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Application of liquid chromatography–thermospray mass spectrometry to the analysis of polyester oligomers

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ABSTRACT

The products obtained by depolymerization of poly(ethylene terephthalate) (PET) with ethylene glycol were characterized by liquid chromatography–thermospray mass spectrometry (LC–TSP-MS). Discharge ionization produced intense negative ion mass spectra containing both acetate attachment and radical molecular anions of PET oligomers. Both full-scan and multiple ion detection modes were evaluated for the structural identification of the LC peaks. Improved performance of the LC–TSP-MS analysis could be obtained by derivatization of the depolymerization mixture with perfluoroanhydrides. This approach gave rise to a tenfold decrease in detection limits and allowed the identification of several additional components of the mixture. Major constituents of the glycolysis mixture were found to be linear and cyclic PET oligomers, diethylene glycol-containing oligomers and monoacetyl derivatives of linear oligomers.

INTRODUCTION

Recycling of plastics is a topic of growing interest, particularly with regard to poly(ethylene terephthalate) (PET) [1–3]. The recycling route consisting in depolymerizing PET from post-consumer soft drink bottles and re-using the so-formed monomer for making new polyester resin is attracting the attention of various chemical companies.

PET bottle scraps may be depolymerized by reaction with either methanol [4] or ethylene glycol (the latter process is referred to as glycolysis in the remainder of the paper) [3,5]. The latter is based on the process depicted in reaction 1. PET reacts with excess of ethylene glycol (EG) in the presence of an alkali or transition metal acetate as the catalyst to give bis(2-hydroxyethyl) terephthalate and homologous oligomers [5]. Among other by products are ethers (mainly diethylene glycol and its terephthalate ester) and cyclic oligomers (macrocyclic esters made up of ethylene terephthalate units) [3].

$$\text{PET} + \text{EG} \rightarrow \underset{M_1}{\text{H–ETE–H}} + \underset{M_2}{\text{H–ETETE–H}} + \underset{M_3}{\text{H–ETETETE–H}} + \ldots \quad (1)$$

where PET = $-(OC-C_6H_4-COO-CH_2CH_2O)_n-$, EG = $HOCH_2CH_2OH$, T = $-CO-C_6H_4-CO-$ and E = $-OCH_2CH_2O-$.

The simplest technique for the quantitative analysis of the mixture of glycolysis products of PET is reversed-phase HPLC with UV detection. However, the structural identification of all the LC peaks requires the employment of a more specific detector. Mass spectrometry has already been applied to the direct characterization of PET and related cyclic oligomers. Polyester oligomers in general have been analysed by fast atom bombardment mass spectrometry (MS)

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[6,7]. Electron impact or negative-ion chemical ionization have been used for the PET polymer (pyrolysis–MS) [8] or its cyclic oligomers [9]. Recently, the use of liquid chromatography–mass spectrometry (LC–MS) with a plasmaspray interface has been reported for the analysis of PET cyclic oligomers [10].

This paper describes the characterization of the glycolysis products of PET by means of LC–MS. The methods we have developed are based on the use of thermospray (TSP) as the LC–MS interface. The performances of both full-scan and multiple ion detection (MID) modes were evaluated. In order to enhance the sensitivity we also investigated the use of a suitable derivatization procedure for the PET glycolysis products with perfluoroanhydrides.

EXPERIMENTAL

Depolymerization of PET

A 96.0-g amount of PET bottle scraps and 124 g of ethylene glycol were refluxed for 6 h in the presence of 0.48 g of $Mn(AcO)_4 \cdot 4H_2O$. The reaction mixture was poured into 1 l of hot distilled water. The suspension was cooled to room temperature and filtered, giving a solution and a solid residue. Suspension and filtration were repeated another six times on the solid portion isolated after each filtration. The final pale-green solid was dried under vacuum, constituting the analyte sample (27.9 g). A 15-mg amount of this sample was dissolved in 10 ml of tetrahydrofuran (THF) and used for subsequent LC–UV and LC–MS analyses.

Flow injection (FI)–TSP-MS, LC–UV and LC–TSP-MS

FI–TSP-MS analysis was performed using a Hewlett-Packard Model 1090 liquid chromatograph interfaced to a Finnigan TSQ700 triple quadrupole mass spectrometer equipped with a Finnigan TSP2 thermospray interface. A 10-μl volume of a THF solution of the sample was injected using a mobile phase of acetonitrile–0.05 *M* ammonium acetate (80:20) at a flow-rate of 1 ml/min. Negative-ion mass spectra were recorded by scanning the third quadrupole (Q3) from m/z 100 to 900 in 1 s. For the thermospray conditions, see Results and Discussion.

