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(18) Rose bengal is a commercial name deriving from the similarity in its color to the cosmetic dye, *sincur*, used as a dot or a line in the center of the forehead of Bengali women. Von Tappeiner used the name tetrachlorotetraiodofluorescein in his 1904 paper. Strictly speaking, that name is closer to what was known about the structure of rose bengal then than is the *Chemical Abstracts* name today. Von Tappeiner clearly used synthetic samples rather than the commercial dye or he would have used the commercial name. The original red Indian dye may be either a root extract or *cinnabar*. The dye was originally to symbolize marriage ("happiness wart") but in recent years has become more cosmetic than symbolic. We are uncertain if rose bengal is actually used today for this cosmetic purpose, but it may be.
(19) The *Chemical Abstracts* name for rose bengal is 4,5,6,7-tetrachloro-3′,6′-dihydroxy-2′,4′,5′,7′-tetraiodospiro[isobenzofuran-1(3*H*),9′-[9*H*]xanthen]-3-one disodium salt. This represent the cyclized form of the dye. The "Color Index" form of the dye (noncyclized) is the structure of the dye that we have chosen to use in this paper. Its *Chemical Abstracts* name is 2,3,4,5-tetrachloro-6-(6-hydroxy-2,4,5,7-tetraiodo-3-oxo-3*H*-xanthen-9-yl)benzoic acid disodium salt. We make no apologies for not using it or for using the commercial name instead. Rose Bengal should, we suppose, always be capitalized. We also opt to use the lower case—rose bengal.
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Thermal Degradation of Aromatic–Aliphatic Polyethers. 1. Direct Pyrolysis–Mass Spectrometry

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ABSTRACT: The thermal degradation of eight aromatic–aliphatic polyethers has been studied by direct pyrolysis–mass spectrometry (DP–MS) and by thermogravimetry. The effect of ammonium polyphosphate was also examined. Polyethers I–III undergo an intramolecular exchange process, which produces cyclic compounds, and a thermal rearrangement, producing compounds with aldehyde and phenyl end groups. Polyethers IV–VI decompose mainly through a β-CH hydrogen transfer to the oxygen atom, producing compounds with hydroxy and olefin end groups. A thermal rearrangement leading to compounds with aldehyde and pentyl end groups is also active in polymers V and VI. Polymers VII and VIII decompose with extensive hydrogen-transfer reactions, leading to compounds with hydroxy and methyl end groups, and through a β-CH hydrogen transfer from the methylene to the phenyl ring, generating compounds with aldehyde and phenyl end groups. Ammonium polyphosphate lowers the thermal stability of polymers I–VI, whereas the other polymers remain unaffected. Our data show that ammonium polyphosphate sometimes changes the distribution of the pyrolytic compounds by inducing an acid-catalyzed thermal degradation of the polymer chain.

Introduction

Direct pyrolysis of polymers in the mass spectrometer (DP–MS) is an excellent method for monitoring the initial thermal fragmentation processes occurring when polymers are heated to decomposition.[1]

We have investigated several classes of polymers by the DP–MS technique to ascertain primary thermal decomposition mechanisms operating in each case.[2–6] Effects of structural factors and/or of the presence of a particular agent on the thermal degradation behavior of polymers have been also studied.[3,5]

Previous MS accounts in the literature on polyethers are confined to totally aromatic polymers[7–9] and some aliphatic oligomers.[10]

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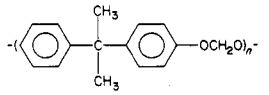
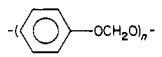
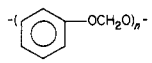
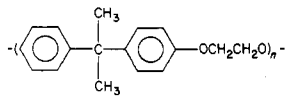
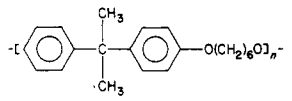
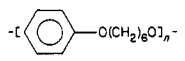
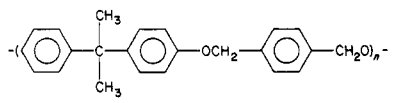
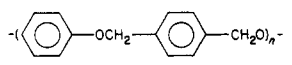
Table I
Structure, TG Data, and Inherent Viscosity of Polyethers Investigated

	structure	η_{inh}[a]	PDT values[b] pure	PDT values[b] with 10% APP	% R[c]
I		0.19[d]	465	350	15
II		ins	445	305	20
III		ins	445	400	30
IV		0.10[d]	465	420	10
V		0.23[d]	460	390	5
VI		0.17[e]	440	350	5
VII		0.27[d]	350	350	40
VIII		0.11[e]	290	290	50

[a] $\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL. $c = 0.5$ g/dL. [b] Maximum of polymer degradation temperature (PDT) in TG experiments under N_2 (flow rate 60 mL/min), heating rate 10 °C min. [c] Residue % of sample at 600 °C in TG experiments. [d] In tetrachloroethane/phenol (2/3) at 30 °C. [e] In *m*-cresol at 70 °C.

In the present work we report a study on the thermal degradation of a series of aromatic–aliphatic polyethers (Table I) and on the effect of ammonium polyphosphate (APP) on their thermal behavior.

It is generally agreed that APP, a precursor of poly(phosphoric acid), is capable of lowering the thermal stability of some polymers, presumably because it promotes acid-hydrolyzed reactions on the substrates.[5,11,12]

Thermogravimetry (TG) data show that the thermal stability of polyethers I–VI is lowered by the presence of APP (Table I), while that of polymers VII and VIII is unaltered.

Our results show that the mechanism of thermal degradation of aromatic–aliphatic polyethers varies with the chemical structure of each polymer, and therefore the presence of APP affects it in different ways.

