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Characterization of Copolymer Sequences by Fast Atom Bombardment Mass Spectrometry. 1. Identification of Oligomers Produced in the Hydrolysis and Photolysis of Random Copolyamides Containing Photolabile Units in the Main Chain

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ABSTRACT: Poly(truxilloylpiperazine) (III), poly(adipoylpiperazine) (IV), and two random copolyamides (I and II) containing different amounts of photolabile units in the main chain were hydrolyzed or photolyzed. Oligomers produced by these degradation processes were identified by performing FAB-MS. The FAB spectra show peaks up to 2000 daltons. Oligomers having cinnamoyl end groups were detected in the photolyzed mixtures, whereas only oligomers with piperazine, truxillic, and/or adipic end groups were observed in the mass spectra of hydrolyzed samples. Therefore, the analysis of oligomers detected in FAB spectra yields information about the polymer structure, the copolymer sequence, and the kind of end groups present in each oligomer.

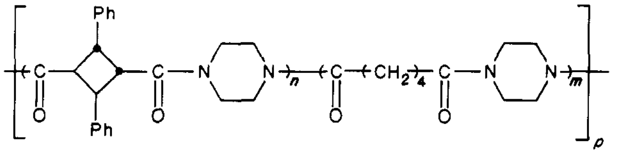
Introduction

The characterization of sequence arrangements in multicomponent condensation polymers having large comonomer subunits cannot be easily determined by current methods, including NMR, which otherwise has proved of general utility in the case of vinyl, olefin, and diene copolymers.[1]

The recent development of fast atom bombardment mass spectrometry (FAB-MS) has shown that this technique is of considerable value in structural characterization of proteins, because it allows the direct analysis of the mixtures of peptides produced by the enzymatic degradation of native and modified proteins.[2,3]

Although FAB mass spectra of synthetic polymer samples have been reported,[4-7] the technique has not yet been applied to the study of the sequence in synthetic copolymers, and there is considerable interest in exploring its potential in this field.

We have used FAB-MS to identify the oligomers formed in the hydrolysis and photolysis of the random copolyamides I and II



I: $n = 0.8, m = 0.2$
II: $n = 0.5, m = 0.5$

and their corresponding homopolyamides III and IV (Table I).

The FAB spectra of the oligomer mixtures show structurally significant peaks up to 1500–2000 daltons, allowing the characterization of the copolymer sequence and the identification of end groups present in each oligomer.

Experimental Section

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 rotating in a rotoevaporator was irradiated under a Q700 Hanau medium-pressure mercury lamp. After 96 h, the solid was repeatedly extracted with ethyl ether. The residue was crystallized from ethanol to give α-truxillic acid, mp 281–283 °C. By treatment of this acid with an excess of thionyl chloride in the presence of a trace of pyridine α-truxilloyl chloride was obtained, mp 122–124 °C.

Poly(truxilloylpiperazine), poly(adipoylpiperazine), and the two copolyamides I and II were prepared by interfacial polycondensation starting from piperazine and the respective acyl chloride or a mixture of two acyl chlorides. In a typical procedure of synthesis of copolyamide I, 0.95 g (0.011 mol) of piperazine and 2.33 g (0.022 mol) of Na_2CO_3 in 25 mL of water were placed in a Waring blender and precooled in a freezer. To the rapidly stirred system was added a solution containing 2.922 g (0.0088 mol) of α-truxilloyl chloride and 0.400 g (0.0022 mol) of adipoyl chloride in 20 mL of THF, in one application. The system was stirred for 5 min and poured into about 300 mL of water.

After some hours, the copolymer was filtered, washed with water, and dried in vacuo at 70 °C.

Polymer and Copolymer Characterization. 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 values of inherent viscosities ($\eta_{inh} = (\ln \eta_r)/c$; $c = 0.5$ g/dL) are reported in Table I.

Thermogravimetric analyses were performed with a Perkin-Elmer TGS-2 apparatus in a nitrogen atmosphere (60 mL/min) by using a heating rate of 10 °C/min. Pertinent values of temperature of maximum rate of polymer degradation (PDT) are reported in Table I.

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 with THF as the eluant at a flow rate of 1 mL/min.