LC separation was performed on the system described above. Sample injections of 5 μl were made on a Shandon Hypersil C_{18} column (250 mm × 4.6 mm I.D.) using linear gradient elution from 30 to 90% B in 20 min (A = 0.05 *M* ammonium acetate; B = acetonitrile) at a flow-rate of 1.0 ml/min.

The LC eluent could be fed either to a Hewlett-Packard Model 1050 UV detector (242 nm) or to the TSP probe. The TSP conditions during LC–MS were the following: vaporizer temperature 70°C, source temperature 180°C, discharge voltage 800 V and repeller voltage −100 V. In the full-scan mode, Q3 was scanned from m/z 200 to 900 in 4 s. In the MID scan mode Q3 was scanned over mass windows 1.0 u wide and centred around m/z 254, 446, 488, 490, 576, 638, 682 and 830, with a total scan cycle time of 5 s.

Derivatization

A 1.0-ml volume of a THF solution of the sample was treated at room temperature with 100 μl of trifluoroacetic anhydride (TFA) or heptafluorobutyric anhydride (HFBA). After 30 min the mixture was dried under a stream of nitrogen, the residue was dissolved in 1.0 ml of THF and 100 μl of TFA or HFBA were added. The mixture was allowed to stand for 30 min, after which the solution was dried and the residue dissolved in 300 μl of acetonitrile. LC–MS analysis of the HFBA derivatives was performed by injecting 15 μl of the acetonitrile solution and using a linear gradient elution (from 80 to 90% B in 5 min; A and B as above). The vaporizer temperature was set at 65°C. Throughout the analysis Q3 was scanned from m/z 400 to 1500 in 4 s. All the other experimental conditions were as described for the underivatized sample. The derivatization yield was determined on the basis of LC–UV peak areas and was found to be almost quantitative (diderivatized/monoderivatized peak-area ratio = 100:1).

Detection limits were determined by flow injection (10 μl) of the appropriately diluted solutions of either the derivatized or the underivatized sample and operating Q3 in the single-

ion detection mode (window width 1 u, scan time 1 s).

Chemicals

HPLC-grade water, ammonium acetate, acetonitrile and THF were purchased from Merck. PET bottle scraps were obtained from Tecoplast (Ferrara, Italy). Analytical-reagent grade ethylene glycol was obtained from Carlo Erba. $Mn(AcO)_4 \cdot 4H_2O$, TFA and HFBA were purchased from Aldrich. All chemicals were used as received.

RESULTS AND DISCUSSION

The search for the optimum TSP conditions was performed by flow injection (FI) analysis with a water–acetonitrile mobile phase containing ammonium acetate as the buffer. These preliminary experiments showed that by far the most intense signals were obtained by recording the negative-ion mass spectra produced by operating the TSP interface in the discharge ionization mode. A typical negative-ion FI–TSP mass spectrum of the glycolysis mixture is reported in Fig. 1. Most of the ions can be easily recognized as corresponding to two types of molecular ions of linear PET oligomers (from monomer M_1 to tetramer M_4; see reaction 1): odd-electron radical anions ($M_n^{\cdot-}$), presumably formed by electron attachment, and even-electron acetate attachment ions $[(M_n + AcO)^-]$. The ratio between the two molecular ions for each oligomer depends on the buffer content of the eluent. Other minor ions can be assigned to either fragment ions or molecular ions of additional components of the mixture.

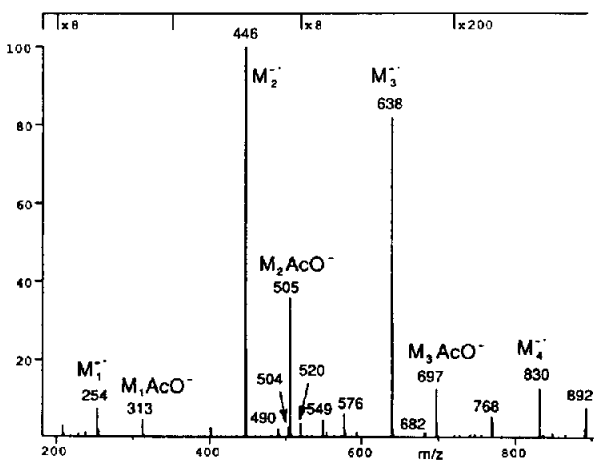

Fig. 1. FI–TSP mass spectrum of the mixture obtained by glycolysis of PET.

