Synthesis and structural characterization by fast-atom bombardment mass spectrometry of exactly alternating copolyesters containing photolabile units in the main chain

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Polycondensation between bis(2-hydroxymethylenephenyl)adipate, bis(3-hydroxypropylene)terephthalate and bis(2-hydroxyethylene)terephthalate with α-truxilloyl chloride were performed to obtain exactly alternating copolyesters containing photoreactive cyclobutane units in the main chain. The resulting copolyesters were characterized by fast-atom bombardment (f.a.b.) mass spectrometry, and the structure of the oligomers detected in the f.a.b.(+) and f.a.b.(−) mass spectra allowed confirmation of the alternating sequence present in the copolymers.

(Keywords: fast-atom bombardment mass spectrometry; copolyesters; photolabile units)

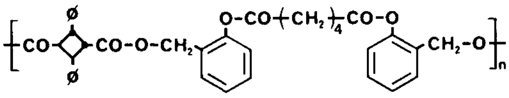
INTRODUCTION

Interest in the synthesis of new condensation copolymers containing one or more functional groups (amide, ester, urethane, urea, etc.) in the main chain has been increasing in the literature[1–4]. Copolyesters of suitable comonomers able to produce thermotropic materials having interesting properties for fibre, membrane or plastic applications have been studied especially in order to ascertain their structure–properties relationships[4–7].

However, relatively little work has been done on the sequential analysis of comonomers in the copolymer chain, because the characterization of the sequence arrangements in condensation copolymers having large comonomer subunits cannot be easily determined by current methods, including the n.m.r. technique which has proved of general utility in the case of vinyl, olefin and diene copolymers[8]. Therefore it is sometimes difficult to establish if a condensation copolymer has exactly alternating, block or random structure. Often the sequence is assumed only on the basis of the synthetic method.

In this report, we describe the synthesis of three exactly alternating copolyesters I–III from α-truxilloyl chloride and bis(2-hydroxymethylenephenyl)adipate, bis(3-hydroxypropylene)terephthalate or bis(2-hydroxyethylene)terephthalate, respectively, by the solution polymerization method. Because of the presence of the cyclobutane units in the main chain, these materials show a marked disposition towards photolysis, as already observed in the polyamide case[9].

We have used the fast-atom bombardment–mass spectrometry (f.a.b.–m.s.) technique to identify the synthetic oligomers contained in the crude samples I–III. The structural analysis of oligomers detected in the f.a.b.(+) and f.a.b.(−) mass spectra allowed us to ascertain the exactly alternating sequence of comonomers in copolyesters I–III.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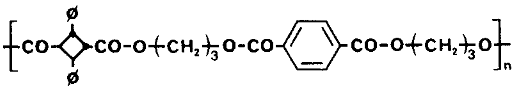
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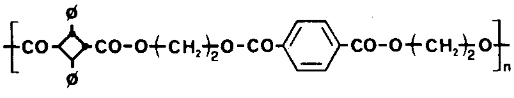
III

EXPERIMENTAL

Materials

Basic materials were commercial products appropriately purified before use.

α-Truxillic acid was prepared according to the following procedure. A water suspension of commercial *trans*-cinnamic acid maintained under stirring was

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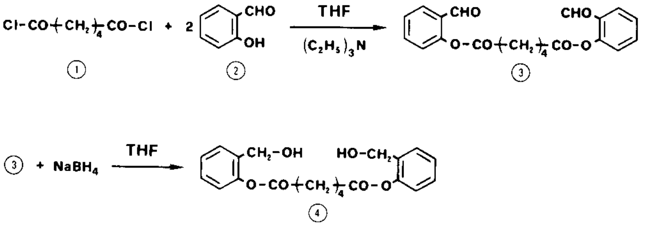


Scheme I

irradiated with the light emitted by a Q 700 Hanau medium-pressure mercury lamp. After four days, the solid was repeatedly extracted with ethyl ether. The residue was crystallized from acetic acid to give α-truxillic acid, m.p. 281–283°C. By treatment of this acid with an excess of thionyl chloride (using a trace of pyridine as catalyst), α-truxilloyl chloride was obtained. After crystallization from toluene, the product showed a m.p. of 122–124°C.

