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Registry No. Poly(butylene terephthalate) (SRU), 24968-12-5; poly(butylene terephthalate) (copolymer), 26062-94-2; (poly(butylene terephthalate))(poly(tetramethylene oxide)) (block copolymer), 106159-00-6.

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Fast Atom Bombardment Mass Spectrometry Identification of Oligomers Contained in Poly(ϵ-caprolactam) and Poly(butylene isophthalate)

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ABSTRACT: Fast atom bombardment mass spectrometry (FAB-MS) and high-performance liquid chromatography (HPLC) were used to identify oligomers formed in polymerization reactions leading to poly(ϵ-caprolactam) and poly(butylene isophthalate). The results indicate that FAB-MS is suitable for the rapid analysis and identification of these complex mixtures, yielding better results with respect to conventional electron impact and chemical ionization–MS modes. Metastable scanning of FAB ions, employing also collision-activated decomposition (CAD), was used in order to ascertain the fragmentation pathways of some molecular ions corresponding to cyclic oligomers of poly(ϵ-caprolactam). Positive and negative FAB mass spectra, CAD B/E and CAD B^2/E scans, are reported and discussed in the text. Definite advantages of the FAB method over conventional MS are the ability to detect labile compounds (as in the case of poly(butylene isophthalate)) and reveal higher molecular weights (up to 1450 amu, in the present case).

Introduction

The production of high molecular weight polymers is often accompanied by the formation of sizable amounts of low molecular weight oligomers.[1-3]

Among the classes of polycondensates, in particular for industrial applications, polyesters and polyamides, where often cyclic and open-chain oligomers are formed during the polymerization reactions, are the most important. In this case, knowledge of the structure and of the amount of these oligomers may be essential for obtaining high-quality industrial polymers.

Current methods for detecting low amounts of oligomers contained in polymeric samples are based almost exclusively on gas–liquid and gel permeation chromatography.[1,2] These separation techniques are indeed powerful, but sometimes low volatility of samples or low solubility in most organic solvents makes alternative and rapid methods of detection and identification for low molecular weight compounds desirable.

Mass spectrometry (MS) is particularly suitable to the detection of these materials. Up to now, the MS method most used for the detection of oligomers contained in

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polymer samples has been based on the direct introduction of the polycondensation mixtures into the ion source of a mass spectrometer by the conventional direct insertion probe for solid samples. The probe temperature is then increased, and oligomers, which evaporate undecomposed in the high vacuum of the ion source, are usually detected as separate peaks in the total ion current curves before the evolution of the thermal decomposition products originating from the polymer pyrolysis.[3-7]

However, if the oligomers are thermally labile or their molecular weights are too high, they cannot be seen before the thermal degradation of the polymer. Moreover, if the oligomers are not stable under electron impact or chemical ionization modes, their molecular ions are absent in the mass spectra, making the identification difficult and sometimes impossible.[6]

Since its introduction in 1981,[8] fast atom bombardment mass spectrometry (FAB-MS) has become widely used for the analysis of high molecular weight and thermally labile compounds. In particular, many studies of natural products (as peptides, saccharides, nucleic acids, and related materials) have been performed in the past years by FAB-MS.[9]

However, little information is today available on the detection of mixtures by FAB-MS in the field of synthetic polymers.

We have resorted to using the FAB-MS technique to detect and identify, without isolation, several cyclic and open-chain oligomers extracted from poly(ϵ-caprolactam) (nylon 6) and poly(butylene isophthalate) (PBIP). In both cases, high-performance liquid chromatography (HPLC) has been used to provide an alternative estimate of oligomers in the mixture. In the present case we have observed that HPLC provides information on compounds with molecular weights up to about 800 amu, whereas the FAB-MS technique allows us to detect products with molecular weights up to about 1450 amu.

Experimental Section

Sample Preparation and HPLC Conditions. Finely powdered polyamide (nylon 6, ASN 27, produced by Tecnopolimeri S.p.A., Snia Group,[10] by hydrolytic polymerization at 270 °C; relative viscosity about 2.65) was extracted with methanol for 40 h. Methanol was evaporated at 60 °C under vacuum, and the residue was dried at 60 °C under vacuum overnight. HPLC column: Lichrosorb RP 8 5 (SUPELCO); eluent CF_3CH_2OH/H_2O 40:60 (density = 1.186 g/cm^3; oven temperature 50 °C; flow rate 0.8 mL/min; detector UV 205 nm (Figure 1A).