Fine tuning of the TSP conditions was accomplished by systematically varying the experimental parameters over reasonable ranges of values. No significant effect was observed by changing the ion source temperature between 150 and 200°C. Lower temperatures were not tested to avoid source contamination and higher temperatures had a detrimental effect on the absolute ion intensities. The optimum discharge voltage was found to be 700–800 V; above this value a plateau was reached. Fig. 2a shows the influence of the vaporizer temperature on the intensities of different molecular ions. It can be seen that within the range 65–80°C radical anions are favoured at low temperatures, whereas the opposite is true for acetate attachment ions. Outside this range the intensities decreased dramatically. The effect of the repeller voltage on the intensity of molecular ions of various size is depicted in Fig. 2b. The voltage required for maximum intensity clearly depends on the size of the ion, and increases as the ion size is increased. A compromise was chosen by setting the repeller voltage at −100 V.

These optimum vaporizer and ion source temperatures are strikingly different from those reported previously [10] for the cyclic PET oligomers, which involved the use of temperatures up to 350°C. Therefore, we tested our "mild" TSP conditions with a pure sample of the cyclic PET trimer (cyclo-M_3). It turned out that the optimum experimental conditions for the cyclic trimer were identical with those found for the linear oligomers. Moreover, our conditions are consistent with the ion evaporation mechanism, which does not require the volatilization of the neutral analyte [11,12]. There seem to be no explanation for this marked disagreement other than differences in vaporizer and ion source design and the temperature control systems of the two TSP interfaces used.

The optimized TSP conditions were used in the subsequent LC–TSP-MS analysis of the

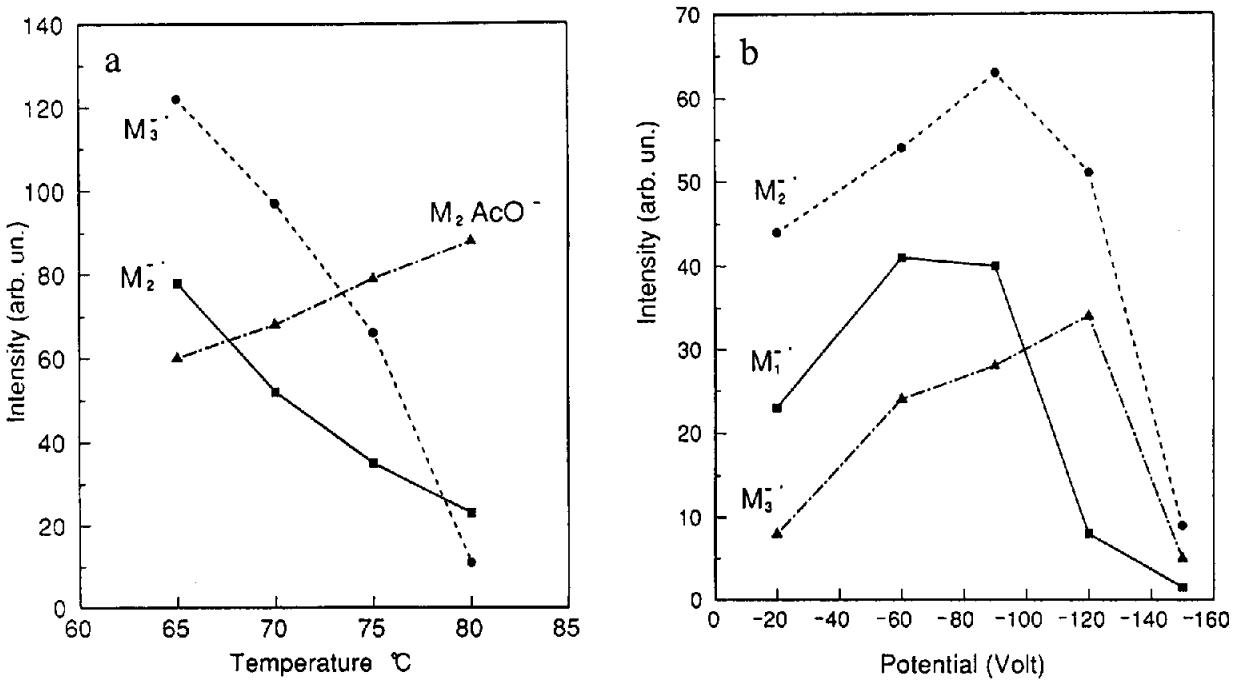

Fig. 2. Effects of (a) vaporizer temperature and (b) repeller voltage on the absolute ion intensities of different molecular ions.

