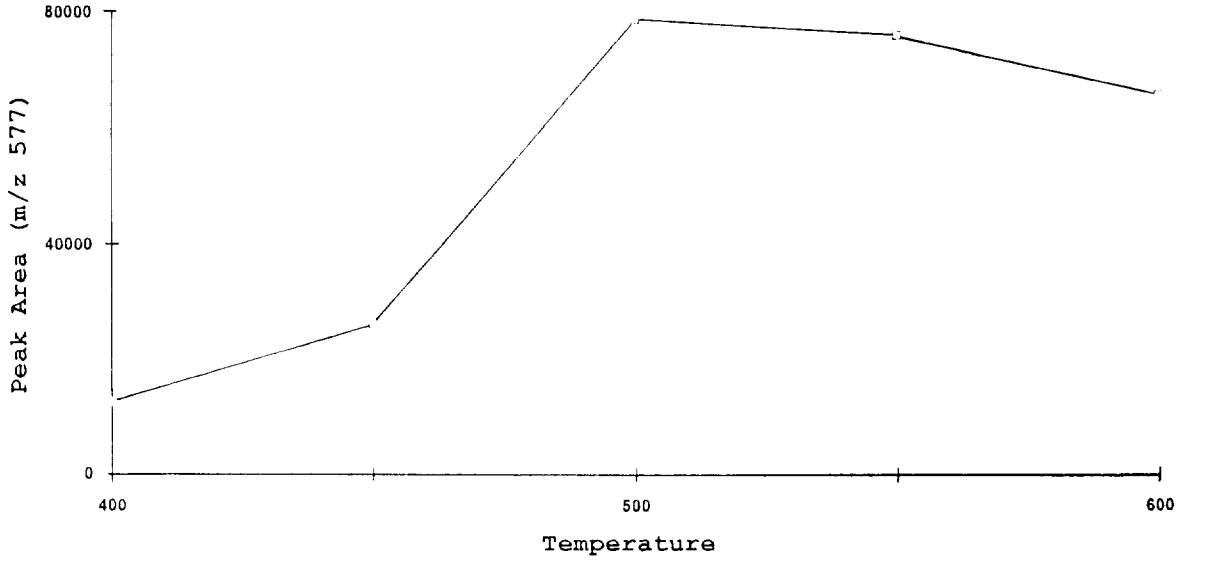

Fig. 1. Effect of APCI probe temperature on ion sensitivity: x-axis: probe temperature (°C), y-axis: peak area for m/z 577 for constant mass of PET cyclic trimer flow injected.

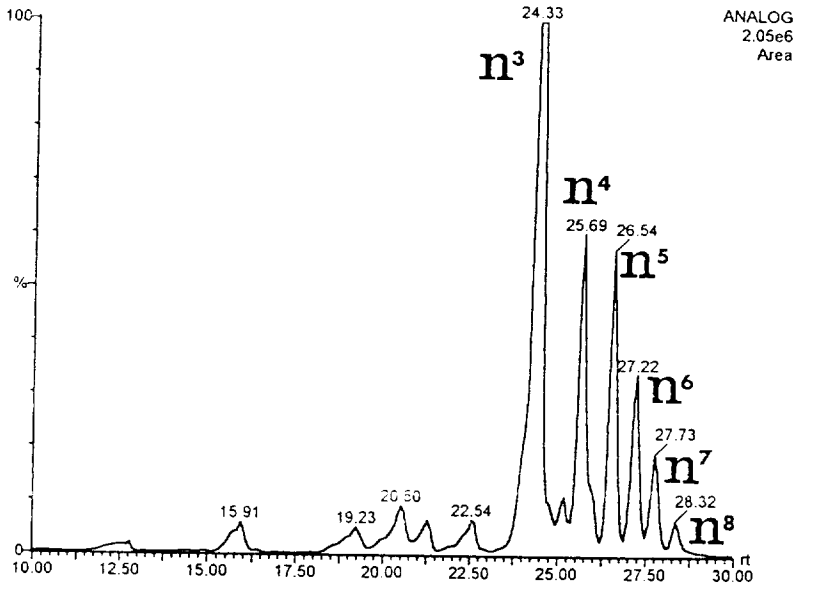

Fig. 2. LC–UV trace for PET extract; *x*-axis: retention time (min); *y*-axis: UV response at 254 nm. Peak assignment cyclic PET oligomers: n^3 = trimer, n^4 = tetramer, n^5 = pentamer, n^6 = hexamer, n^7 = heptamer, n^8 = octamer.