FAB analyses were performed on a double-focusing Kratos MS 50 S mass spectrometer equipped with the standard FAB source. Mass spectra were recorded by using a UV recorder. Xenon was used as the bombarding gas, with an energy of 8 KV. The mass resolution was approximately 2000. A mixture of CsI/RbI (50/50 w/w) was used as a calibrant (calibration range 28–2000 daltons). Spectra were obtained by using 3-nitrobenzyl alcohol (3-NBA) as a matrix. B/E and B^2/E scans were performed by using a linked scan unit, at a scan rate of 20 s/decade, and were recorded on an UV recorder.

Photolyses of polymers and copolymers were performed by means of a low-pressure mercury lamp NN 15/44 (Quarzlampaugesellschaft Hanau) in spectrophotometric quartz cells (20-mm

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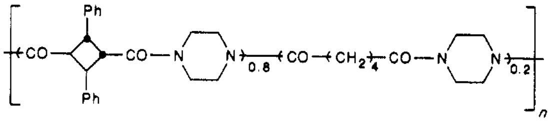
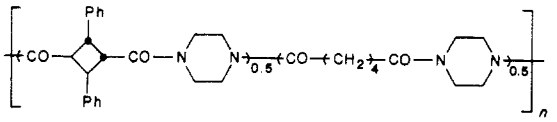
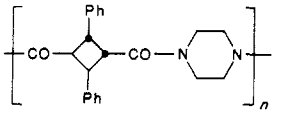
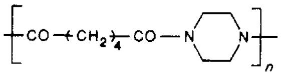
Table I
Structure, Viscosity, and Thermal Stability of Copolyamides I and II and Homopolyamides III and IV

samples	η_{inh}[a]	PDT,[b] °C
 I	0.11	420
 II	0.09	420
 III	0.08	415
 IV	0.10	440

[a] $\eta_{inh} = (\ln \eta_r)/c$; c = 0.5 g/dL. Experiments were carried out in trifluoroethanol. [b] TG experiments under N_2, flow rate 60 mL/min, heating rate 10 °C/min.

optical path) placed 10 cm from the lamp. Concentrations of the solutions were about 0.5 g of sample in 100 mL of solvent. At regular times, the solution was transferred in a Desreux-Bischoff suspended level viscometer for measuring the viscosity.

Hydrolyses of polymers and copolymers were performed in MSA + 30% H_2O solutions maintained at 70 °C for 5 days. In each case, after neutralization with NH_4OH solution, the insoluble residue was filtered, washed with water, and dried under vacuum.

Results and Discussion

Truxillic polyamides are photodegradable and photochromic materials, and the addition of small amounts of strong acids to solutions of these polymers induces a large increase in the rate of photolysis.[8] The latter finding produced the first example of an acid-catalyzed photoreaction, and subsequent studies allowed elucidation of the mechanism of the acid catalysis in terms of acid–base equilibria of the ground and excited states involved in the photolysis.[8-10]

Amides are very weak bases in the ground state but become much stronger bases in the first excited singlet state. Therefore, protonation of the amide group by means of strong acids occurs more efficiently when the sample is irradiated by UV light. In the case of polyamides containing truxillic units in the main chain, protonation of the amide group weakens the cyclobutane ring, and a strong catalytic effect on the photocleavage is observed.

This mechanism of action does not appear to be confined to amides, and other functional groups show similar effects.

The effect of the UV irradiation on the viscosity of copolyamide I in TFE and MSA solutions is compared in Figure 1, and it is apparent that the viscosity decrease is faster in MSA.

In Figure 2 the GPC traces of irradiated samples of copolyamide I in TFE + 1% MSA at different exposure times are reported; a marked lowering of the copolymer molecular weight was observed.

The photolytic cleavage of the cyclobutane rings generates oligomers containing cinnamoyl end groups. The lower molecular weights fraction of these oligomers (up to about 2000 daltons) can be detected by direct FAB-MS analysis of the irradiated crude samples.

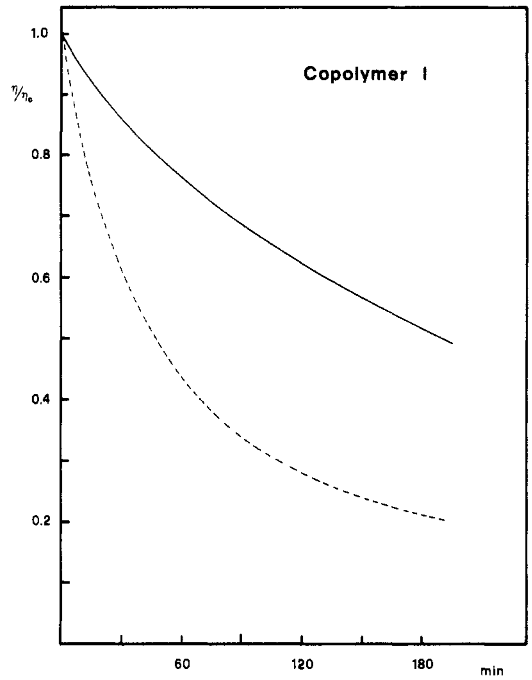


Figure 1. Effect of UV irradiation time on the viscosity of copolyamide I in TFE (—) and MSA (- - -) solutions.