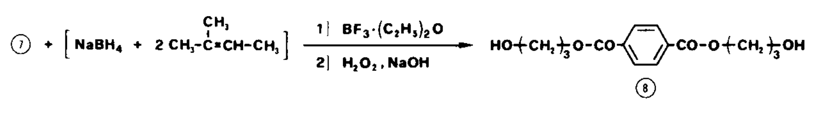
Comonomer syntheses

Bis(2-hydroxymethylenephenyl)adipate (*scheme 1*). First 17 g (0.093 mol) of adipoyl chloride **1** in 40 ml of tetrahydrofuran (THF) were slowly added to a solution of 23.2 g (0.19 mol) of salicylaldehyde **2** and 19 g (0.19 mol) of triethylamine (TEA) in 100 ml of THF at 0°C, under stirring. The solution was then refluxed for 1 h, cooled in a freezer and filtered to remove the TEA hydrochloride formed in the reaction. After distillation of the THF, the bis(salicylaldehyde)adipate **3** was crystallized from $CHCl_3/(C_2H_5)_2O$: m.p. 70–71°C. The white crystals obtained were analysed by ^1H n.m.r. and electron impact mass spectrometry (e.i.–m.s.).

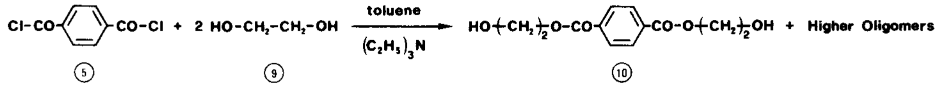
The reduction of compound **3** to obtain the bis(2-hydroxymethylenephenyl)adipate **4** was performed by using sodium borohydride. First 21.7 g (0.061 mol) of **3** were dissolved in 100 ml of THF and cooled at about −10°C. Then a 10% solution of $NaBH_4$ in H_2O was slowly added maintaining the temperature at less than −5°C, until all the aldehyde was reduced to alcohol and a drop of this THF solution poured into dilute H_2SO_4 produced H_2 (indicating the presence of $NaBH_4$ in excess). After neutralization of the solution with dilute H_2SO_4, the THF was distilled and the residue extracted by $CHCl_3$. The bis(2-hydroxymethylenephenyl)adipate **4** so obtained was purified by preparative h.p.l.c. (Whatman, Partisil M9 10/25; eluant, $CHCl_3$ with 2% of $(C_2H_5)_2O$) and then crystallized from $(C_2H_5)_2O$: m.p. 96–97°C. The white crystals obtained were analysed by ^1H n.m.r. in $CDCl_3$ (singlet at 7.59 ppm: hydroxylic hydrogen atoms; multiplet at 6.8–7.3 ppm: aromatic hydrogen atoms; singlet at 5.11 ppm: benzylic hydrogen atoms; multiplets at 2.34 and 1.61 ppm: methylene hydrogen atoms) and e.i.–m.s. (molecular ion at m/z 358).

Bis(3-hydroxypropylene)terephthalate (*scheme 2*). First of all 20.3 g (0.1 mol) of terephthaloyl chloride **5** in 50 ml of THF were slowly added to a solution of 11.9 g (0.205 mol) of allyl alcohol **6** and 20.7 g (0.205 mol) of TEA in 100 ml of THF at 0°C, under stirring. After 1 h of refluxing, the solution was cooled in a freezer and the TEA hydrochloride formed in the reaction filtered. The pale yellow oil obtained after distillation of THF was then purified by preparative h.p.l.c. (Whatman, Partisil M9 10/25; eluant, petroleum ether with 30% $CHCl_3$). The bis(allyl)terephthalate **7**, recovered as a colourless oil that solidified in a freezer, was characterized by e.i.–m.s. (molecular ion at m/z 246).

The hydroboronation–oxidation of **7** to obtain the bis(3-hydroxypropylene)terephthalate **8** was performed according to the procedure of Brown and Zweifel[10]. First 2.6 g (0.068 mol) of $NaBH_4$ were dissolved in 50 ml of diglyme at 0°C under stirring and N_2 flow, and 12.6 g (0.18 mol) of 2-methyl-2-butene were added. Then 12.8 g (0.09 mol) of BF_3–$(C_2H_5)_2O$ were added in 30 min (a white suspension was formed). After 1 h at 0°C, 8.4 g (0.034 mol) of **7** in 5 ml of diglyme were added in 5 min, and the solution heated at room temperature. After 2 h, the solution was cooled to 0°C and the boron derivative oxidized by a solution of 3 g of NaOH in 25 ml of H_2O and 27 ml of 30% H_2O_2. The diglyme/water solution so obtained was then extracted with 300 ml of $CHCl_3$ which, after distillation, gave a white residue. The bis(3-hydroxypropylene)terephthalate **8** was recovered from this residue by preparative h.p.l.c. (Whatman, Partisil M9 10/25; eluant, CH_2Cl_2 with 15% CH_3–CO–CH_3) and crystallized from acetone/toluene: m.p. 83–85°C. It was characterized by ^1H n.m.r. in $CDCl_3$ (singlet at 8.09 ppm: aromatic hydrogen atoms; two triplets at 4.41 and 3.70 ppm and a multiplet at 1.93 ppm: methylene hydrogen atoms; singlet at 2.86 ppm: hydroxylic hydrogen atoms) and by e.i.–m.s. (protonated molecular ion at m/z 283).