PET [1]. One involves the direct esterification of terephthalic acid with ethylene glycol to form a mixture comprising largely of the intermediate monomer bis(2-hydroxyethyl) terephthalate (BHET) and its linear oligomers. The alternative route starts at dimethyl terephthalate and uses transesterification with MEG to form BHET. Both routes then form PET by prepolymerisation and polycondensation of the BHET reaction mass.

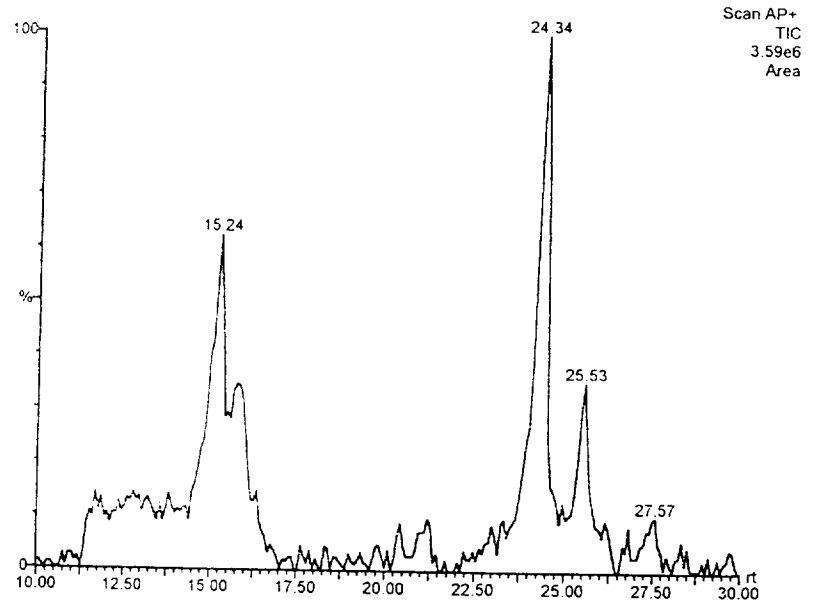

Fig. 3. LC–APCI-MS TIC chromatogram for PET extract; *x*-axis: retention time (min); *y*-axis: total ion current (normalised).