Experimental Section

Synthesis of Polymers and Model Compounds. Polymer I was synthesized starting from bisphenol-A and dichloromethane according to the method described by Hay et al.[13] In a three-necked flask equipped with magnetic stirrer, reflux condenser and a tube for the introduction of N_2 were placed 11.4 g (0.05 mol) of bisphenol-A, 20 mL of dichloromethane, and 25 mL of *N*-methylpyrrolidone. The mixture was stirred until an homogeneous solution was obtained. At this point 4.2 g (0.105 mol) of NaOH pellets was added, and the mixture was heated at 75 °C in an oil bath under stirring and N_2 flow. After 20 h the solution was cooled and poured in 1 L of water acidified with HCl to obtain a white polymer. The polymer was washed with hot *N,N*-dimethylformamide (DMF) and then with acetone. The polymer was dried in vacuo at 70 °C.

Polymers II and III were synthesized in the same way, using hydroquinone or resorcinol, respectively, rather than bisphenol-A.

Polymer IV was synthesized with the same apparatus as for polymer I. Bisphenol-A (6.8 g, 0.03 mol), 3.5 g (0.035 mol) of 1,2-dichloroethane, 3.8 g (0.01 mol) of tetrabutylammonium bromide (phase-transfer agent), 40 mL of water, and 40 mL of toluene were placed in a three-necked flask and stirred under N_2 flow; then 6 g (0.15 mol) of NaOH pellets was added, and the dispersion was heated at 75 °C. After 20 h the solution was cooled and the insoluble white solid was filtered, washed with water, and dried. The polymer was purified by desolving in DMF and then pouring the solution in methanol acifidied with HCl.

Polymers V and VI were synthesized in the same way of polymer IV by using 1,6-dichlorohexane and bisphenol-A or hydroquinone, respectively.

Polymers VII and VIII were synthesized in the same way of polymer IV by using α,α'-dibromo-*p*-xylene and bisphenol-A or hydroquinone, respectively.

Cyclic compounds IX and X were obtained by extraction with boiling DMF from polymer I together to other oligomers having higher molecular weight.[13] The oligomers were characterized by mass spectrometry.

Cyclic compound XI was obtained from the reaction between cathecol and dichloromethane using the method described for polymer I. No polymer was formed in this reaction. The compound was crystallized from toluene/methanol (1:3) (mp 258–260 °C) and identified by ^{1}H NMR spectroscopy [δ 2.72 (m, 8 H), δ 4.26 (s, 4 H)] and by mass spectrometry.

Thermogravimetry. A Perkin-Elmer thermal analyzer TGS-2 was used to determine the thermal behavior of the samples. Experiments were carried out on a sample of about 2 mg under an N_2 flow rate of 60 mL/min and a furnace heating rate of 10 °C/min up to 800 °C.

Mass Spectrometry. Pyrolysis was carried out by the direct insertion inlet of a Kratos MS 50 S double focusing mass spectrometer, according to a technique described elsewhere;[1] the heating rate was 10 °C/min. Mass spectra were obtained at 18 eV.

Under these electron impact (EI) conditions all compounds containing bisphenol-A units undergo methyl loss in the first free field region of the mass spectrometer.[14] Therefore all the thermal fragments, reported in Tables I–VII, generate metastable peaks that are not reported for brevity.

Viscometry. Inherent viscosities of the polymers investigated ($\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL) were measured in a Desruex–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 are reported in Table I.

Results and Discussion

Thermogravimetry. To characterize the thermal stability of polyethers I–VIII and of their mixtures with APP, TG experiments under N_2 flow and a heating rate of 10 °C/min were performed. Temperatures of the maximum rate of polymer degradation (PDT) are collected in Table I. Comparing the PDT value of pure and APP-doped polyethers, one can note that the thermal stability of polyethers I–VI is lowered by the presence of APP, while that of polymers VII and VIII remains unaffected.

Mass Spectrometry. In the DP–MS technique,[1] polymers are introduced via the direct insertion probe, and the temperature is increased gradually up to a point at which thermal degradation reactions occur; the volatile compounds formed are then ionized and detected.

The mass spectrum of a polymer obtained under these conditions is therefore that of a mixture of compounds formed by pyrolysis. In this method, mass spectra are scanned repetitively, stored, and analyzed individually.

The advantage of examining a series of successive scans, rather than the sum of the mass spectra over the entire thermal decomposition envelope, consists in the possibility of detecting eventual differences among the spectra and to attribute them to different processes of thermal decomposition.[1] The alternative of summing and averaging the overall mass spectra obtained would be very useful for analytical purposes, such as materials fingerprinting.[25]

When the mass spectral analysis of polymers is performed with a linear heating rate, total ion current (TIC) curves essentially reproduce the differential gravimetric curves (DTG), so that their maxima (PDT) closely match the maximum volatilization temperatures of the pyrolytic compounds in the MS experiments.[15]

The use of TG and MS data allows one to evaluate simultaneously the pyrolysis temperature, the composition, and the amount of volatile compounds formed during the thermal decomposition. When DTG and/or TIC curves show several relative maxima, as many mass spectra are reported, since they most likely correspond to different thermal decomposition stages.

The mass spectra selected herein are therefore those obtained at the maximum evolution rates, as can be deduced from the inspection of Table I and Figures 3–8.

A general advantage of the DP–MS technique is that pyrolysis is accomplished under high vacuum, and therefore the thermal compounds formed are volatilized and removed readily from the hot zone. This fact, together with the low probability of molecular collisions and with fast detection, reduces to a great extent the occurrence of secondary reactions, so that almost exclusively primary fragments are detected. Consequently, the information obtained is of particular importance in assessing the primary thermal degradation mechanisms of a polymer.

Furthermore, since pyrolysis is achieved very close to the ion source, no problem of transport exists; fragments of high mass, often essential for the structural characterization of the polymer, can be detected, whereas they are often lost using other techniques.

The main problem connected with this technique is, however, the identification of the products in the spectrum of a multicomponent mixture produced by thermal degradation. In fact, in the spectrum of a polymer, the molecular ions of the thermally formed compounds will appear mixed with the fragment ions formed by EI.

