copolymers. The photolytic activity of the homopoly(adipoylpiperazine) IV is negligible, but it is degraded by hydrolysis. The FAB mass spectrum of the hydrolyzates is shown in Figure 6, and the structural assignments of the peaks are reported in Table III. Oligomers with all three kinds of end groups expected (acid/acid, acid/amine, and amine/amine) are found.

**Acknowledgment.** Partial financial support from the Italian Ministry of Public Education and from Consiglio Nazionale delle Ricerche (Roma) is gratefully acknowledged.

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# Characterization of Copolymer Sequences by Fast Atom Bombardment Mass Spectrometry. 2. Identification of Oligomers Contained in Alternating and Random Copolyesters with Photolabile Units in the Main Chain

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ABSTRACT: An exactly alternating copolyester containing ethylene truxillate and ethylene terephthalate units and three random copolyesters with different truxillic/terephthalic ratios were synthesized. The oligomers contained in each crude copolymer were directly analyzed by FAB mass spectrometry. Peaks at $m/z$ 1700 corresponding to oligomers at the heptad level were recorded, yielding diagnostic information about the copolymer sequences.

## Introduction

In the accompanying paper[1] we have reported the FAB-MS characterization of copolymer sequence by identifying the oligomers produced in the photolytic and hydrolytic degradation of some copolyamides.

The data permitted the characterizion of the copolymer sequence and the identification of end groups present in each oligomer, establishing the value of the FAB technique for the structural analysis of copolymer.[1]

In the examples given above, however, it was necessary to degrade the copolymer to obtain a mixture of low molecular weight oligomers in order to get meaningful FAB spectra.

Here we wish to discuss some cases where it is possible to proceed to the direct FAB analysis of copolymers by identifying the preformed synthetic oligomers contained in these materials.

This application derives from the finding that a pure, high molecular weight polymer does not yield significant peaks in the FAB mode,[2] implying that fast atom bombardment in a liquid matrix does not cause a selective fragmentation of the polymer backbone.

The formation of oligomers in polycondensation reactions is not limited only to the case of low monomer conversion, which must necessarily yield low molecular weight oligomers; the formation of oligomers also includes, high conversion, where the molecular weight distribution is shifted toward relatively high polymers.

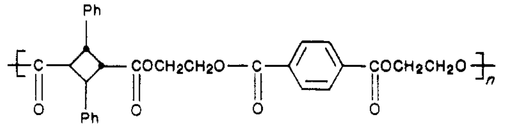
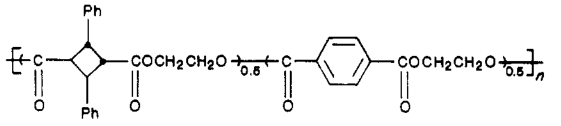
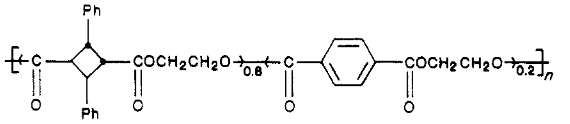
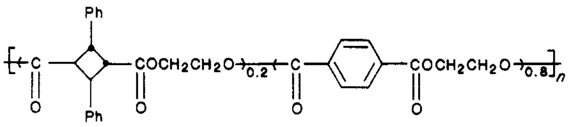
Oligomers contained in a crude polymer sample can be open-chain or cyclic compounds. The latter, formed through end-to-end biting or ring–chain equilibration processes,[3] might be partly hydrolyzed to linear oligomers both in the course of the polymerization reaction or during the work-up process (extraction, precipitation, washing, and drying).

Some common examples of cyclic oligomer hydrolysis are polyesters,[4,5] polycarbonates[6,7] (very sensitive to acids and humidity), and nylons.[8]

Therefore, the occurrence of cyclic and linear oligomers in a crude condensation copolymer sample appears to be quite general, and their structural analysis may lead to the characterization of the copolymer sequence.