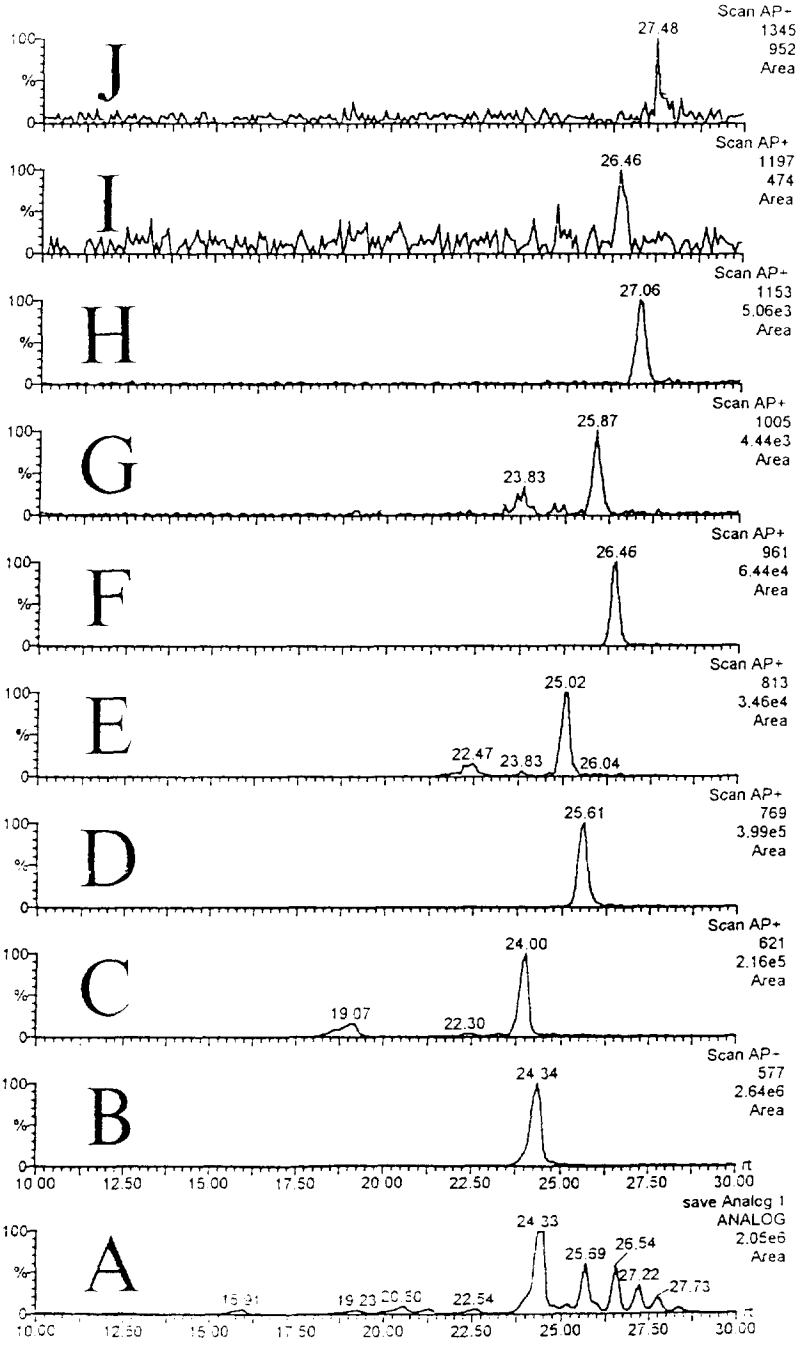

Fig. 4. LC–APCI-MS SIM traces for PET extract; *x*-axis: retention time (min), *y*-axis: selected ion intensity (reconstructed and normalised). (A) Analog trace at 254 nm, (B) cyclic trimer at *m/z* 577, (C) DEG-trimer at 621, (D) tetramer at 769, (E) DEG-tetramer at 813, (F) pentamer at 961, (G) DEG-pentamer at 1005, (H) hexamer at 1153, (I) DEG-hexamer at 1197, (J) heptamer at 1345 (for formula see Table 1).

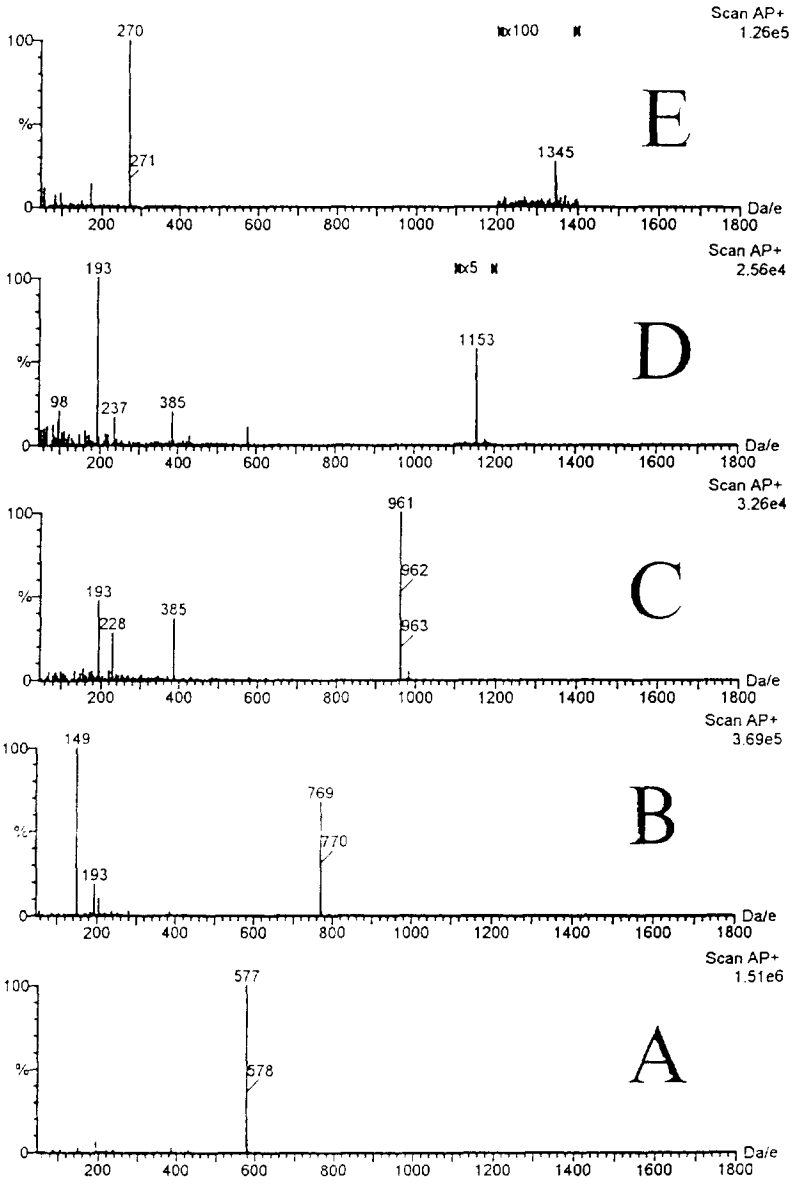

Fig. 5. LC–APCI-MS spectra for cyclic PET oligomers; *x*-axis: *m/z* ratio; *y*-axis: ion intensity (normalised, note that magnification has been used at the top end of the spectra for the weaker, high-molecular-mass, substances). (A) Trimer, (B) tetramer, (C) pentamer, (D) hexamer, (E) heptamer.