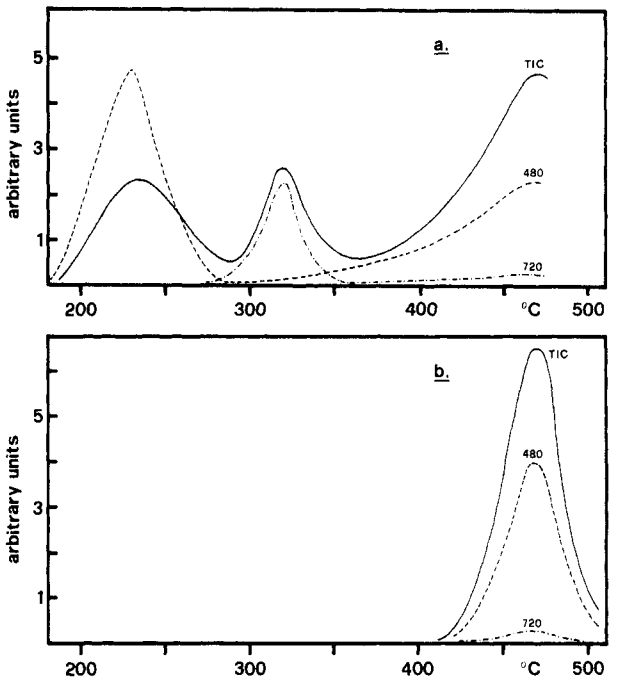


Figure 1. Total ion current (TIC) of (a) crude sample of polymer I, and (b) sample of polymer I after oligomer extraction.

In some instances, identification of thermal degradation products can be achieved by using soft ionization methods, by using exact mass measurements, or by matching spectra of model samples.[16] In other cases, MS–MS methods have been applied with success.[17]

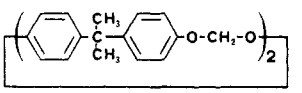
It might be feared that using linear-programmed heating of the MS probe, one might be observing mostly evaporating oligomers rather than pyrolysis products. However, gradual heating allows one to detect oligomers contained in a polymer sample since they are already volatile under high vacuum at relatively mild temperatures, at which the corresponding polymers remain undecomposed. We have provided several examples of this fact.[18] In the case of polymer I (Table I), two pre-formed oligomers are detected. Figure 1a reports the total ion current (TIC) vs. temperature of a crude sample of polymer I. The two peaks at 220 and 320 °C correspond to the evolution of the cyclic oligomers IX and X, respectively.

The evolving products were analyzed by repetitive mass scans, so that the two oligomers could be directly identified through the mass spectra.

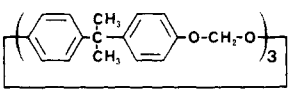
Once detected and identified by this procedure, the two cyclic oligomers were separated from polymer I by solvent extraction.

The TIC curve in Figure 1b, corresponding to a sample of polymer I after oligomer extraction, shows a negligible ion current below 400 °C.

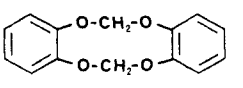
Model Compounds. To differentiate the thermal and EI fragments in the case of polymers I, II, and III (Table I), we investigated the mass spectra of three cyclic model compounds IX, X, and XI.