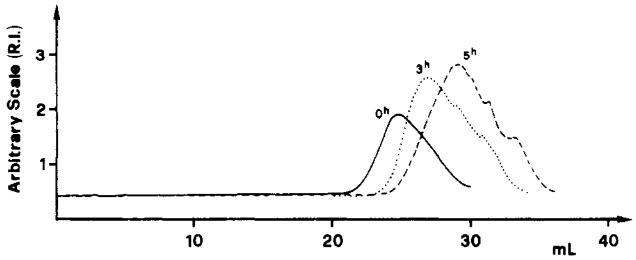


Figure 2. GPC traces (with THF as eluant) of irradiated samples of copolyamide I in TFE + 1% MSA at different exposition times.

In Figure 3 the positive FAB spectrum of the mixture of oligomers generated by irradiation UV of copolyamide

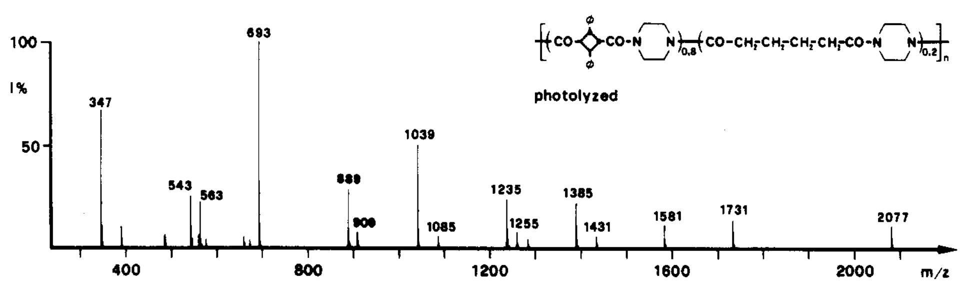


Figure 3. Positive FAB mass spectrum of oligomers generated by photolysis (5 h) of copolyamide I.

Table II
Oligomers Present in Polymer IV and Copolymers I and II Detected in the FAB(+) Mass Spectra

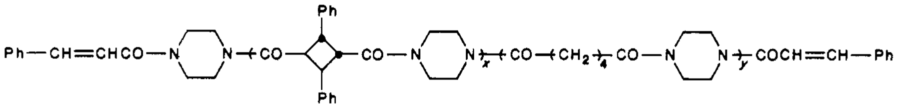
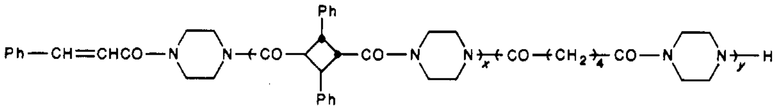
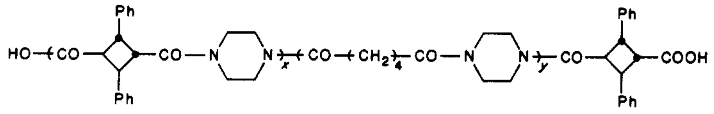
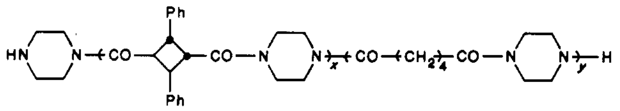
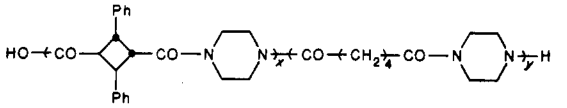
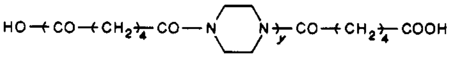
structures	polymer III, *m/z* (*x*, *y*)	copolymer I, *m/z* (*x*, *y*)	copolymer II, *m/z* (*x*, *y*)
	347 (0, 0) 693 (1, 0) 1039 (2, 0) 1385 (3, 0) 1731 (4, 0)	347 (0, 0) 543 (0, 1) 693 (1, 0) 889 (1, 1) 1039 (2, 0) 1085 (1, 2) 1235 (2, 1) 1385 (3, 0) 1431 (2, 2) 1581 (3, 1) 1731 (4, 0) 2077 (5, 0)	347 (0, 0) 543 (0, 1) 693 (1, 0) 739 (0, 2) 889 (1, 1) 1039 (2, 0) 1085 (1, 2) 1235 (2, 1) 1431 (2, 2)
	563 (1, 0) 909 (2, 0) 1255 (3, 0)	563 (1, 0) 909 (2, 0) 1255 (3, 0)	563 (1, 0) 609 (0, 2) 759 (1, 1) 909 (2, 0)