Crude PBIP (produced by high-temperature polycondensation of dimethyl isophthalate and butanediol in the presence of $Ti(OBu)_4$ as a catalyst[11]) was dissolved in chloroform and then reprecipitated in acetone. The solid precipitated was filtered, and the operation (dissolution–precipitation) was repeated two times.

The mixture (obtained by evaporating under vacuum the solutions collected all together) was dried at 60 °C under vacuum overnight: HPLC column Spherisorb SSCN; eluent CH_3CN/H_2O 45:55; oven temperature 45 °C; flow rate 0.9 mL/min (Figure 1B).

Peaks in the HPLC tracings in Figure 1 were identified by comparison with the retention times of authentic oligomer samples.[10,11]

Mass Spectrometry. FAB analyses were performed on a double focusing Kratos MS 50S mass spectrometer equipped with the standard FAB source.

Mass spectra were recorded by using a DS 55 data system or an UV recorder. Xenon and argon were used as bombarding gases, with an energy of 8 kV. Mass resolution was approximately 2000. A mixture of CsI/RbI (50/50 wt) was used as a calibrant (calibration range m/z 28–1531). Spectra were obtained by using glycerol (Gly) and/or thioglycerol (Thiogly) as matrices. In the case of PBIP mixture, a homogenous solution of Gly/Thiogly/HCl 1 M (1:1:1 v/v) was used and applied to the copper target. Peak intensity values shown in mass spectra represent the average of five separate mass spectra.

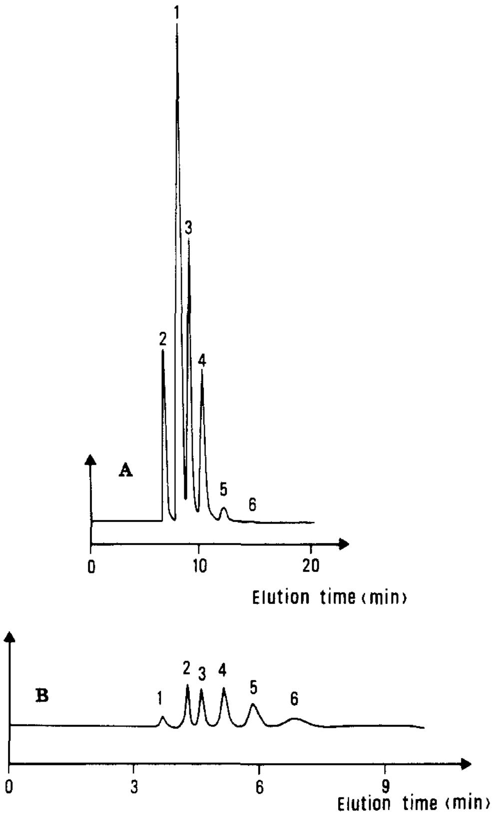


Figure 1. (A) HPLC separation of cyclooligoamides extracted from nylon 6 (mixture I): (1) caprolactam; (2) cyclic dimer; (3) cyclic trimer; (4) cyclic tetramer; (5) cyclic pentamer; (6) cyclic hexamer. (B) HPLC separation of open-chain and cyclooligoesters extracted from poly(butylene isophthalate) (mixture II): (1) linear monomer; (2) linear dimer; (3) cyclic monomer; (4) cyclic dimer; (5) cyclic trimer; (6) cyclic tetramer

Collision-activated decomposition (CAD) MS/MS analyses were performed on the same mass spectrometer equipped with a collision chamber in the first free field region.

Metastable decompositions were activated by using argon as collision gas. The pressure in the collision chamber was set in such a way as to reduce the ion beam to 10% of its usual value.

Accelerating voltage was set at 8 kV.

B/E and B^2/E scans were performed by using a linked scan unit, at a scan rate of 20 s/decade, and recorded on an UV recorder.

Results and Discussion

In Figure 1A is reported the HPLC trace showing the separation of cyclooligoamides (mixture I) of a methanolic extract from nylon 6. The conditions described give perfect separation of oligomers up to the hexamer.

In Figure 1B is reported the HPLC trace showing the separation of several open-chain and cyclooligoesters of chloroform extracts from the PBIP (mixture II). The conditions described allow separation of linear monomer and dimer and of cyclic oligomers up to tetramer.

In Figure 2 is reported the positive FAB mass spectrum of mixture I, recorded by using argon as bombarding gas and glycerol/HCl as matrix.