IX; m/z 480



X; m/z 720



XI; m/z 244

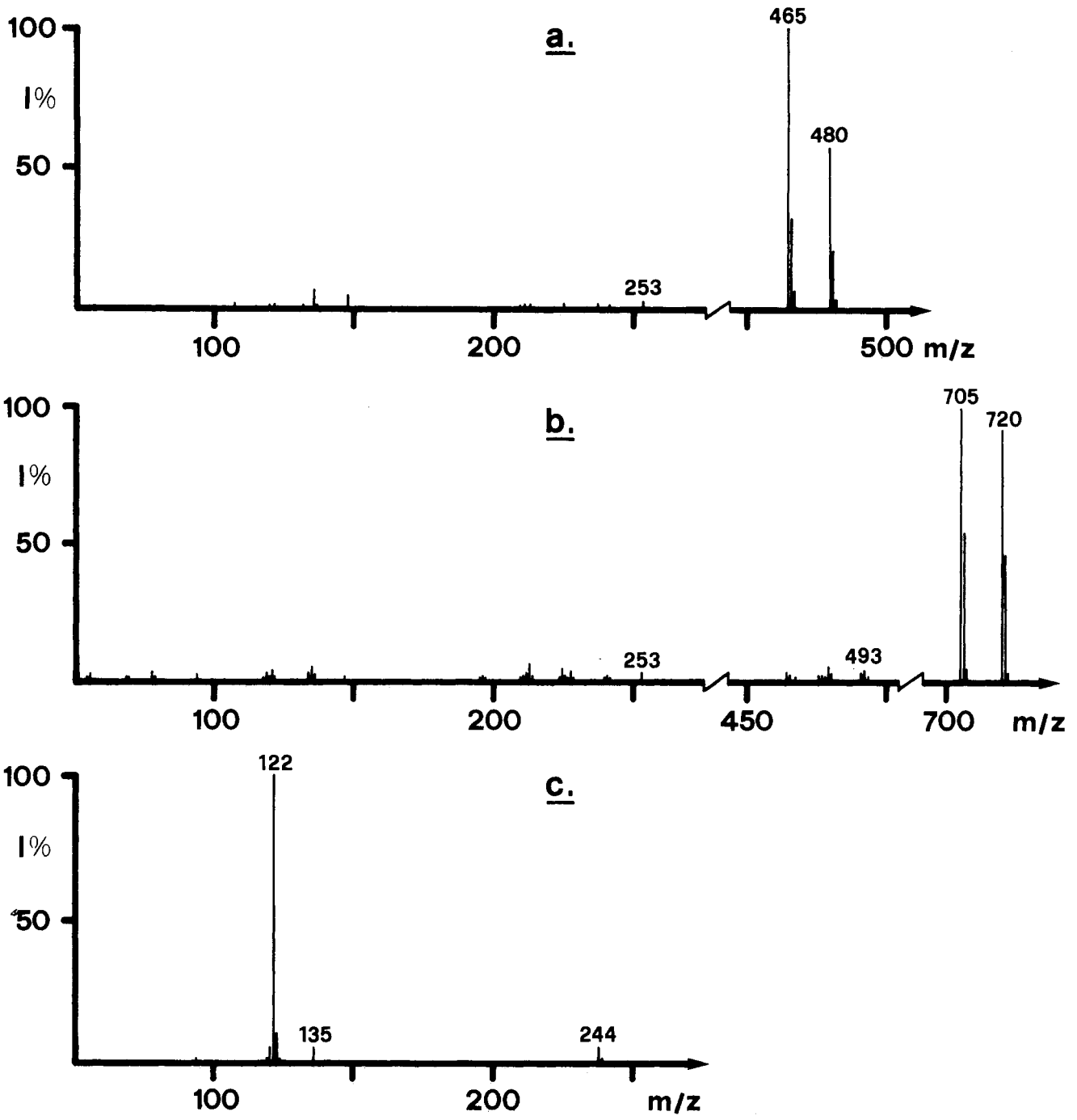


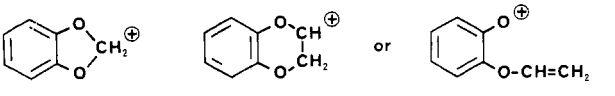
Figure 2. Mass spectrum of (a) cyclic dimer IX, (b) cyclic trimer X, and (c) cyclic dimer XI.

These model compounds, when heated under high-vacuum conditions of the MS, volatilize undecomposed; therefore their fragmentation products by EI can be studied conveniently.

Figure 2a shows the spectrum recorded at a probe temperature of 220 °C of the cyclic compound IX. The spectrum appears essentially to be constituted of two peaks at m/z 480 (molecular ion) and m/z 465 (base peak), which originates from the parent ion through a methyl loss. This transition, characteristic of bisphenol-A derivatives, is substantiated by a metastable peak at m/z 450.5.

In Figure 2b the mass spectrum recorded at a probe temperature of 320 °C of the cyclic compound X is reported. The inspection of the spectrum reveals the presence of two intense peaks at m/z 720 and m/z 705 (base peak), respectively corresponding to the molecular ion and the EI fragment originating from it by methyl loss (metastable transition peak at m/z 690.3).

Figure 2c shows the mass spectrum of cyclic compound XI recorded at a probe temperature of 210 °C. The peak at m/z 244, corresponding to the molecular ion, appears with low intensity. Peaks due to EI fragmentation are detected at m/z 122 (base peak), corresponding to half of molecule XI, and at m/z 135. Likely structures for these ion are



XII; m/z 122 **XIII; m/z 135** **XIV; m/z 135**

Comparison of the mass spectrum in Figure 2c with those in Figure 2, parts a and b shows that cyclic compound XI is much less stable to EI fragmentation than the