Table III
Oligomers Present in the Hydrolyzed Samples Detected in the FAB(-) Mass Spectra

structures	polymer IV, *m/z* (*x*, *y*)	polymer III, *m/z* (*x*, *y*)	copolymer II, *m/z* (*x*, *y*)
		365 (1, 0) 711 (2, 0) 1057 (3, 0) 1403 (4, 0) 1749 (5, 0)	365 (1, 0) 561 (1, 1) 711 (2, 0) 907 (2, 1) 1057 (3, 0) 1103 (2, 2) 1253 (3, 1) 1403 (4, 0) 1449 (3, 2) 1599 (4, 1) 1749 (5, 0) 1795 (4, 2)
	283 (0, 1) 479 (0, 2) 675 (0, 3) 871 (0, 4)	433 (1, 0) 779 (2, 0) 1125 (3, 0) 1471 (4, 0) 1817 (5, 0)	433 (1, 0) 779 (2, 0) 1125 (3, 0) 1471 (4, 0) 1817 (5, 0)
	411 (0, 2) 607 (0, 3) 803 (0, 4) 999 (0, 5) 1195 (0, 6)	643 (1, 0) 989 (2, 0) 1335 (3, 0) 1681 (4, 0)	493 (0, 1) 643 (1, 0) 689 (0, 2) 839 (1, 1) 989 (2, 0) 1035 (1, 2) 1185 (2, 1) 1335 (3, 0) 1381 (2, 2) 1531 (3, 1) 1681 (4, 0) 1727 (3, 2)
	343 (0, 1) 539 (0, 2) 735 (0, 3) 931 (0, 4) 1127 (0, 5)		

I, is reported. The structures corresponding to peaks appearing in Figure 3 are identified in Table II. As expected, they have cinnamoyl end groups, and the oligomer sequences detected reach the heptad level. Due to the high truxillic content in copolyamide I, only a few oligomers containing adipic units are formed by photolysis and de-

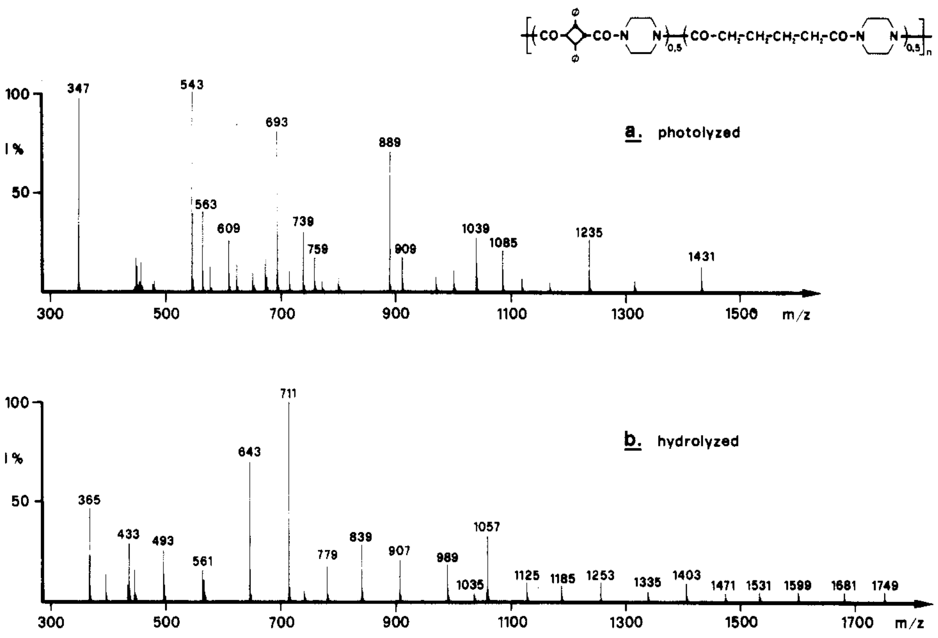


Figure 4. Positive FAB mass spectra of oligomers generated by (a) photolysis (in a TFE + 1% MSA solution after 5 h of exposition time) and (b) hydrolysis (after 5 days in a MSA + 30% H_2O solution) of copolyamide II.