The positive FAB mass spectrum in Figure 2 shows the protonated molecular ions of the oligomers from the monomer to the decamer (m/z 114 + n113; n = 0–9), indicating that FAB is useful for the detection of high molecular weight oligomers (above 1100 amu) in the mixture.

In Figure 3 is reported the negative FAB mass spectrum of mixture I, recorded by using glycerol as matrix and xenon as bombarding gas. The quasi-molecular ions (M–

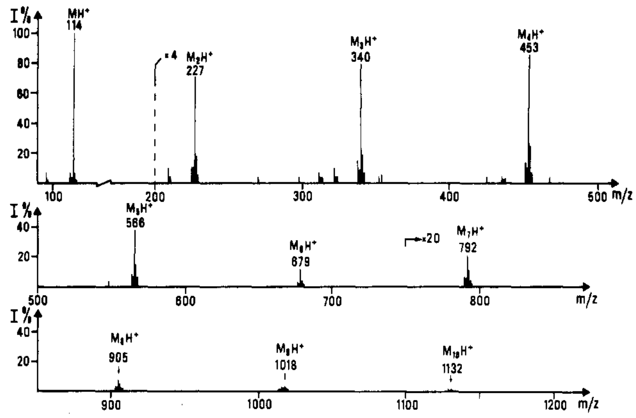


Figure 2. Positive FAB mass spectrum of mixture I.

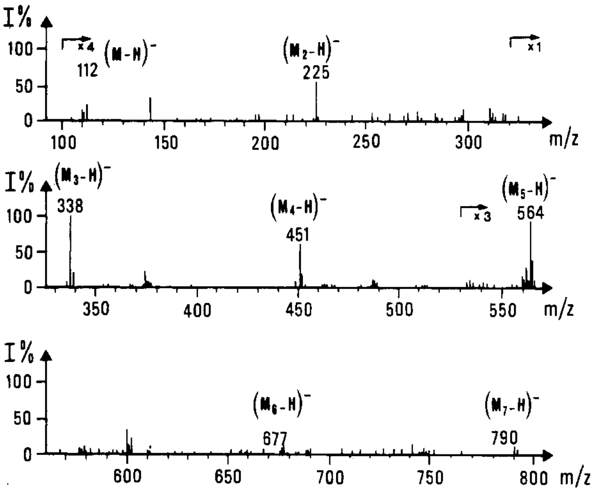


Figure 3. Negative FAB mass spectrum of mixture I.

H)⁻ of the oligomers from the monomer to the heptamer (m/z 112 + n113; n = 0–6) are present in the mass spectrum in Figure 3. However, in this case peak intensities of the molecular ions of the cyclic monomer and dimer are much lower than expected, whereas the molecular ion of the cyclic trimer is the base peak of the spectrum. Therefore, it appears that negative FAB-MS is less useful than positive FAB mode, at least in the present case.

In order to estimate the reliability of the distribution of cyclic products obtained by FAB analysis, we have tried to link FAB with HPLC data. However, the correlation is not good and the hypothesis was made that a fragmentation of the higher molecular weight ions to yield lower oligomers might be occurring in FAB mode.

FAB linked scans[12] of some molecular ions corresponding to cyclic oligomers in mixture I were therefore performed.

In parts A and B of Figure 4 are reported the collision-activated decomposition (CAD) B/E spectra (daughter ions) of the ions corresponding to cyclic trimer $(M_3 + H)^+$ (m/z 340) and cyclic tetramer $(M_4 + H)^+$ (m/z 453), respectively. As it can be seen, cyclic dimer $(M_2 + H)^+$ (m/z 227) and cyclic monomer $(M + H)^+$ (m/z 114) (Figure 4A) and cyclic trimer $(M_3 + H)^+$ (m/z 340), cyclic dimer $(M_2 + H)^+$ (m/z 227), and cyclic monomer $(M + H)^+$ (m/z 114) (Figure 4B) are obtained as daughter ions from the parent ions at m/z 340 (protonated cyclic trimer) and at m/z 453 (protonated cyclic tetramer), respectively. Other peaks present in the spectra in Figure 4 are due to the loss of 18 amu (presumably water) from ions corresponding to cyclic oligomers. Loss of 18 amu was already observed in the FAB mass spectrum in Figure 2; in that case metastable transitions were found at m/z 80.8 (transition 114 → 96), m/z 192.4 (transition 227 → 209), m/z 305.0 (transition 340 → 322), m/z 417.7 (transition 453 → 435), and m/z 530.6 (transition 566 → 548).