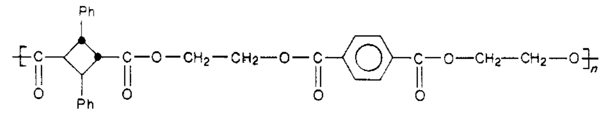
0024-9297/89/2222-0627$01.50/0

Table I
**Structure, Viscosity, Thermal Stability, and Composition of the Copolyesters I–IV Investigated**

| structure | $\eta_{inh}$[a] | PDT,[b] °C | truxillic/terephthalic ratio calcd | truxillic/terephthalic ratio found[c] |
|---|---|---|---|---|
|  I | 0.11 | 420 | 1 | 0.97 |
|  II | 0.09 | 420 | 1 | 1.04 |
|  III | 0.08 | 415 | 4 | 3.8 |
|  IV | 0.1 | 440 | 0.25 | 0.28 |

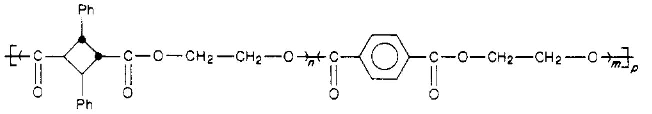
[a] $\eta_{inh} = (\ln \eta_r)/c$; $c$ = 0.5 g/dL in trifluoroethanol. [b] TG experiments under $N_2$, flow rate 60 mL/min, heating rate 10 °C/min. [c] By $^1H$ NMR spectra in DMSO-$d_6$.

We have synthesized an exactly alternating copolyester (I) containing ethylene terephthalate and ethylene truxillate units



I

and three random copolyesters corresponding to the same general formula:



II: $n$ = 0.5, $m$ = 0.5
III: $n$ = 0.8, $m$ = 0.2
IV: $n$ = 0.2, $m$ = 0.8

The FAB spectra of the crude copolyester samples show the presence of peaks corresponding to alternating or random sequences in a very clear way, allowing characterization of the sequence of subunits in these copolymers.

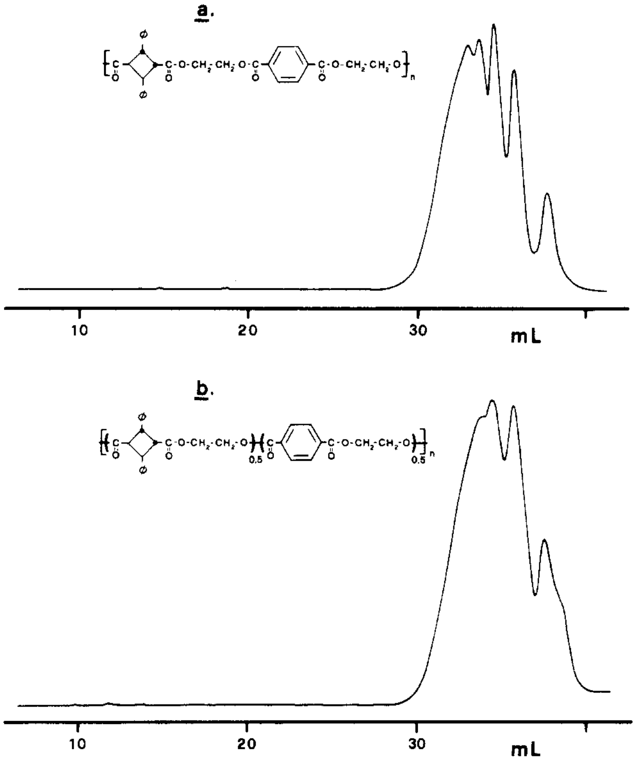


**Figure 1.** GPC traces (with THF as eluant) of (a) alternating copolyester I and (b) random copolyester (50:50) II.

## Experimental Section

**Materials.** Basic materials were commercial products appropriately purified before use.

**Bis(2-hydroxyethylene) Terephthalate Synthesis.** Bis(2-hydroxyethylene) terephthalate was synthesized by condensation of terephthaloyl chloride and a large excess of ethylene glycol (5 times the stoichiometric amount). The product was crystallized from boiling water (mp 106–107 °C[9]). The $^1H$ NMR spectrum (in acetonitrile-$d_3$) exhibited a singlet at 8.14 ppm (aromatic hydrogen atoms) and two triplets at 4.38 and at 3.81 ppm (methylene hydrogen atoms).