In the solid state polycondensation process, PET is heated above its glass transition temperature but below its crystalline melting point, in an inert atmosphere or in vacuo to increase the molecular mass of the polymer [8]. This process does not remove entirely the low-molecular-mass oligomers, however, since the molecular mass distribution for condensation polymers is characterised by the most probable distribution. The equilibrium distribution is reached by ester interchange reactions which can be quite rapid in the melt, with equilibrium reached within 10 min [9]. Thus, there is always a fraction of low-molecular-mass oligomers present.

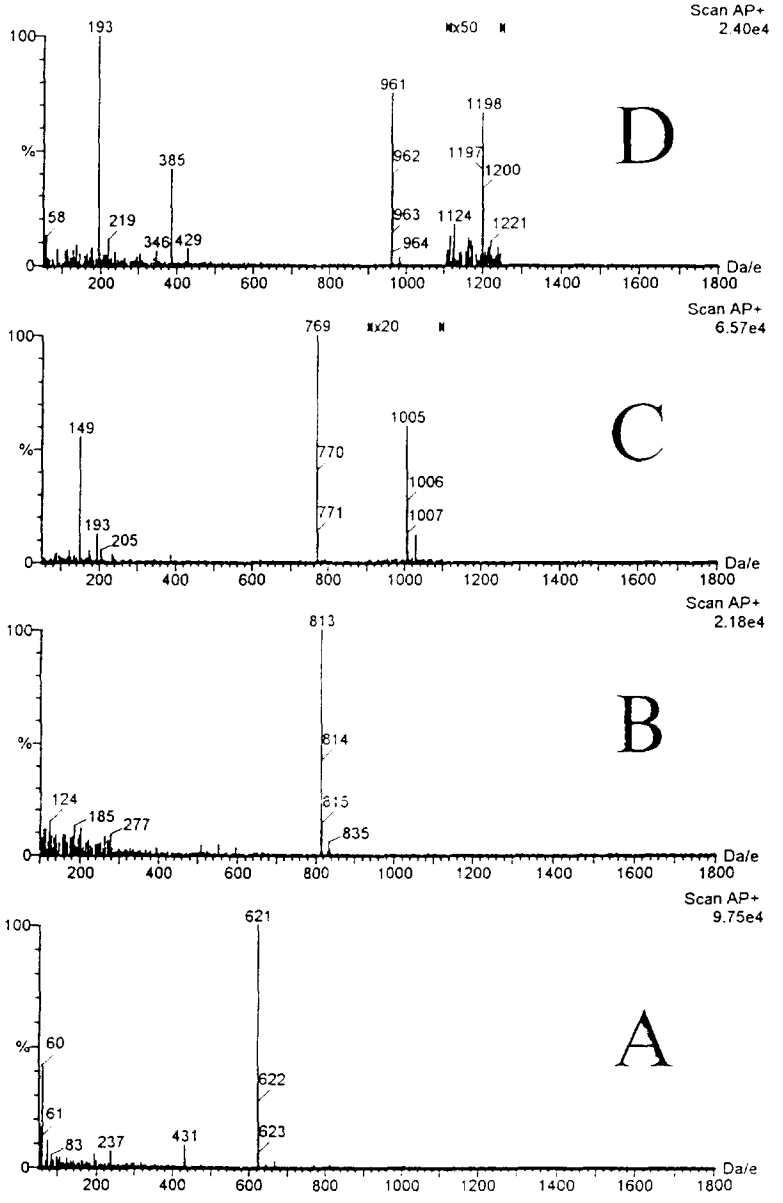

Fig. 6. LC–APCI-MS spectra for cyclic DEG-PET oligomers; *x*-axis: *m/z* ratio; *y*-axis: ion intensity (normalised, magnification used, see legend Fig. 5). (A) Trimer, (B) tetramer, (C) pentamer, (D) hexamer.