Scheme II



Scheme III

Bis(2-hydroxyethylene)terephthalate (*scheme 3*). This monomer was synthesized by adding a solution of 20.3 g (0.1 mol) of terephthaloyl chloride **5** in 50 ml of toluene to a solution of 26 g (1 mol, five times the stoichiometric amount) of ethylene glycol and 20.2 g (0.2 mol) of TEA, under stirring. After 1 h the solvent (toluene and the excess of ethylene glycol) was distilled and the residue (bis(2-hydroxyethylene)terephthalate **10**, higher oligomers and TEA hydrochloride) was extracted by boiling water. The compound **10**, crystallized by cooling of this solution (m.p. 106–107°C according to the literature[11]), was characterized by ^{1}H n.m.r. (singlet at 8.14 ppm: aromatic hydrogen atoms; two triplets at 4.38 and 3.81 ppm: methylene hydrogen atoms; singlet at 3.02 ppm: hydroxylic hydrogen atoms) and e.i.–m.s. (protonated molecular ion at *m/z* 255).

Alternating copolyester syntheses

Alternating copolymers I–III were synthesized by reaction of truxilloyl chloride with bis(2-hydroxymethylenephenyl)adipate, bis(3-hydroxypropylene)-terephthalate or bis(2-hydroxyethylene)terephthalate, respectively, according to the solution polycondensation method, using THF as solvent and TEA as HCl acceptor. After filtration of the formed TEA hydrochloride, the crude copolymers were recovered by distillation of the solvent. In this way, oligomer-rich copolyesters suitable for direct f.a.b.–m.s. analysis were obtained.

G.p.c. analysis

A Waters 6000 A apparatus equipped with four micro-Styragel columns (in the order 1000, 500, 10 000, 100 Å pore size) was used. The analyses were performed at 25°C using THF as eluant at a flow rate of 0.7 ml min^{-1}.

Viscometry

Inherent viscosities of the polymers investigated ($\eta_{\text{inh}} = \ln \eta_r / C$; $C = 0.5\,\text{g dl}^{-1}$) were measured in a Desreux–Bishoff suspended level viscometer containing a coarse sintered glass filter attached just below the reservoir through which the solution passes as it rises into the capillary. THF was used as solvent at a temperature of 30±0.01°C. Pertinent values are: polymer I, $\eta_{\text{inh}} = 0.09$; polymer II, $\eta_{\text{inh}} = 0.12$; polymer III, $\eta_{\text{inh}} = 0.10$.

Thermogravimetry

Thermogravimetric analyses were performed with a Perkin–Elmer TGS-2 apparatus in an N_2 atmosphere (flow rate of 60 ml min^{-1}) using a heating rate of 10°C min^{-1}. Pertinent values of the temperature of maximum rate of polymer degradation (*PDT*) are: polymer I, *PDT* = 365°C; polymer II, *PDT* = 400°C; polymer III, *PDT* = 420°C.

Mass spectrometry

F.a.b. analyses were performed on a double-focusing Kratos MS 50 S mass spectrometer equipped with the standard f.a.b. source. Mass spectra were recorded by using a u.v. recorder. Xenon was used as bombarding gas, with an energy of 8 kV. Mass resolution was approximately 2000. A mixture of CsI/RbI (50/50 wt%) was used as calibrant (calibration range: *m/z* 28–1900). Spectra were obtained by using 3-nitrobenzyl alcohol as matrix.

B/E and B^2/E f.a.b. mass spectra[12] were performed by using a linked scan unit, at a scan rate of 30 s/decade, and recorded on a u.v. recorder.

The e.i. mass spectra were achieved at 18 eV.

RESULTS AND DISCUSSION

In order to obtain exactly alternating copolyesters, suitable monomeric diols containing an adipic (bis(2-hydroxymethylenephenyl)adipate) or terephthalic (bis(3-hydroxypropylene)terephthalate and bis(2-hydroxyethylene)terephthalate) unit were synthesized (see 'Experimental' section).