**Alternating Copolyester I Synthesis.** Copolymer I (Table I) was prepared by solution polycondensation of bis(2-hydroxyethylene) terephthalate and $\alpha$-truxilloyl chloride[1] using THF as solvent and triethylamine as acceptor of HCl. After filtration of insoluble triethylamine hydrogen chloride, the solution was poured into water and the copolymer recovered by filtration.

**Random Copolyesters II–IV Syntheses.** Copolyesters II–IV were prepared in the same way as copolymer I, starting from

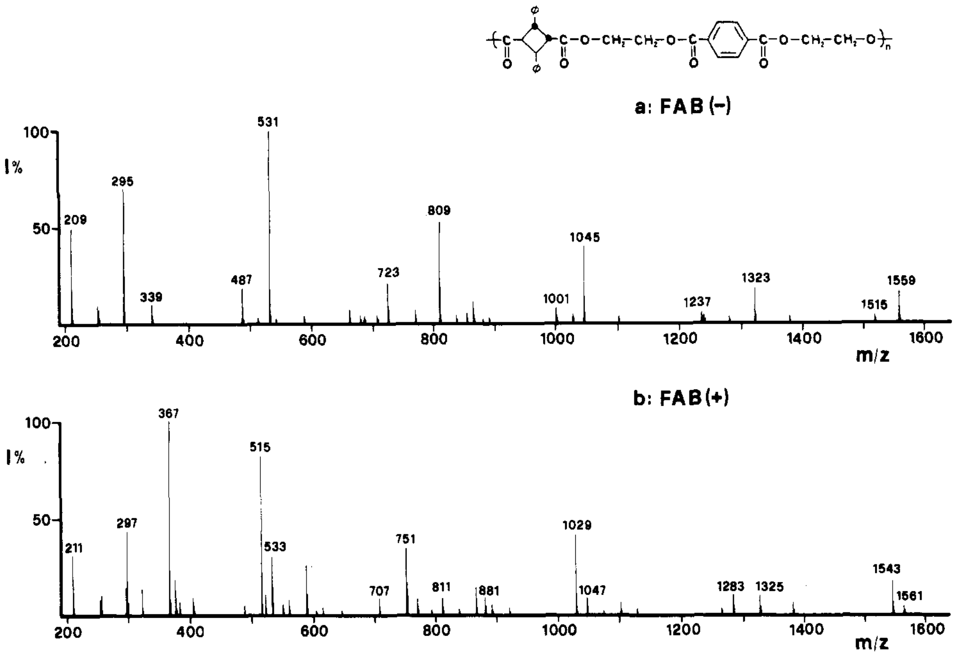
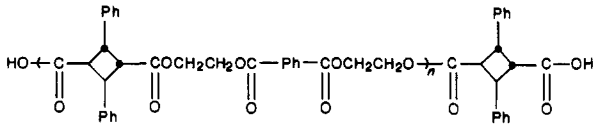
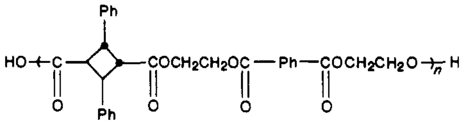
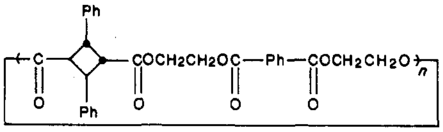
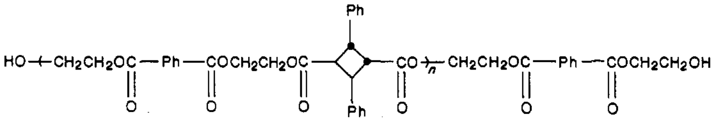