mixture of the glycolysis products of PET. The chromatograms obtained with UV and full-scan MS detection are reported in Fig. 3. The MS trace is actually a reconstructed ion chromatogram made up only by the ion currents corresponding to the most abundant ions of the FI–TSP mass spectrum (Fig. 1). This data manipulation was necessary because the total ion current chromatogram was too noisy and mainly due to high-intensity background ions.

The comparison between the two traces reported in Fig. 3 clearly indicates that sensitivity in the TSP-MS mode is poorer than that in the UV mode. Peaks B and F are completely missing from the MS trace and peaks D and G are barely detectable.

The mass spectra of peaks C and E (Fig. 4) show both M^- and $[M + AcO]^-$ molecular ions of the linear PET dimer (m/z 446 and 505) and trimer (m/z 638 and 697), respectively. Fragment ions originated from the loss of 192 u, corresponding to the elimination of a repeating unit ($-COC_6H_4COOC_2H_4O-$). The mass spectrum taken on the left shoulder of peak C (Fig. 4) can be attributed to a linear PET dimer containing a diethylene glycol moiety instead of one of the three ethylene glycol groups (M^- at m/z 490 and $[M + AcO]^-$ at m/z 549), with a molecular mass 44 u higher than that of the normal dimer [13]. Similarly, peak A was the linear PET monomer (M^- at m/z 254 and $[M + AcO]^-$ at m/z 313). Unfortunately, the mass spectra of peaks D and G were too weak for unambiguous interpretation.

In the attempt to obtain at least the molecular mass of all the LC–UV peaks, we tried to use the mass analyser in the MID mode instead of the usual full-scan mode. The set of m/z values chosen for the MID scan included the most significant ions (that is, adduct ions were excluded) contained in the FI–TSP mass spectrum of the sample (see Fig. 1). The total ion chromatogram produced by the LC–TSP-MID analysis is reported in Fig. 5. All the peaks previously observed in the UV trace can be easily recognized in the MID trace. The ion responsible for each peak was tentatively considered to be the molecular ion of the corresponding component.

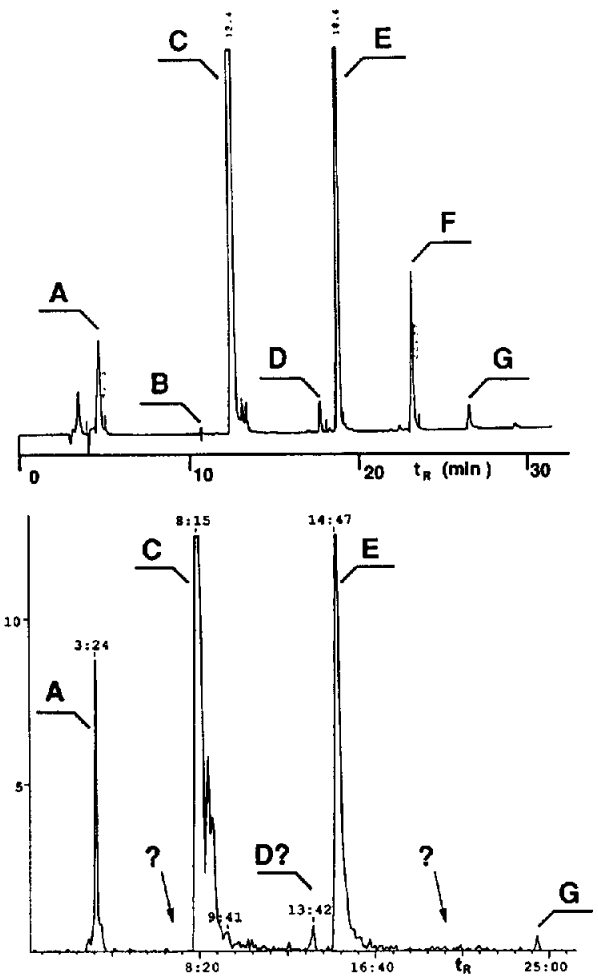

Fig. 3. LC–UV (top) and LC–TSP-MS (full-scan mode, bottom) traces for the glycolysis mixture of PET. The same amount of sample was injected in both instances. Time scales in min.