A careful purification of these monomers and an accurate analysis (t.l.c., n.m.r., m.s.) of their purity was made before their polycondensation reaction with α-truxilloyl chloride, to assure the exactly alternating structure of the resulting copolyesters I–III.

The polymerization solution method was selected to obtain copolymeric materials with a large amount of low-molecular-weight oligomers, which can be directly analysed by f.a.b.–m.s.[13]. As expected, the g.p.c. traces (*Figure 1*) of the crude copolyesters I–III showed numerous peaks.

In order to obtain a more accurate identification of the species present in the mixtures, both positive and negative ions emitted during the f.a.b. analyses of crude copolyesters I–III samples were recorded, because different families of oligomers show remarkably different responses to positive or negative detection modes. This behaviour is particularly evident in *Figure 2*, in which the negative and positive f.a.b. mass spectra of alternating copolyester I are compared.

Open-chain oligomers having truxillic acid and/or benzyl alcohol end-groups (**1**, **2** and **3**, *Figure 2* and *Table 1*) are the molecular ions appearing in the f.a.b.(−) mass spectrum. Only two molecular ions (*m/z* 619 and 1237)

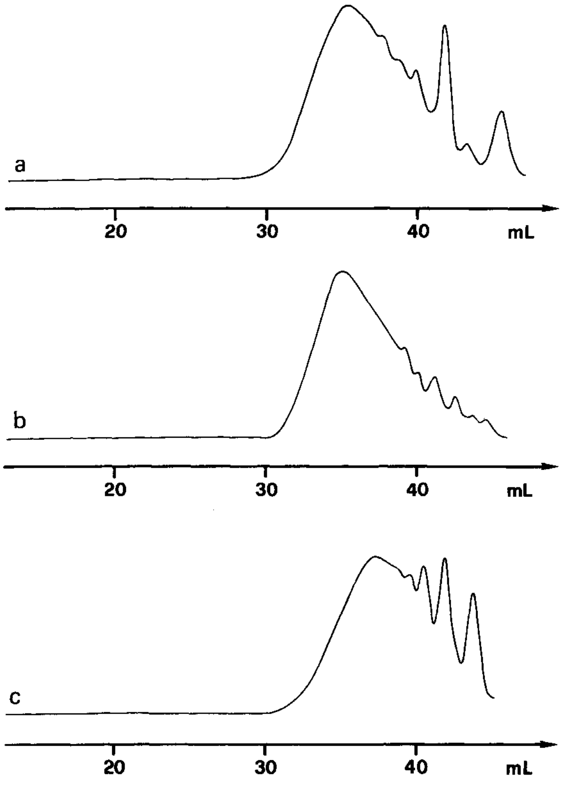


Figure 1 G.p.c. tracts (THF as eluant) of (a) alternating copolyester I, (b) alternating copolyester II and (c) alternating copolyester III