**Figure 2.** (a) Negative FAB mass spectrum and (b) positive FAB mass spectrum of the crude alternating copolyester I.

**Table II**
**Open-Chain and Cyclic Oligomers Present in Copolymer I and Their Second Fragment Ions Detected in the FAB(−) and FAB(+) Mass Spectra**

| | open-chain and cyclic oligomers | | second fragment ions | |
|---|---|---|---|---|
| structure | FAB(−), m/z (n) | FAB(+), m/z (n) | FAB(−), m/z | FAB(+), m/z |
|  1 | 295 (0) | 297 (0) | | |
| | 809 (1) | 811 (1) | (−148) 661 | |
| | 1323 (2) | 1325 (2) | | |
|  2 | 531 (1) | 533 (1) | ($B^2/E$, 446.6) 487, ($B/E$) 339 | |
| | 1045 (2) | 1047 (2) | ($B^2/E$, 958.8) 1001, 853 | |
| | 1559 (3) | 1561 (3) | 1515 | |
|  3 | | 515 (1) | | ($B/E$) 367 |
| | | 1029 (2) | | ($B/E$) 881 |
| | | 1543 (3) | | |
|  4 | | 255 (0) | (−44) 209 | (−44) 211 |
| | | 769 (1) | (−44) 723 | (−18) 751 |
| | | 1283 (2) | (−44) 1237 | (−18) 1265 |

[a] Secondary fragmentations were in some cases confirmed by $B/E$ or $B^2/E$ experiments, as indicated beside the mass values of the corresponding fragment ions. The mass value reported beside the $B^2/E$ value (in parentheses) corresponds to the metastable transition peak detected in the $B^2/E$ experiment.

ethylene glycol and a mixture of terephthaloyl and α-truxilloyl chlorides in the appropriate amount.

The truxillic/terephthalic ratio in each copolymer was determined by $^1H$ NMR spectra (Table I).

**Copolymer Characterization Techniques.** Viscosity measurements were carried out at 30 ± 0.01 °C in TFE by using a Desreux-Bishoff suspended level viscometer that contains a coarse sintered glass filter attached just below the reservoir through which the solution passes as it rises into the capillary. Pertinent inherent viscosities ($\eta_{inh} = (\ln \eta_r)/c$; $c = 0.5$ g/dL) are listed in Table I.

$^1H$ NMR spectra were recorded in DMSO-$d_6$ solution with TMS as an internal standard on a Bruker P 80 spectrometer.

Thermogravimetric analyses were performed on a Perkin-Elmer TGS-2 apparatus in a nitrogen atmosphere (60 mL/min) using