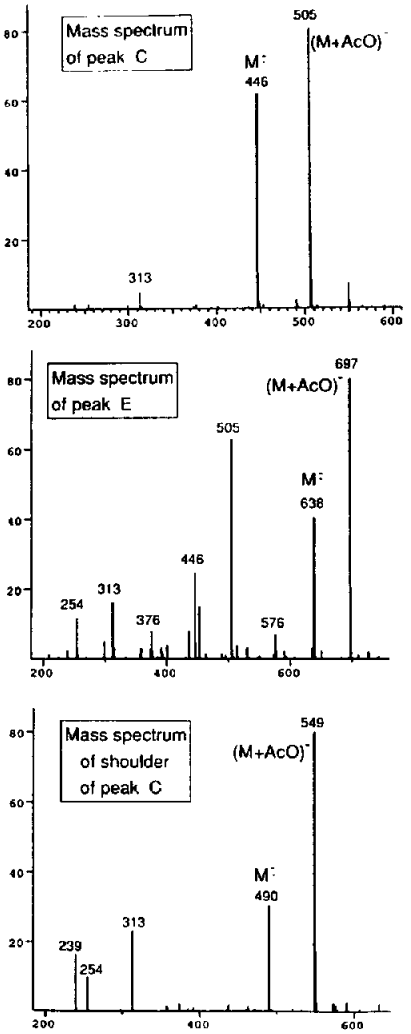

Fig. 4. TSP mass spectra of peak C (top), peak E (centre) and left shoulder of peak C (bottom) in the LC–TSP-MS trace in Fig. 3.

This assumption allowed the assignment of a tentative structure for peaks B, D, F and G. Peak B was an isomer of the diethylene glycol-containing dimer (m/z 490). Peak D was a mixture of the diethylene glycol-containing trimer (m/z 682) and the monoacetyl derivative of the linear PET dimer (m/z 488), the latter presumably formed by reaction between the oligomer and acetate from the catalyst. Peak F turned out to be the linear PET tetramer (m/z 830) and peak G could be assigned to the cyclic PET trimer (m/z 576). The results for the remaining peaks (A, C and E) were in agreement with the structural assignments obtained previously by LC–MS analysis in the full-scan mode.

It is worth noting that the proper use of the information derived from the FI–TSP mass spectrum allowed us to take advantage of the improved sensitivity typical of the MID mode (normally employed for target-compound analysis) for the characterization of an unknown mixture. On the other hand, the full-scan mode

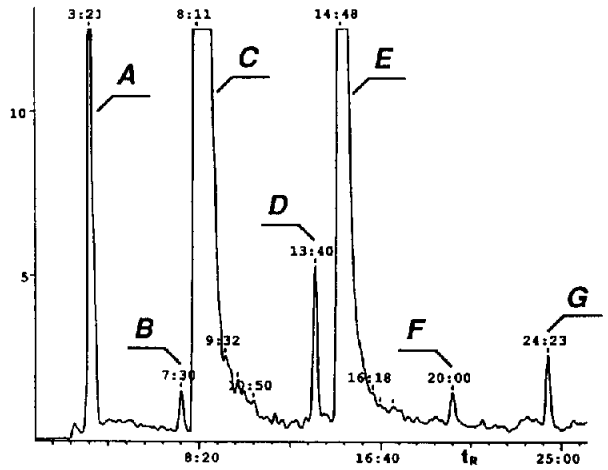

Fig. 5. LC–TSP-MS (MID mode) trace for the glycolysis mixture of PET. Time scale in min.

is certainly more reliable than the MID mode for the determination of the molecular mass of an unknown substance. However, mass spectra of minor components of the glycolysis mixture could not be recorded by LC–TSP-MS analysis, because the signal-to-noise ratio was too low. The causes of poor sensitivity could be (i) poor ionization efficiency, (ii) high-intensity background ions in the m/z range of interest and (iii) low volatility of the analytes. Another problem was the low solubility of the sample mixture. Maximum sample concentrations (about 1.5 mg/ml) could be obtained by using THF as the solvent. Unfortunately, the use of THF limited the injection volume to 5 μl to avoid peak-splitting problems. Therefore, no more than about 7–8 μg of the sample mixture could be injected.