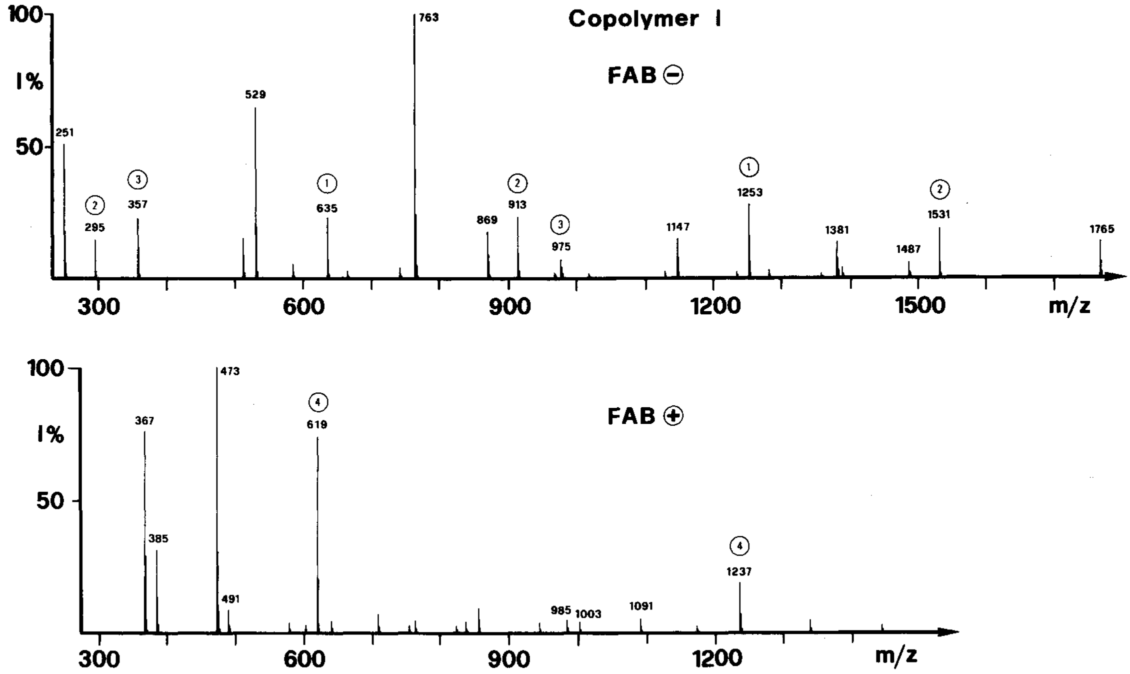
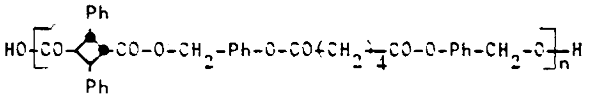
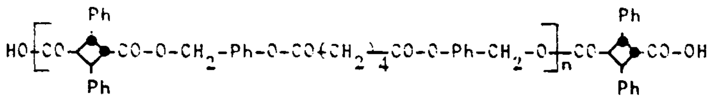
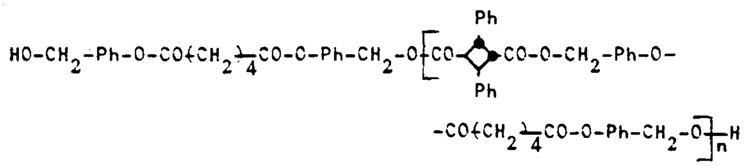
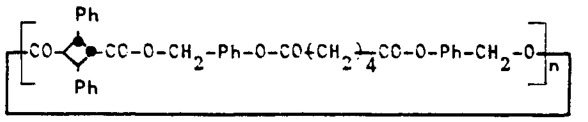


Figure 2 Negative and positive f.a.b. mass spectra of the crude alternating copolyester I. In the spectra are also indicated, according to the symbols used in *Table 1*, the molecular ions of oligomers having the same end-groups

Table 1 Open-chain and cyclic oligomers present in the copolyester I and their second fragment ions detected in the f.a.b.(−) and f.a.b.(+) mass spectra

Symbol and structure of oligomers	Molecular ions		Secondary fragment ions	
	F.a.b.(−) *m/z*(*n*)	F.a.b.(+) *m/z*(*n*)	F.a.b.(−) *m/z*	F.a.b.(+) *m/z*
1 	635(1) 1253(2) [1871(3)][b]		529[a] 1147[a] 1765	
2 	295(0) 913(1) 1531(2)			
3 	357(0) 975(1) [1593(2)][b]		251[a] 869[a], 763[a] 1487, 1381[a]	
4 		619(1) 1237(2)		491[a], 473[a], 385[a], 367[a] 1091, 1003, 985

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[a] Transition confirmed by *B*/*E* experiments

[b] The presence of these molecular ions is deduced on the basis of their secondary fragment ions at *m*/*z* 1765 and *m*/*z* 1487 and 1381, respectively

corresponding to cyclic oligomers (**4**, *Figure 2* and *Table 1*) are detected in the f.a.b.(+) mass spectrum. All the other peaks present in the two mass spectra (*Figure 2*) have been identified as secondary fragment ions of oligomers at higher molecular weight (parent ions) on the basis of f.a.b. linked scans (B/E or B^2E) analyses (*Table 1*).

In *Figure 3* the negative and positive f.a.b. mass spectra of the oligomers present in the crude alternating copolyester II are reported. The structures corresponding to the peaks appearing in *Figure 3* are identified in *Table 2*.