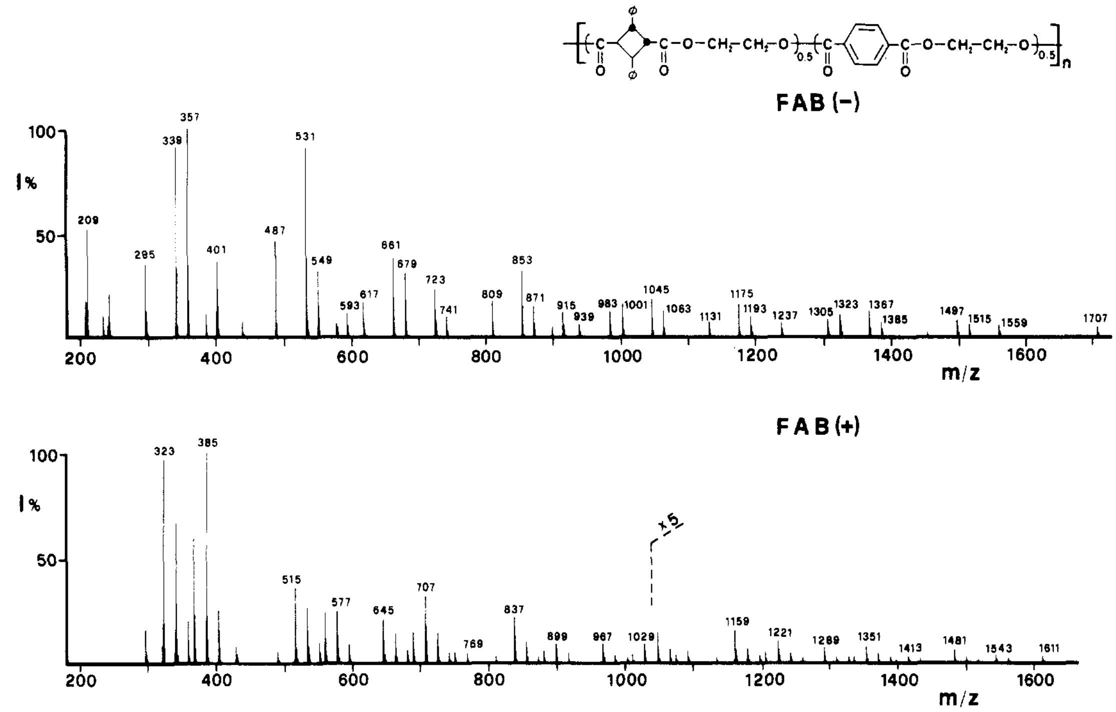
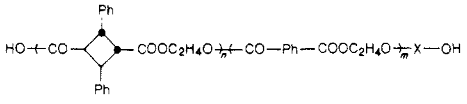
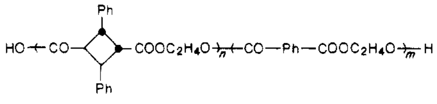
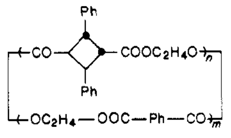


**Figure 3.** (a) Negative FAB mass spectrum and (b) positive FAB mass spectrum of the crude random copolyester (50:50) II.

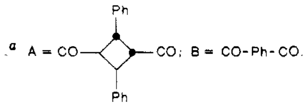
**Table III**
**Open-Chain and Cyclic Oligomers Present in the Random Copolymer II Detected in the FAB(-) and FAB(+) Mass Spectra**


x


y


z

| | | x | | | y | | z |
|---|---|---|---|---|---|---|---|
| *n* | *m* | X[a] | FAB(-), *m/z* | FAB(+), *m/z* | FAB(-), *m/z* | FAB(+), *m/z* | FAB(+),[b] *m/z* |
| 0 | 0 | A | 295 | 297 | | | |
| | | B | | | | | |
| 0 | 1 | A | 487 | 489 | 209 | | |
| | | B | 357 | 359 | | | |
| 0 | 2 | A | 679 | 681 | 401 | 403 | 385 |
| | | B | 549 | 551 | | | |
| 0 | 3 | A | 871 | 873 | 593 | 595 | 577 |
| | | B | 741 | 743 | | | |
| 0 | 4 | A | 1063 | 1065 | | | 769 |
| | | B | | | | | |
| 0 | 5 | A | | 1257 | | | |
| | | B | | | | | |
| 1 | 0 | A | 617 | | 339 | 341 | |
| 1 | 1 | A | 809 | 811 | 531 | 533 | 515 |
| 1 | 2 | A | 1001 | 1003 | 723 | 725 | 707 |
| 1 | 3 | A | 1193 | 1195 | 915 | 917 | 899 |
| 1 | 4 | A | 1385 | 1387 | | | 1091 |
| 2 | 0 | A | 939 | | 661 | 663 | 645 |
| 2 | 1 | A | 1131 | 1133 | 853 | 855 | 837 |
| 2 | 2 | A | 1323 | 1325 | 1045 | 1047 | 1029 |
| 2 | 3 | A | 1515 | 1517 | 1237 | 1239 | 1221 |
| 2 | 4 | A | 1707 | | | 1431 | 1413 |
| 3 | 0 | A | | | 983 | 985 | 967 |
| 3 | 1 | A | 1453 | | 1175 | 1177 | 1159 |
| 3 | 2 | A | | | 1367 | 1369 | 1351 |
| 3 | 3 | A | | | 1559 | 1561 | 1543 |
| 4 | 0 | A | | | 1305 | 1307 | 1289 |
| 4 | 1 | A | | | 1497 | 1499 | 1481 |
| 4 | 2 | A | | | | | |
| 5 | 0 | A | | | | | 1611 |