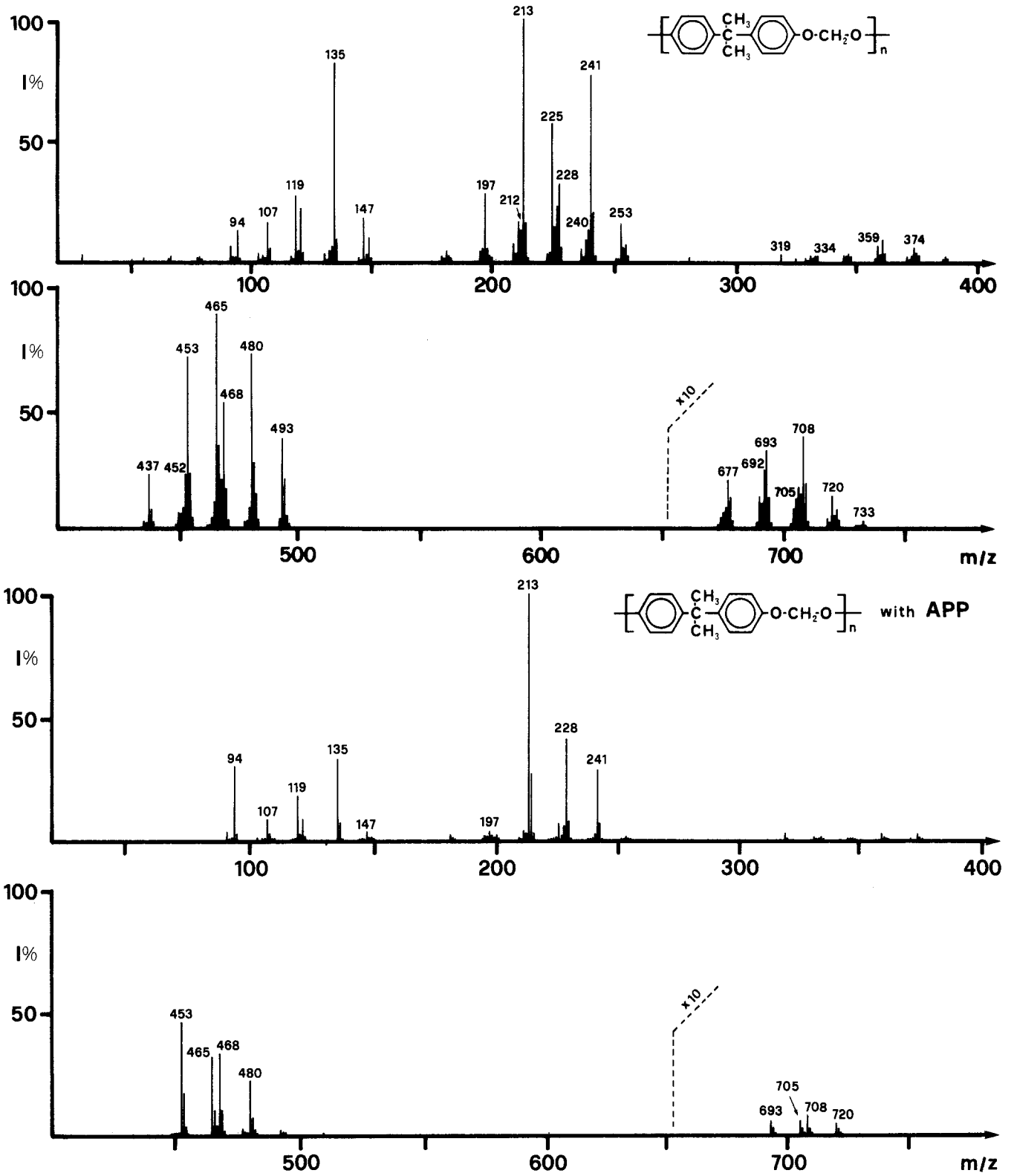


Figure 3. Mass spectrum of the thermal degradation products of (a) polymer I at a probe temperature of 465 °C, and (b) polymer I/APP mixture at 350 °C.

cyclic compounds IX and X.

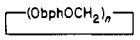
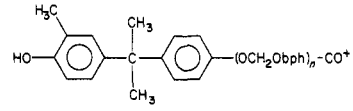
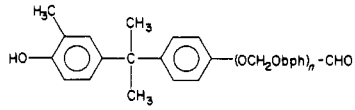
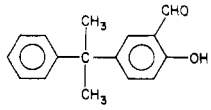
Polymer I. Figure 3a shows the mass spectrum of polymer I (Table I) recorded at a probe temperature of 465 °C.

The structural assignments for the most intense thermal and EI fragments are given in Table II. The spectrum exhibits an intense peak at m/z 480 corresponding to the molecular ion of the cyclic dimer and a peak at m/z 720 due to the cyclic trimer. The assignment of these peaks to cyclic structures comes straightforwardly from the comparison with the EI spectra of pure cyclic formals in Figure 2, parts a and b, respectively.

Another series of thermal compounds corresponding to bisphenol-A (m/z 228) and its higher homologues (m/z 468, 708) are present in the spectrum (Figure 3), accompanied by the EI fragmentation characteristic of bisphenol-A, due to the methyl loss from the parent ion.[14]

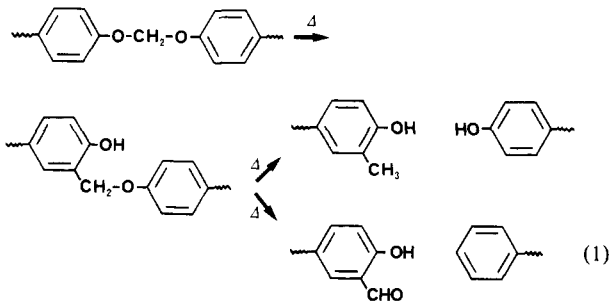
In Figure 3a is also present an intense peak at m/z 225, arising from the parent ion at m/z 240 (Table II) after methyl loss. This transition is substantiated by a meta-

Table II
Thermal and EI Fragments of Polymer I[a]

thermal fragments	m/z (n)	EI fragments	m/z (n)
	480 (2), 720 (3)	HO-(bphOCH$_2$O)$_n$-bphOCH$_2^+$	241 (0), 481 (1), 721 (2)
HO-(bphOCH$_2$O)$_n$-bphOH	228 (0), 468 (1), 708 (2)	HO-(bphOCH$_2$O)$_n$-phC$^+$(CH$_3$)$_2$	135 (0), 375 (1)
HO-(bphOCH$_2$O)$_n$-bphH	212 (0), 452 (1), 692 (2)	HO-(bphOCH$_2$O)$_n$-ph$^+$	93 (0), 333 (1)
HO-(bphOCH$_2$O)$_n$-phH	94 (0), 334 (1)		253 (0), 493 (1), 733 (2)
HO-(bphOCH$_2$O)$_n$-phC(CH$_3$)=CH$_2$	134 (0), 374 (1)		
	254 (0), 494 (1), 734 (2)		
	240		

[a] bph = -C$_6$H$_4$-*p*-C(CH$_3$)$_2$-*p*-C$_6$H$_4$-; ph = 1,4-phenylene.

stable peak at m/z 210.9. Most likely the peak at m/z 240 is generated through a fragmentation arising from the thermal rearrangement (eq 1)



(1)

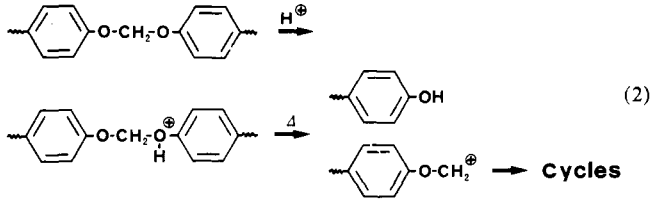
The structural assignment of the peak at m/z 240 to 4-cumyl-2-hydroxybenzaldehyde is confirmed by flash pyrolysis–GC–MS data.[19]

Another family of peaks corresponding to compounds having aldehyde, hydroxy, and methyl end groups (Table II), are present in the spectrum at m/z 254, 494, and 734, accompanied by the respective M-1 ions with higher intensities.

In Figure 3b is shown the mass spectrum taken at a probe temperature of 350 °C of a polymer I/APP mixture.

In the spectrum appear, with sizeable intensity, peaks arising from bisphenol-A, its higher homologues (m/z 468, 708), and cyclic formals (Table II). The peak at m/z 240 and its M-15 fragment ion disappear, and the peaks at m/z 253 and m/z 493 appear with very low intensities.