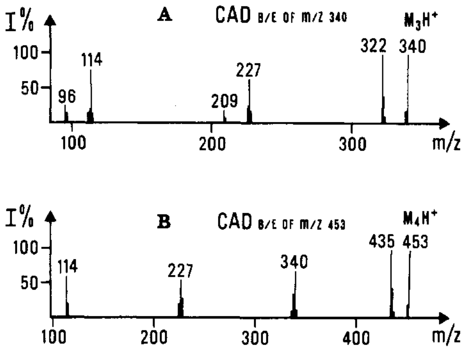


Figure 4. (A) FAB MS/MS spectrum (CAD B/E) of the $(M_3 + H)^+$ molecular ion, m/z 340, of cyclic trimer from mixture I. (B) FAB MS/MS spectrum (CAD B/E) of the $(M_4 + H)^+$ molecular ion, m/z 453, of cyclic tetramer from mixture I.

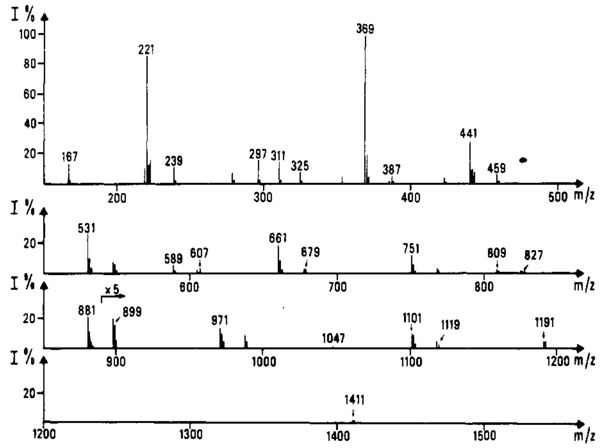


Figure 5. Positive FAB mass spectrum of mixture II. Structural assignments are reported in Table I.

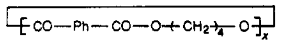
CAD B^2/E spectra (parent ions) of the ions corresponding to cyclic monomer $(M + H)^+$ (m/z 114) and cyclic dimer $(M_2 + H)^+$ (m/z 227), in mixture I, confirm the results obtained by CAD B/E spectra. In fact, they show a metastable transition at m/z 57.25, indicating that the cyclic monomer originates from the cyclic dimer (transition 227 → 114), and a metastable transition at m/z 151.56, indicating that the parent ion of the peak at m/z 227 (protonated cyclic dimer) is the cyclic trimer $(M_3 + H)^+$ (m/z 340).

From these results it might be inferred that, in this case, the FAB method cannot be used for quantitative determination.

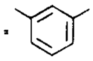
In Figure 5 is reported the positive FAB mass spectrum of mixture II, recorded by using glycerol/thioglycerol/HCl as matrix and argon as bombarding gas.

This spectrum, containing peaks up to about m/z 1450, shows several peaks (Table I) corresponding to the protonated molecular ions of cyclic oligomers (m/z 221, 441, 661, 881, and 1101), linear oligomers (with hydroxyl and carboxyl end groups) (m/z 239, 459, 679, 899, and 1119), compounds with two hydroxyl end groups (m/z 311, 531, 751, 971, 1191, and 1411), and compounds with two carboxyl end groups (m/z 167, 387, 607, 827, and 1047), respectively. Also present in the FAB mass spectrum are several peaks corresponding to fragment ions (i.e., m/z 297, 325, 369, 589, and 809). They come from the protonated molecular ions of the cyclic oligomers by the loss of 72 amu (presumably tetrahydrofuran, transitions confirmed by metastable peaks) and/or 44 amu (carbon dioxide).

Table I
Cyclic and Open-Chain Oligoesters Present in Mixture II

compound[a]	x	MH$^+$ m/z
 $\overline{[\mathrm{CO{-}Ph{-}CO{-}O{-}(CH_2)_4{-}O}]_x}$	1	221
	2	441
	3	661
	4	881
	5	1101
$\mathrm{HO{-}[CO{-}Ph{-}CO{-}O{-}(CH_2)_4{-}O]_x H}$	1	239
	2	459
	3	679
	4	899
	5	1119
$\mathrm{HO{-}(CH_2)_4{-}O{-}[CO{-}Ph{-}CO{-}O{-}(CH_2)_4{-}O]_x H}$	1	311
	2	531
	3	751
	4	971
	5	1191
	6	1411
$\mathrm{HO{-}[CO{-}Ph{-}CO{-}O{-}(CH_2)_4{-}O]_x CO{-}Ph{-}COOH}$	0	167
	1	387
	2	607
	3	827
	4	1047

[a] Ph =



As it can be observed from the FAB mass spectrum in Figure 5, all the series of oligomers theoretically expected are detected: the cyclic oligomers and the three families of open-chain compounds.