In the f.a.b.(−) mass spectrum (*Figure 3*) oligomeric

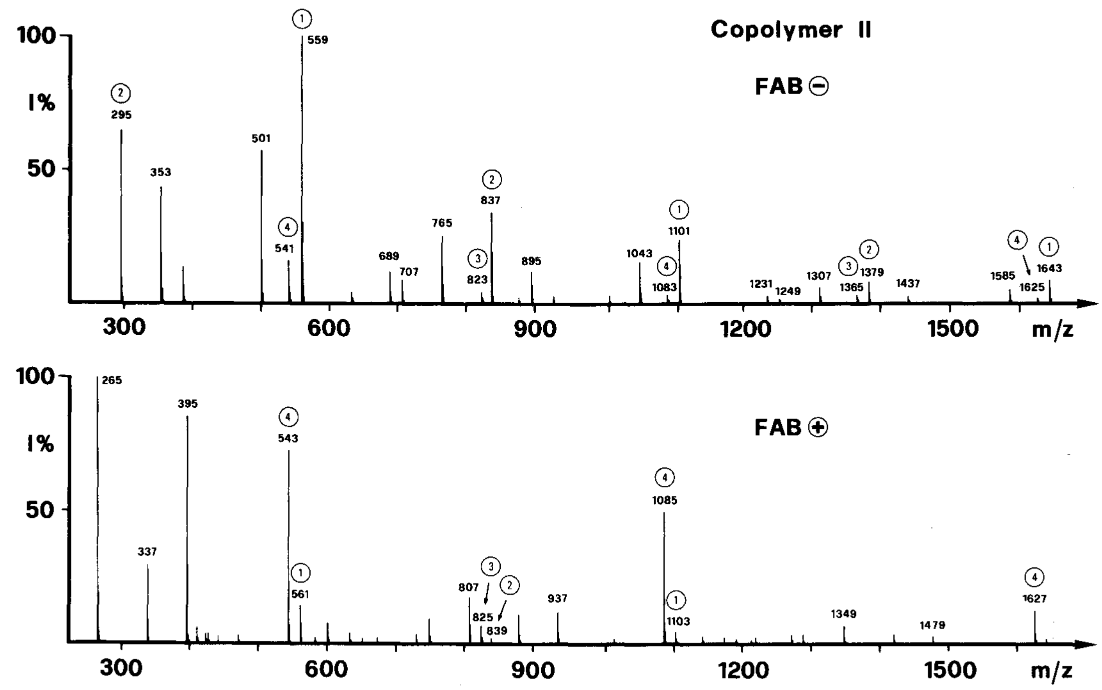
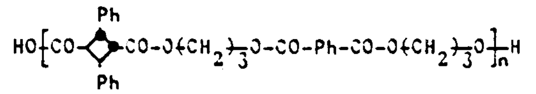
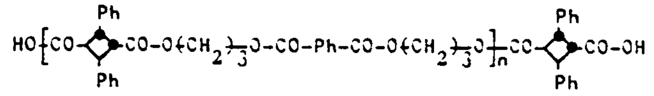
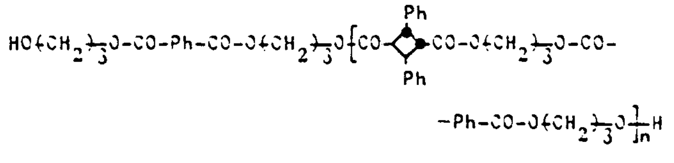
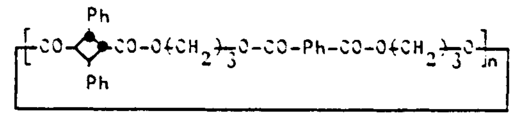


Figure 3 Negative and positive f.a.b. mass spectra of the crude alternating copolyester II. In the spectra are also indicated, according to the symbols used in *Table 2*, the molecular ions of oligomers having the same end-groups

Table 2 Open-chain and cyclic oligomers present in the copolyester II and their second fragment ions detected in the f.a.b.(−) and f.a.b.(+) mass spectra

Symbol and structure of oligomers		Molecular ions		Secondary fragment ions		
		F.a.b.(−) *m/z(n)*	F.a.b.(+) *m/z(n)*	F.a.b.(−) *B/E*	F.a.b.(+) *B/E*	F.a.b.(+) B^2/E^a
1		559(1) 1101(2) 1643(3)	561(1) 1103(2)	501, 353 1043, 895 1585, 1437		
2		295(0) 837(1) 1379(2)	839(1)	689 1231		
3		823(1) 1365(2)	825(1)	765, 707 1307, 1249		
4		541(1) 1083(2) 1625(3)	543(1) 1085(2) 1627(3)		395, 265 937, 807 1479, 1349	395^b(287.3) 937(808)

[a] Values of the metastable transition peaks are given in parentheses

[b] This secondary fragment ion is subjected to another transition confirmed by B^2/E f.a.b. spectrum: 337(287.5)

species having acid/acid (*m/z(n)* 295(0), 837(1), 1379(2)) or acid/hydroxy (*m/z(n)* 559(1), 1101(2), 1643(3)) end-groups (**2** and **1**, *Table 2*) are present. On the contrary, the f.a.b.(+) mass spectrum clearly reveals the presence of cyclic oligomers (*m/z(n)* 543(1), 1085(2), 1627(3)) (**4**, *Table 2*), whereas the peaks corresponding to open-chain molecular ions appear with very low intensity. The oligomeric species having hydroxy/hydroxy end-groups (**3**, *Table 2*) are present in both the mass spectra with very low intensity, probably because of their low ionizability in these conditions.