APP is a precursor of poly(phosphoric acid), and therefore the acid-catalyzed thermal degradation of polymer I occurs at a lower temperature through a selective pathway (eq 2), which produces hydroxy end groups and carbenium ions responsible for the formation of cyclic formals by a back-biting mechanism[20-22]



(2)

Under these conditions, no aldehydes can be formed in the pyrolysis through the mechanism illustrated in eq 1, and therefore the peaks at m/z 253 and m/z 493 (Figure 3b) appear with very low intensities. Actually, here they are generated by EI fragmentation of cyclic formals (m/z 480 and 720), while in the spectrum of pure polymer I (Figure 3a) they mainly arise (by H loss) from compounds with aldehyde end groups, and they have a much higher intensities.

Polymer II. In Figure 4a is shown the mass spectrum of polymer II recorded at a probe temperature of 445 °C.

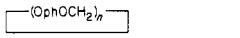
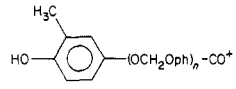
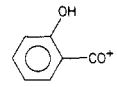
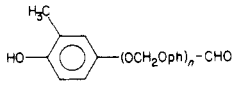
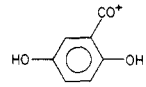
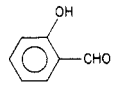
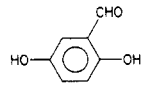
The structural assignments for the thermal and EI fragments are reported in Table III. The spectrum exhibits peaks due to thermal fragments corresponding to hydroquinone (m/z 110) and its higher homologues (m/z 232, 354, 476, and 598). The peaks at m/z 122 and m/z 138, with the corresponding M-1 fragments at m/z 121 and m/z 137, respectively, due to compounds having hydroxy and aldehyde groups (eq 1), also appear in the spectrum.

Another series of four peaks at m/z 244, 366, 488, and 610, corresponding to the molecular ions of cyclic formals, are present (Table III). EI fragments at m/z 135, 257, 379, and 501 might originate from aldehydes by H loss (Table III), but there is no firm basis for this assignment. However, data obtained for a mixture of polymer II with APP allow one to remove this ambiguity.

In Figure 4b is reported the mass spectrum of a polymer II/APP mixture taken at a probe temperature of 305 °C. It can be noted that only peaks due to hydroquinone (m/z 110), its higher homologues (m/z 232, 354, 476, and 598) and cyclic formals (m/z 244, 366, 488, and 610) appear in the spectrum. The peaks at m/z 135, 257, 379, and 501 have now very low intensities as a consequence of the selective thermal process (eq 2) induced by APP. These data suggest than in the spectrum of pure polymer II (Figure 4a), peaks at m/z 135, 257, 379, and 501 are mainly generated from aldehydes by H loss (Table III). Also peaks at m/z 121 and m/z 137 (aldehydes, Table III) are almost absent in the mass spectrum (Figure 4b).

Polymer III. The synthesis of the meta isomer was undertaken in the hope of inducing a greater tendency to form cyclic oligomers with respect to the para isomer (polymer II). However the mass spectral data obtained for polymer III (Table I) are analogous to those of polymer II, and therefore they are not discussed here. The results obtained for polyethers II and III show that the amounts of cyclic oligomers formed by the thermal-exchange process for the two isomeric polymers are comparable because the

Table III
Thermal and EI Fragments of Polymer II[a]

thermal fragments	m/z (n)	EI fragments	m/z (n)
	244 (2), 366 (3), 488 (4), 610 (5)	HO-(phOCH$_2$O)$_n$-phOCH$_2^+$	123 (0), 245 (1), 367 (2), 489 (3), 611 (4)
HO-(phOCH$_2$O)$_n$-phOH	110 (0), 232 (1), 354 (2), 476 (3), 598 (4)		135 (0), 257 (1), 379 (2), 501 (3)
HO-(phOCH$_2$O)$_n$-phH	94 (0), 216 (1), 338 (2), 460 (3), 582 (4)		121
	136 (0), 258 (1), 380 (2), 502 (3)		137
	122		
	138		

[a] ph = 1,4-phenylene.

Table IV
Thermal and EI Fragments of Polymer IV[a]

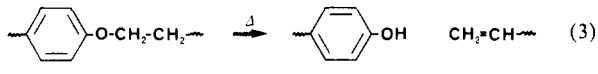
thermal fragments	m/z (n)	EI fragments	m/z (n)
HO-(bphOCH$_2$CH$_2$O)$_n$-bphOH	228 (0), 482 (1), 736 (2), 990 (3)	HO-(bphOCH$_2$CH$_2$O)$_n$-bphOCH$_2^+$	241 (0), 495 (1), 749 (2)
HO-(bphOCH$_2$CH$_2$O)$_n$-bphOCH=CH$_2$	254 (0), 508 (1), 762 (2), 1016 (3)	HO-(bphOCH$_2$CH$_2$O)$_n$-bphOCH$_2$CH$_2^+$	255 (0), 509 (1), 763 (2)
CH$_2$=CH-(ObphOCH$_2$CH$_2$)$_n$-ObphOCH=CH$_2$	280 (0), 534 (1), 788 (2)	HO-(bphOCH$_2$CH$_2$O)$_n$-phC$^+$(CH$_3$)$_2$	135 (0), 389 (1), 643 (2), 897 (3)
HO-(bphOCH$_2$CH$_2$O)$_n$-phH	94 (0), 348 (1), 602 (2)	CH$_2$=CH-(ObphOCH$_2$CH$_2$)$_n$-OphC$^+$(CH$_3$)$_2$	161 (0), 415 (1), 669 (2), 923 (3)
HO-(bphOCH$_2$CH$_2$O)$_n$-phC(CH$_3$)=CH$_2$	134 (0), 388 (1), 642 (2), 896 (3)		
CH$_2$=CH-(ObphOCH$_2$CH$_2$)$_n$-C(CH$_3$)=CH$_2$	160 (0), 414 (1), 668 (2), 922 (3)		

[a] bph = -C$_6$H$_4$-p-C(CH$_3$)$_2$-p-C$_6$H$_4$-; ph = 1,4-phenylene.