Derivatization is usually employed in order to improve both the solubility and detectability of difficult analytes [14]. As one of the ionization mechanisms in the TSP–MS analysis of PET oligomers was electron attachment, we tried to enhance the ionization efficiency by derivatizing the terminal hydoxyl groups with perfluoroanhydrides. The derivatization procedure with either trifluoroacetic anhydride (TFA) or heptafluorobutyric anhydride (HFBA) was simple and gave rise to high conversion yields (>99%). The sole modification of the TSP parameters required by the derivatized samples was the lowering of the vaporizer temperature to 65°C. The detection limits for the derivatized (with HFBA) and underivatized samples were determined under optimized TSP–MS conditions. On flow injection of 100 pg of the derivatized sample [which contains *ca.* 120 fmole of the HFBA derivative of the linear PET dimer (M_r 838), since this compound is by far the most abundant component of the sample mixture], a signal-to-noise ratio of 20 was obtained in the single-ion detection mode (m/z 838). A similar experiment with the underivatized sample required the injection of 300 pg (*ca.* 670 fmol of the linear dimer) to obtain a signal-to-noise ratio of 10. The resulting detection limit (signal-to-noise ratio ≈ 3) for the derivatized dimer (about 20 fmol) turned out to be an order of magnitude lower than for the underivatized dimer (about 200 fmol). The results for the trimers were even better, as derivatization with HFBA resulted in a 30-fold increase in the signal-to-noise ratio, indicating that the derivatization reduced the discrimination against high-molecular-mass components, presumably because of the improved volatility of the perfluoroacyl derivatives.

Another advantage of the HFBA derivatives is that their solubility in the organic mobile phase (acetonitrile) is dramatically increased relative to that of the untreated sample. The use of acetonitrile instead of THF as the sample solvent allowed the injection of a much higher volume of a more concentrated solution. Fig. 6 shows the total ion chromatogram (unmanipulated data) obtained from the LC–TSP-MS analysis in full-scan mode of the sample derivatized with HFBA (50 μg injected). The chromatogram reproduced fairly well the LC–UV trace of the same sample (not shown). Most of the negative-ion mass spectra contained the molecular radical anion only, but some of the minor peaks had mass spectra containing more than a single ion. The results and the structural assignments for all the LC–MS peaks are summarized in Table I. As can be seen from these data, the LC–TSP-MS analysis of the derivatized sample confirmed the results obtained from the underivatized mixture, but it was also able to reveal the presence of some additional components. Heptafluorobutyric acid (peak 1), the monoderivatized linear dimer

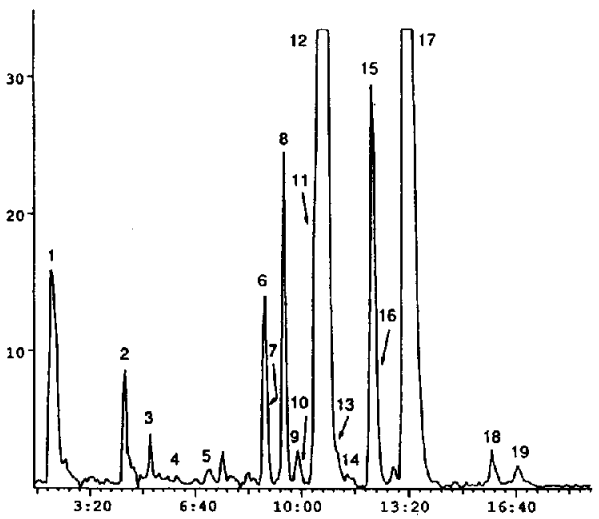

Fig. 6. LC–TSP-MS (full-scan mode) trace for the glycolysis mixture of PET derivatized with HFBA. Time scale in min.