[a] 

[b] Only the FAB(+) spectrum yields molecular ions corresponding to cyclic oligomers.

a heating rate of 10 °C/min. Pertinent temperatures of the maximum rate of polymer degradation (PDT) are reported in Table I.

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 an UV recorder. Xenon was used as the bombarding gas, with an energy of 8 kV. Mass resolution was approximately 2000. A mixture of CsI/RbI (50/50 w/w) was used as the calibrant (calibration range: $m/z$ 28–1800). Spectra were obtained by using 3-nitrobenzyl alcohol (3-NBA) as the matrix.

$B/E$ and $B^2/E$ scans were performed by using a linked scan unit, at a scan rate of 30 s/decade, and recorded on a UV recorder.

GPC analyses were performed by a Waters 6000 A apparatus equipped with four columns of micro-Styragel (in the order $10^3$-, 500-, $10^4$-, and $10^2$-Å pore size). A differential refractometer Model R 401 from Waters was used as the detector. The analyses were performed at 25 °C by using THF as eluant at a flow rate of 1 mL/min. As an example, in Figure 1 the GPC traces of copolymers I and II are reported.

## Results and Discussion

Both positive and negative ions emitted during the FAB analyses of copolyesters I–IV were recorded. This allows a more complete detection of the species present in the mixture, because different families of molecules show remarkably different responses in positive and negative modes.

This effect is particularly evident in Figure 2, where the positive and negative FAB spectra of alternating copolyester I are compared. In fact, linear oligomers bearing acid end groups (denoted **1** and **2** in Table II) are the only molecular ions appearing in Figure 2a, because the preformed carbanions are most easily desorbed in the negative FAB mode. Their intensity decreases in the positive FAB mode (Figure 2b), in which the cyclic oligomers (denoted **3** in Table II) show the highest response. The oligomeric species having hydroxy end groups (compounds **4** in Table II) are also present in Figure 2b, although with low intensity. No information can be extracted from these FAB spectra on the relative abundance of the oligomers present in the mixture, because secondary fragmentation of the higher molecular weight ions is occurring.

FAB linked scans[10] of the molecular ions corresponding to the oligomers listed in Table II were performed; it was found that some peaks are obtained as daughter ions ($B/E$ spectra) from higher molecular weight ions (parent ions). Other peaks present in the spectra in Figure 2 are due to secondary fragment ions, identified in Table II. Parent ions ($B^2/E$ spectra) confirm the results obtained by the $B/E$ spectra and allow us to identify appropriate metastable transitions (Table II).

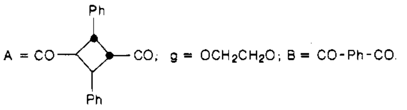
Correlation of FAB and GPC data (Figures 2 and 3 and Figure 1, respectively) is not possible in the present case. In fact, several compounds detected in the FAB spectra, corresponding to the series of cyclic and open-chain oligomers theorically expected, show similar retention times in the GPC traces, so that each peak actually is the convolution of more signals.