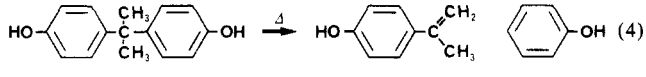
conformational flexibility of the polymeric chain is already good in the para isomer.

Polymer IV. Figure 5 shows the mass spectrum of polymer IV (Table I) recorded at a probe temperature of 465 °C.

The structural assignments for the thermal and EI fragments are reported in Table IV. Most peaks present in the spectrum can be directly related to fragments with hydroxy and olefin end groups (Table IV) originated by a β-CH hydrogen-transfer process (eq 3)


(3)

Peaks corresponding to compounds originated by thermal cleavage of the bisphenol-A unit (eq 4) were also detected

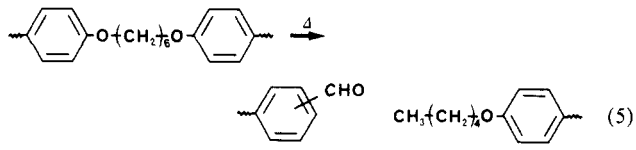

(4)

This thermal process of disproportionation, already encountered for other classes of polymers containing bisphenol-A units,[6,7] is catalyzed selectively by APP, resulting in the lowering of the polymer PDT value (Table I).

Polymer V. Figure 6 shows the mass spectrum of polymer V (Table I) recorded at a probe temperature of 460 °C.

The structural assignments of the thermal and EI fragments are reported in Table V. The most intense peaks in the spectrum are directly related to compounds with hydroxy and olefin end groups (Table V) originated by a β-CH hydrogen-transfer process (eq 3).

The base peak at m/z 225 arises from the parent ion at m/z 240 after methyl loss; this transition is substantiated by a metastable peak at m/z 210.9. The fragment ion at m/z 240 and its homologues at higher masses (Table V) arise from a thermal rearrangement leading to aldehyde end groups, for which examples are reported in the literature[19,23,24] (eq 5)


(5)

According to eq 5, ions containing saturated pentyl end groups at m/z 298, 368, and 380, respectively, and their homologues at higher masses (Table V) are found in the spectrum (Figure 6).

Thermal fragments due to bisphenol disproportionation are also present in the spectrum, according to eq 4 (Table V).

The presence of APP lowers the PDT value of polymer V. Mass spectral data (omitted for brevity) show that APP enhances the intensities of the peaks having hydroxy and olefin end groups because the acid-catalyzed thermal degradation favors these reactions. The formation of compounds having aldehyde end groups is unfavored. Consequently peaks at m/z 240, 550, and 860 are very low