The MS results agree with the expectations above and confirmed that the main extractable fraction from PET comprised the cyclic oligomers. LC–APCI-MS analysis resulted in tentative molecular masses for the peaks present in Fig. 4 and these masses along with the oligomer formulae are given in Table 1. Characteristic spectra of the cyclic oligomers from the trimer to the heptamer were obtained (Fig. 5).

4.2. Identity of the second oligomer series

A second homologous series of substances 44 mass units higher than each PET oligomer was

Table 1
PET cyclic oligomer series

Oligomer	Formula ($+H^+$)	Protonated molecular mass
PET oligomers		
$[TPA]_3[MEG]_3$	$C_{30}H_{25}O_{12}$	577.13
$[TPA]_4[MEG]_4$	$C_{40}H_{33}O_{16}$	769.17
$[TPA]_5[MEG]_5$	$C_{50}H_{41}O_{20}$	961.21
$[TPA]_6[MEG]_6$	$C_{60}H_{49}O_{24}$	1153.25
$[TPA]_7[MEG]_7$	$C_{70}H_{57}O_{28}$	1345.30
Second oligomer series with one DEG in place of MEG		
$[TPA]_3[MEG]_2[DEG]_1$	$C_{32}H_{29}O_{13}$	621.12
$[TPA]_4[MEG]_3[DEG]_1$	$C_{42}H_{37}O_{17}$	813.23
$[TPA]_5[MEG]_4[DEG]_1$	$C_{52}H_{45}O_{21}$	1005.24
$[TPA]_6[MEG]_5[DEG]_1$	$C_{62}H_{53}O_{25}$	1197.23

observed eluting prior to each oligomer. It is postulated (Table 1) that these are substances similar to the oligomers but with one MEG unit replaced by a diethylene glycol (DEG) unit. These results confirm those reported in the literature [7,10] where the secondary series of peaks was suspected of being cyclic oligomer ethers. The high temperature and acid conditions of PET polymerisation can cause the formation of traces of diethylene glycol from MEG – a process of etherification with elimination of water from two MEG molecules [8]. As a diol, DEG is capable of participating in the polymerisation process and so is incorporated into oligomer and polymer chains. The formation of DEG is closely controlled since it can have adverse effects on the chemical stability and physical properties of the polymer [8]. A typical DEG content would be quite low at 1–2% by mass of polymer [1] and this is the reason why the second oligomer series (with DEG incorporated) is relatively minor. Statistically, the likelihood of replacing 2 MEG units with DEG is very small and the failure to detect a third oligomer series is not unexpected.

4.3. Advantages of LC–APCI-MS

There are very few published papers dealing with LC–MS analysis of PET oligomers and reaction by-products. Milon [10] extracted the PET film from a microwave susceptor and analysed the extract by plasmaspray LC–MS in the negative-ion mode using acetonitrile with formic acid as the mobile phase. Milon observed that an unusually high probe tip temperature of 370°C was required and could only confirm the cyclic trimer and tetramer. The tetramer gave a poor peak shape and low ion abundance. There was a severe loss of sensitivity at the lower tip temperature of 290°C and the cyclic tetramer was then not observed. In the TIC mode the LC–MS procedure [10] was at least 10-times less sensitive than LC–UV and this agrees with the findings here.

More recently, Guarini et al. [11] examined depolymerisation reaction mixtures obtained by the glycolysis of PET, again using negative-ion thermospray. With acetonitrile and ammonium acetate as mobile phase, they observed negative-ion mass spectra with ions from both electron attachment and acetate attachment. The sensitivity was not changed on varying the source temperature between 150 and 200°C – although higher temperatures led to reduced sensitivity. The authors reported that the TIC was noisy due to high intensity background ions and sensitivity was poorer than with the UV detector. In the SIM mode, sensitivity was comparable with that of the UV detector. Mass spectra of oligomers larger than the linear $TPA_2MEG_2DEG_1$ were too weak for unambiguous interpretation. Sensitivity was improved by the reaction of terminal hydroxyl groups with perfluoroanhydrides and

oligomers up to the linear tetramer were observed for derivatised samples with good full-scan spectra obtained for 50 μg of glycolysis mixture injected.

In comparison, the work reported here observed cyclic PET oligomers up to the heptamer plus a minor series of related cyclic oligomers. To the authors knowledge, this is the first time that PET oligomers above the cyclic tetramer have been confirmed by positive-ion LC–MS. On the question of sensitivity, the SIM chromatograms and spectra shown in Figs. 4 and 5 correspond to 25 μg (trimer) down to 0.6 μg (heptamer) injected. The advantages of LC–APCI-MS as an MS techniques over thermospray are therefore clearly demonstrated.

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