Summarizing our results, FAB-MS appears to be a suitable method for the rapid analysis of mixtures of cyclic oligomers or open-chain compounds contained in synthetic polymers.

In the case of nylon 6, the FAB-MS technique shows its high potential in detecting compounds present in trace amounts in the mixture. In fact, the HPLC tracing (Figure 1A) shows peaks up to only the cyclic hexamer. On the other hand, gradual heating of the mixture into the ion source of the mass spectrometer does not lead to good results. In fact, low molecular weight oligomers (from monomer to pentamer) are detected by electron impact MS, whereas oligomers from hexamer to decamer are not volatilized and remain therefore unrevealed. Instead, in the FAB mass spectrum in Figure 2 peaks corresponding to protonated molecular ions from monomer to decamer are present.

In the case of PBIP, the FAB-MS method (Figure 5 and Table I) allows the detection and identification of about 20 compounds present in mixture II, while with HPLC (Figure 1B) only 6 compounds were detected. Moreover, among these compounds some are very labile (i.e., open-chain products; Table I); it is possible that they might be lost when other techniques (such as HPLC, GC-MS, or EI-MS) are used and are instead detected by using the FAB-MS method.

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Registry No. PBIP (SRU), 28087-45-8; PBIP (copolymer), 38317-19-0; nylon 6, 25038-54-4; $\overline{\mathrm{(COPhCOO(CH_2)_4O)}}$, 89182-72-9; $\overline{\mathrm{(COPhCO_2(CH_2)_4O)}}_2$, 106929-20-8; $\overline{\mathrm{(COPhCO_2(CH_2)_4O)}}_3$, 106929-21-9; $\overline{\mathrm{(COPhCO_2(CH_2)_4O)}}_4$, 106929-22-0; $\overline{\mathrm{(COPhCO_2(CH_2)_4O)}}_5$, 106929-23-1; $\mathrm{HO(COPhCO_2(CH_2)_4O)H}$, 106929-24-2; $\mathrm{HO(COPhCO_2(CH_2)_4O)_2H}$, 106929-25-3; $\mathrm{HO(COPhCO_2(CH_2)_4O)_3H}$, 106929-26-4; $\mathrm{HO(COPhCO_2(CH_2)_4O)_4H}$, 106929-27-5; $\mathrm{HO(COPhCO_2(CH_2)_4O)_5H}$, 106929-28-6; $\mathrm{HO(CH_2)_4O_2CPhCO_2(CH_2)_4OH}$, 17773-48-7; $\mathrm{HO(CH_2)_4O(COPhCO_2(CH_2)_4O)_2H}$, 106929-29-7; $\mathrm{HO(CH_2)_4O(COPhCO_2(CH_2)_4O)_3H}$, 106929-30-0; $\mathrm{HO(CH_2)_4O(COPhCO_2(CH_2)_4O)_4H}$, 106929-31-1; $\mathrm{HO(CH_2)_4O(COPhCO_2(CH_2)_4O)_5H}$, 106929-32-2; $\mathrm{HO(CH_2)_4O(COPhCO_2(CH_2)_4O)_6H}$, 106929-33-3; $\mathrm{HO_2CPhCO_2(CH_2)_4O_2CPhCO_2H}$, 106929-34-4; $\mathrm{HO_2CPhCO_2H}$, 121-91-5; $\mathrm{HO(COPhCO_2(CH_2)_4O)_2COPhCO_2H}$, 106929-35-5; $\mathrm{HO(COPhCO_2(CH_2)_4O)_3COPhCO_2H}$, 106929-36-6; $\mathrm{HO(COPhCO_2(CH_2)_4O)_4COPhCO_2H}$, 106929-37-7; caprolactam, 105-60-2; caprolactam cyclic dimer, 56403-09-9; caprolactam cyclic trimer, 56403-08-8; caprolactam cyclic tetramer, 5834-63-9; caprolactam cyclic pentamer, 864-90-4; caprolactam cyclic hexamer, 865-14-5.

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