However, quantitative analysis of the mixture components is not necessary in order to characterize the sequence of copolyester I by FAB-MS data in Figure 2 and Table II, and its alternating structure is evident in each oligomer reported in Table II. All the peaks in the spectra in Figure 2 are identified (Table II), and they represent the four oligomer series that can be expected from the synthetic scheme (terephthalic acid cannot appear as an end group).

On the contrary, the FAB spectra in Figure 3 clearly reveal the random structure of the 50/50 copolyester II, as can be seen from the peak assignments reported in Table III.

**Table IV**
**Open-Chain and Cyclic Oligomers Present in the Copolyesters II–IV Detected in the FAB(–) and FAB(+) Mass Spectra**

| oligomers[a] formula | | FAB(–), $m/z$ $(M-1)^-$ | | |
|---|---|---|---|---|
| | | $HO-\underset{\underset{O}{\|}}{C}\sim\sim\sim\underset{\underset{O}{\|}}{C}-OH$ [b] | $HO-\underset{\underset{O}{\|}}{C}\sim\sim\sim CH_2-CH_2OH$ [c] | $\boxed{-\underset{\underset{O}{\|}}{C}\sim\sim\sim O-}$ [d] |
| A | [e] | 295 | 339 | |
| B | | | 209 | |
| ABg | | 487 | 531 | 513 |
| $AB_2g_2$ | | 679 | 723 | 707 |
| $A_2Bg_2$ | | 809 | 853 | 837 |
| $A_2B_2g_3$ | | 1001 | 1045 | 1029 |
| $A_2B_3g_4$ | | 1193 | 1237 | 1221 |
| $A_3B_2g_4$ | | 1323 | 1367 | 1351 |
| $A_3B_3g_5$ | | 1515 | 1559 | 1543 |
| $A_3B_4g_6$ | | 1707 | | |
| $A_2g$ | [f] | 617 | 661 | 645 |
| $A_3g_2$ | | 939 | 983 | 966 |
| $A_3Bg_3$ | | 1131 | 1175 | 1159 |
| $A_4g_3$ | | 1261 | 1305 | 1289 |
| $A_4Bg_4$ | | 1453 | 1497 | 1481 |
| $A_5g_4$ | | 1583 | 1627 | 1611 |
| $A_4B_2g_5$ | | 1645 | 1689 | |
| $B_2g$ | [g] | 357 | 401 | 385 |
| $B_3g_2$ | | 549 | 593 | 577 |
| $B_4g_3$ | | 741 | | 769 |
| $AB_3g_3$ | | 871 | 915 | 899 |
| $B_5g_4$ | | 933 | 977 | 961 |
| $AB_4g_4$ | | 1063 | 1107 | 1091 |
| $B_6g_5$ | | | 1169 | 1153 |
| $AB_5g_5$ | | | | 1283 |
| $B_7g_6$ | | | | 1345 |
| $A_2B_4g_5$ | | 1385 | | 1413 |
| $AB_6g_6$ | | | | 1475 |
| $A_2B_5g_6$ | | | | 1605 |



A = CO–◇–CO; g = $OCH_2CH_2O$; B = CO-Ph-CO.

[a] Abbreviated symbols corresponding to structural formula of oligomers with acid end groups are reported. Corresponding symbols for oligomers with acid and hydroxy end groups and for cyclic oligomers can be obtained by adding an ethylene glycol unit (g) to the symbols reported in the first column. [b] Oligomers with acid end groups. [c] Oligomers with acid and hydroxy end groups. [d] Cyclic oligomers. [e] Oligomers present also in the mass spectrum of alternating copolyester. [f] Oligomers with a higher truxillic unit content with respect to an alternating structure. [g] Oligomers with a higher terephthalic unit content with respect to an alternating structure.

Terephthalic acid end groups are present here (Figure 3 and Table III), and the oligomers detected show a variety of sequences ranging from ethylene truxillate oligoesters to ethylene terephthalate oligoesters (Table III).

Sequence lengths of oligomers detected reach the heptad level, as summarized in Table IV.