F.a.b. linked scans (*B/E*) of the molecular ions corresponding to the oligomers detected in both f.a.b.(−) and f.a.b.(+) mass spectra and listed in *Table 2* were

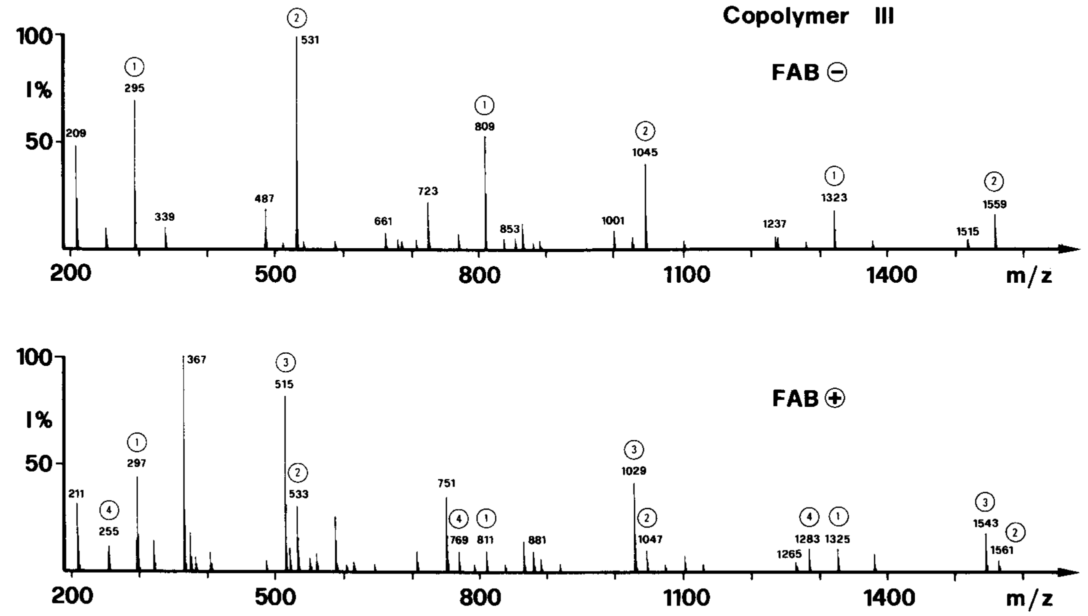
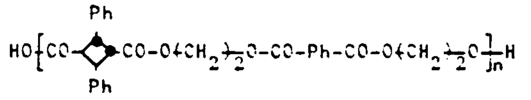
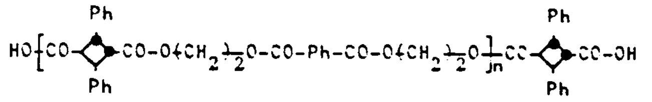
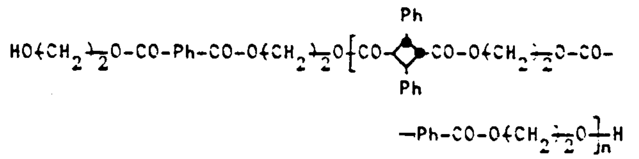
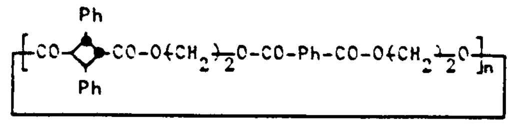


Figure 4 Negative and positive f.a.b. mass spectra of the crude alternating copolyester III. In the spectra are also indicated, according to the symbols used in *Table 3*, the molecular ions of oligomers having the same end-groups

Table 3 Open-chain and cyclic oligomers present in the copolyester III and their second fragment ions detected in the f.a.b.(−) and f.a.b.(+) mass spectra