(peak 3) and the linear dimer (peak 8) and trimer (peak 14) derivatized with a C_3F_7CO and a C_2F_5CO group (pentafluoropropionic anhydride is likely to be an impurity of HFBA) can be regarded as components originating from the derivatization step. The monoacetyl derivative of the linear trimer (peak 9) could not be detected in the underivatized sample. Unfortunately, it was not possible to assign a structure to the other impurities on the basis of the sole TSP mass spectrum. However, peaks 10 and 13 (although unresolved from adjacent peaks) could be recognized as the di-HFBA derivatives of two impurities that were observed in the FI–TSP mass spectrum of the sample (Fig. 1, *m/z* 504 and 520) but could not be found in the LC–TSP-MS chromatogram (Fig. 3, bottom). Therefore, the derivatization provided confirmation that these two ions were actually molecular anions of two

TABLE I

MASS SPECTRAL DATA FOR THE LC–MS PEAKS IN THE ANALYSIS OF THE HFBA-DERIVATIZED SAMPLE

Peak No.	*m/z* (relative abundance, %)	Structural assignment[a]	Proposed M_r for underivatized molecule
1	427 (100), 641 (20)	C_3F_7COOH	214
2	611 (100), 519 (50), 414 (50)	Unknown	?
3	642 (100), 701 (30)	M_2(HFB)	446
4	576 (100)	Cyclo-M_3	576(G)[b]
5	684 (100), 743 (30)	M_2Ac(HFB)	488(D)
6	646 (100)	M_1(HFB)$_2$	254(A)
7	541 (100), 522 (35), 502 (19), 462 (79), 460 (95)	Unknown	?
8	788 (100), 847 (12)	M_2(HFB)(PFP)	446
9	876 (100)	M_3Ac(HFB)	680
10	896 (100)	Unknown	504[c]
11	882 (100), 941 (15)	(M_2 + 44)(HFB)$_2$	490(B)
12	838 (100), 897 (18)	M_2(HFB)$_2$	446(C)
13	912 (100), 971 (9)	Unknown	520[c]
14	980 (100), 1039 (18)	M_3(HFB)(PFP)	638
15	613 (100), 594 (45), 574 (10), 534 (60), 532 (68)	Unknown	?
16	1074 (100), 1133 (20)	(M_3 + 44)(HFB)$_2$	682(D)
17	1030 (100), 1089 (7)	M_3(HFB)$_2$	638(E)
18	685 (100), 666 (40), 646 (16), 606 (57), 608 (61)	Unknown	?
19	838 (100), 1222 (25), 1030 (20)	M_4(HFB)$_2$	830(F)

[a] HFB = heptafluorobutyryl derivative; PFP = pentafluoropropionyl derivative; Ac = acetyl derivative; (M_n + 44) = linear oligomer containing a diethylene glycol unit.

[b] Peak labels used in Figs. 3a, 3b and 5.

[c] Assumed on the basis of the FI–TSP mass spectrum of the underivatized sample (see text for explanation).

components of the glycolysis mixture. The mass spectra relative to peaks 7, 15 and 18 displayed exactly the same group of ions, with an overall increment of 72 u between each couple of adjacent spectra (see, for example, the doublets at m/z 460/462, 532/534 and 604/606 in Table I). This suggests that the peaks correspond to a set of three closely related substances. Further work is under way on the determination of the structure of the unknown components with the aid of other mass spectrometric techniques (*e.g.*, MS–MS).

Three different LC–MS methods have been investigated. The first, involving full-scan acquisition, was the simplest as it did not require any previous knowledge about the sample and provided true mass spectra. The disadvantage was that the sensitivity was too low for the detection of several minor components.

The second approach was the MID mode analysis, which significantly reduced the detection limits but required a hypothesis to be formulated regarding the nature of the compounds analysed. In other words, given a set of expected molecular masses, *e.g.*, those of a series of oligomers, the MID mode allowed the identification of the corresponding LC peaks in the chromatogram.

The third method, namely HFBA derivatization combined with full-scan analysis, was actually able to provide true mass spectra with sufficiently low detection limits. On the other hand, it required some additional effort (cost and time) for the preparation of the sample and, of course, it was effective only for those components which were converted into the derivative. Undesired derivatives (*e.g.*, incompletely derivatized substances) were not a real problem as they could be easily recognized.

CONCLUSIONS

We have applied LC–TSP-MS to the characterization of the mixture obtained by glycolysis of PET. Structural assignment was achieved for all the major constituents and several minor components could also be identified.

We believe that the use of the thermospray interface with discharge ionization in the negative ion mode can be successfully applied to the LC–MS analysis of the depolymerization products of various aromatic polyesters. The use of derivatization with perfluoroanhydrides, although adding some complexity to the analysis, should extend the range of application of discharge TSP ionization to aliphatic polyesters and, in general, to compounds containing hydroxyl groups.

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