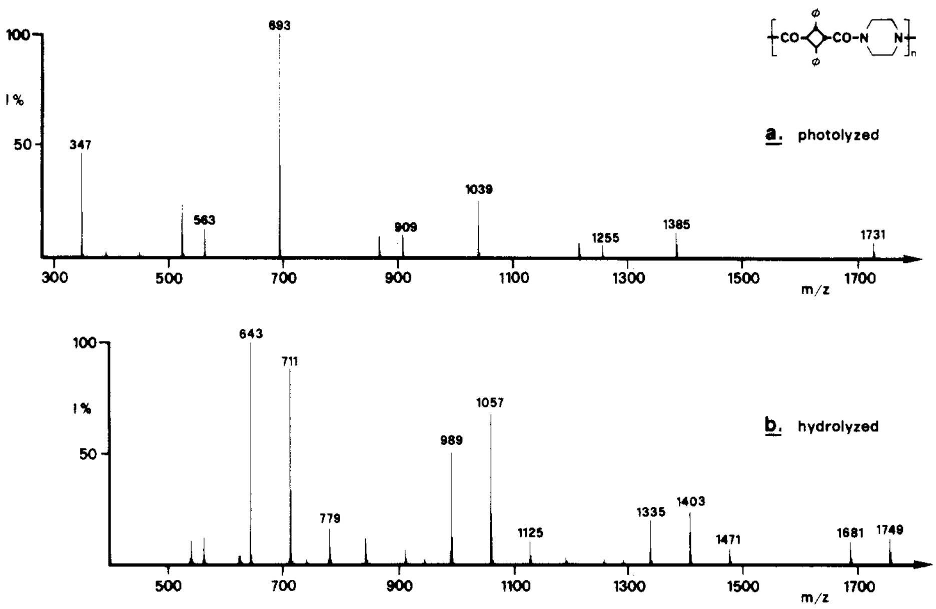


Figure 5. Positive FAB mass spectra of oligomers generated by (a) photolysis (in a TFE + 1% MSA solution after 5 h of exposition time) and (b) hydrolysis (after 5 days in a MSA + 30% H_2O solution) of poly(truxilloylpiperazine) (polymer III).

tected in the FAB mass spectrum (Figure 3 and Table II).

This is not the case for copolyamide II, where the FAB spectrum reported in Figure 4a shows several peaks that can be assigned (Table II) to oligomers containing both adipic and truxillic units and cinnamoyl end groups.

It is interesting to compare the structure of the oligomers originated in the photolysis with those obtained by hydrolysis of copolyamide II, which are reported in the FAB spectrum of Figure 4b and identified in Table III.

It can be observed that the hydrolysis produces oligomers with piperazine, truxillic, and/or adipic end groups, whereas the oligomers with cinnamoyl end groups are absent (Table III).

The FAB spectra yield, therefore, all the information that would be expected from the knowledge of the copolymer structure and of the degradation method used.

The difference between oligomers with different end groups generated by photolysis and hydrolysis is also clearly visible in the case of the homotruxilloylpiperazine

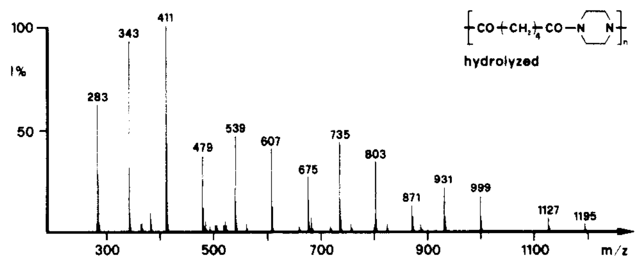


Figure 6. Positive FAB mass spectrum of oligomers generated by hydrolysis (5 days) in a MSA + 30% H_2O solution of poly(adipoylpiperazine) (polymer IV).

(III) (parts a and b of Figure 5, respectively). The structural assignments corresponding to specific peaks can be found in Tables II and III.

The FAB analysis of oligomers originating from the degradation of homopolymer III is therefore very useful in the process of assigning the structures of FAB peaks in 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.

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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.

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