		Molecular ions		Secondary fragment ions	
Symbol and structure of oligomers		F.a.b.(−) *m/z*(*n*)	F.a.b.(+) *m/z*(*n*)	F.a.b.(−) *m/z*	F.a.b.(+) *m/z*
2		531(1) 1045(2) 1559(3)	533(1) 1047(2) 1561(3)	487^{a}(446.6), 339^{b} 1001^{a}(958.8), 853 1515	
1		295(0) 809(1) 1323(2)	297(0) 811(1) 1325(2)	661	
4			255(0) 769(1) 1283(2)	209 723 1237	211 751 1265
3			515(1) 1029(2) 1543(3)		367^{b} 881^{b}

[a] Confirmed by B^2/E experiments; the corresponding metastable transition peaks are given in parentheses
[b] Confirmed by B/E experiments

performed. It was found that almost all the other peaks present in the spectra in *Figure 3* are due to secondary fragment ions, identified in *Table 2*. In some cases, parent ions (B^2/E mass spectra) allowed us to identify appropriate metastable transitions (*Table 2*).

In *Figure 4* the negative and positive f.a.b. mass spectra of alternating copolyester III are compared. Also in this case the molecular ions corresponding to linear oligomers having acid/acid (*m/z* 295, 809, 1323) or acid/hydroxy (*m/z* 531, 1045, 1559) end-groups (**2** and **1**, *Table 3*) are detected in the negative f.a.b. mass spectrum. As expected, their intensity decreases in the positive f.a.b. mass spectrum, in which cyclic oligomers (*m/z* 515, 1029, 1543) (**4**, *Table 3*) appear with higher intensity.

Also in this case, linked scans B/E and B^2/E (*Table 3* allowed us to identify some peaks in the two f.a.b. mass spectra (*Figure 4*) as deriving from oligomers at higher molecular weight by secondary ion fragmentation.

CONCLUSIONS

The f.a.b.–m.s. analysis appears to be a suitable method for the rapid identification of oligomers contained in synthetic copolyesters I–III.

In principle, f.a.b.–m.s. data only give information about the molecular weights of the oligomers contained in the crude copolymer sample, from which it is possible to determine the composition of the oligomers, but not the order in which the comonomers are arranged in their structure.

However, in the case of an alternating sequence of comonomers (A and B), one must find only f.a.b.–m.s. peaks of open-chain oligomers for which the number of comonomer A units is the same as or only one more or less than the number of comonomer B units, in the same molecule. In the case of cyclic oligomers, the number of comonomer A and B units in the same molecule must be the same.

This situation is actually reflected in the f.a.b. mass spectra of the copolyesters I–III (*Tables* 1–3), confirming the exactly alternating structure of these copolymers, the validity of the synthetic methods used and the analytical power of f.a.b.–m.s.

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REFERENCES

1 Tingerthal, J. M., Nava, H. and Percec, V. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 2043

2 Pedemonte, E., Leva, M., Gattiglia, E. and Turturro, A. *Polymer* 1985, **26**, 1202

3 De Candia, F., Petrocelli, V., Russo, R., Maglio, G. and Palumbo, R. *Polymer* 1986, **27**, 797

4 Ober, C., Lenz, R. W., Galli, G. and Chiellini, E. *Macromolecules* 1983, **16**, 1034

5 Lenz, R. W., Jin, J. and Feichtinger, K. A. *Polymer* 1983, **24**, 327

6 Jackson, W. J. Jr and Huhfuss, H. F. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 2043

7 Onwumere, F. C. and Polk, M. B. *J. Polym. Sci., Polym. Chem. Edn.* 1986, **24**, 2239

8 Kricheldorf, H. R., Joshi, S. V. and Hull, W. E. *J. Polym. Sci., Polym. Chem. Edn.* 1981, **20**, 2791; *Makromol. Chem.* 1978, **17**, 2133

9 Montaudo, G. and Scamporrino, E. in 'Developments in Polymer Degradation – 5' (Ed. N. Grassie), Applied Science, London, 1984, Ch. 4, p. 121

10 Brown, H. C. and Zweifel, G. *J. Am. Chem. Soc.* 1960, **82**, 3222

11 Sorenson, W. and Campbell, T. W. in 'Preparative Methods of Polymer Chemistry', Interscience, New York, 1968, p. 152

12 Jennings, K. R. and Mason, R. S. in 'Tandem Mass Spectrometry' (Ed. F. W. McLafferty), Wiley, New York, 1983, p. 197

13 Montaudo, G., Scamporrino, E. and Vitalini, D. *Macromolecules* in press