The relative abundance of oligomers containing different amounts of truxillic and terephthalic subunits is subject to change with the copolyester composition; this fact is reflected in the FAB spectra. In Figure 4 are compared the positive FAB spectra of three random copolyesters II–IV of different composition (Figure 4a, 80/20; Figure 4b, 50/50; Figure 4c, 20/80) in truxillic and terephthalic units.

Only peaks corresponding to cyclic oligomers have been reported in Figure 4. As expected, the oligomers detected in the case of the truxillic-rich copolyester (Figure 4a) show a higher truxillic units content with respect to the other two cases (parts b and c of Figure 4).

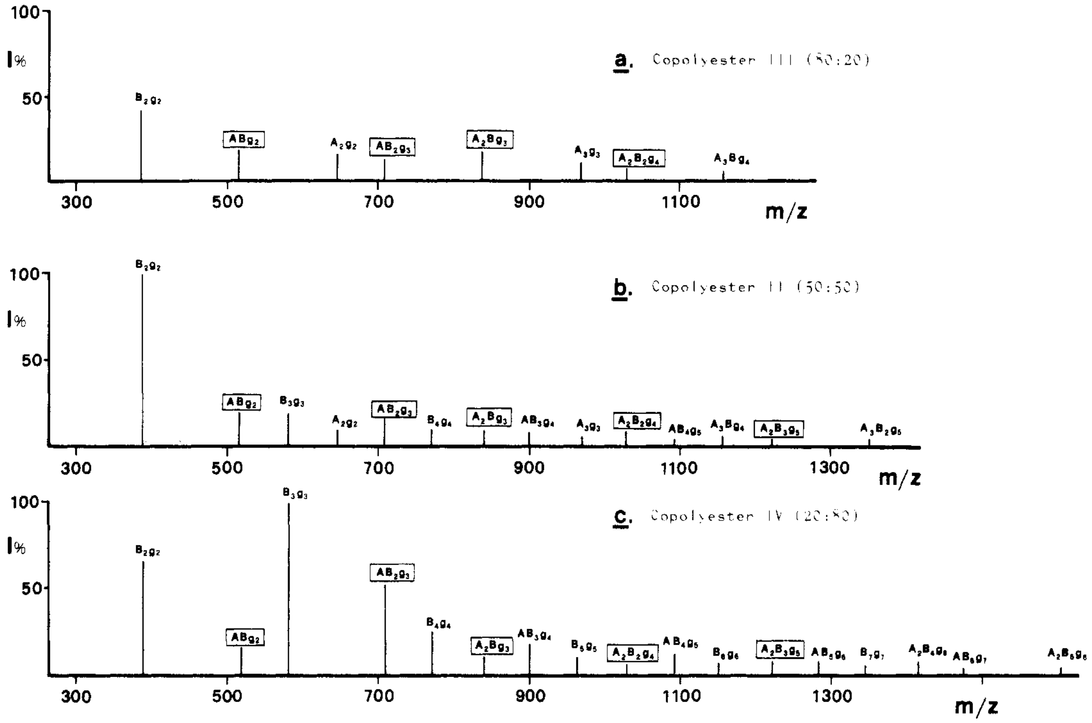


**Figure 4.** Quantitative comparison of the cyclic oligomers (for the *m/z* values and symbol identification see Table IV and footnotes *a* and *d*) detected in the positive FAB mass spectra of (a) random copolyester (80:20) III, (b) random copolyester (50:50) II, and (c) random copolyester (20:80) IV. The possible alternating structures are evidenced.

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**Registry No.** (Bis(2-hydroxyethylene)terephthalate)(α-truxilloyl chloride) (copolymer), 116558-26-0; (bis(2-hydroxyethylene) terephthalate)(α-truxilloyl chloride) (SRU), 116437-86-6; (ethylene glycol)(terephthaloyl chloride)(α-truxilloyl chloride) (copolymer), 116558-27-1.

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