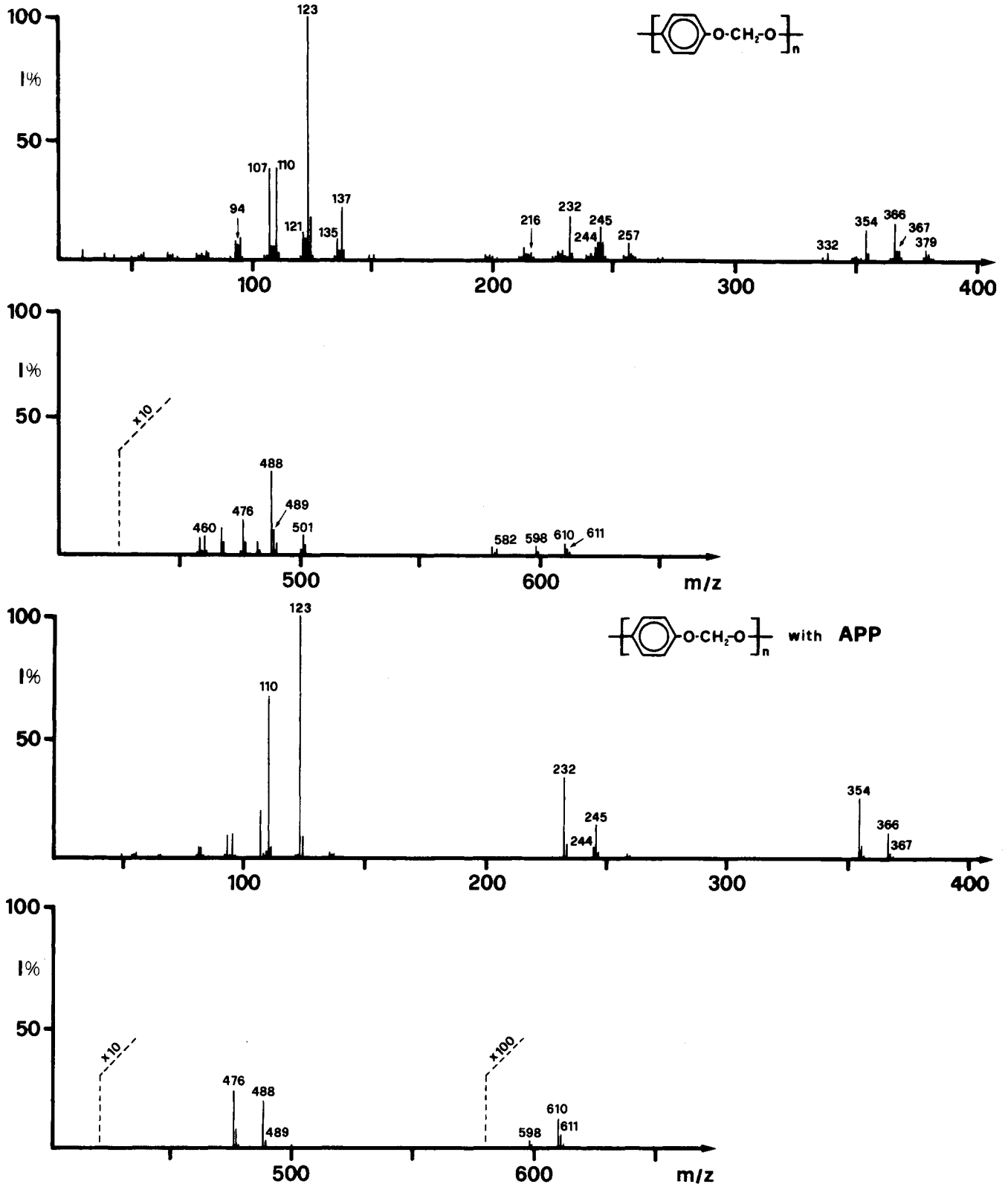


Figure 4. Mass spectrum of the thermal degradation products of (a) polymer II at a probe temperature of 445 °C, and (b) polymer II/APP mixture at 305 °C.

in the spectrum of the polymer V/APP mixture, as well as peaks at m/z 298, 608, 918, 368, 678, 380, and 690 (Table V), corresponding to compounds having pentyl end groups, which are generated in the same reaction (eq 4).

In presence of APP, the thermal disproportionation of bisphenol-A units is also favored.

Polymer VI. The thermal degradation pathway of polymer VI is quite similar to that of polymer V. The peak at m/z 110, corresponding to hydroquinone, and the peak at m/z 83 ($CH_2{=}CHCH_2CH_2CH_2^+$) are the most intense.

The presence of APP, as in the case of polymer V, lowers the PDT value of polymer VI and enhances the intensities of the peaks due to compounds having hydroxy and olefin end groups, originated by hydrogen-transfer reactions in the pure polymer.

Polymer VII. In Figure 7 the mass spectrum of polymer VII recorded at a probe temperature of 350 °C is reported.

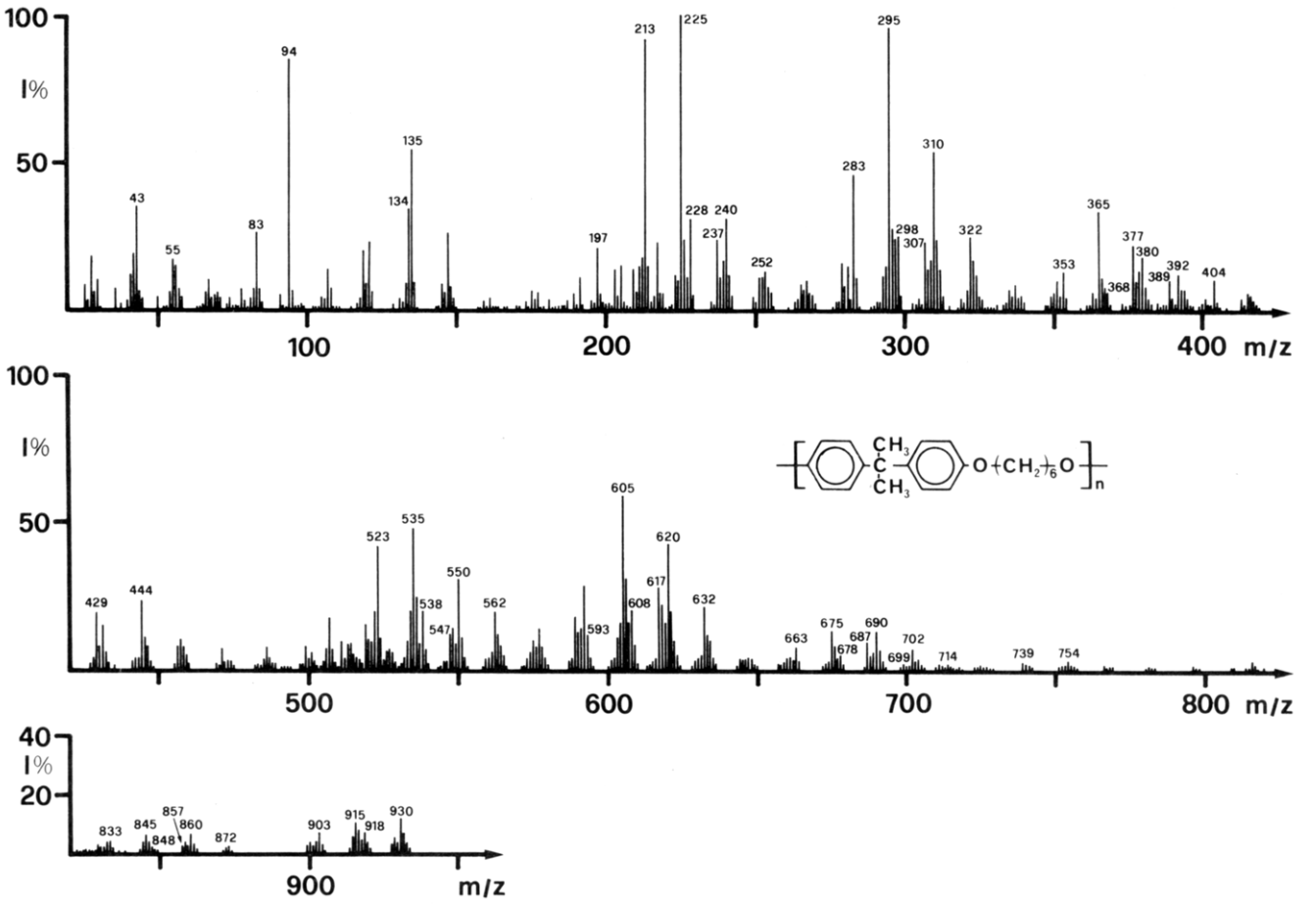


Figure 5. Mass spectrum of the thermal degradation products of polymer IV at a probe temperature of 465 °C.

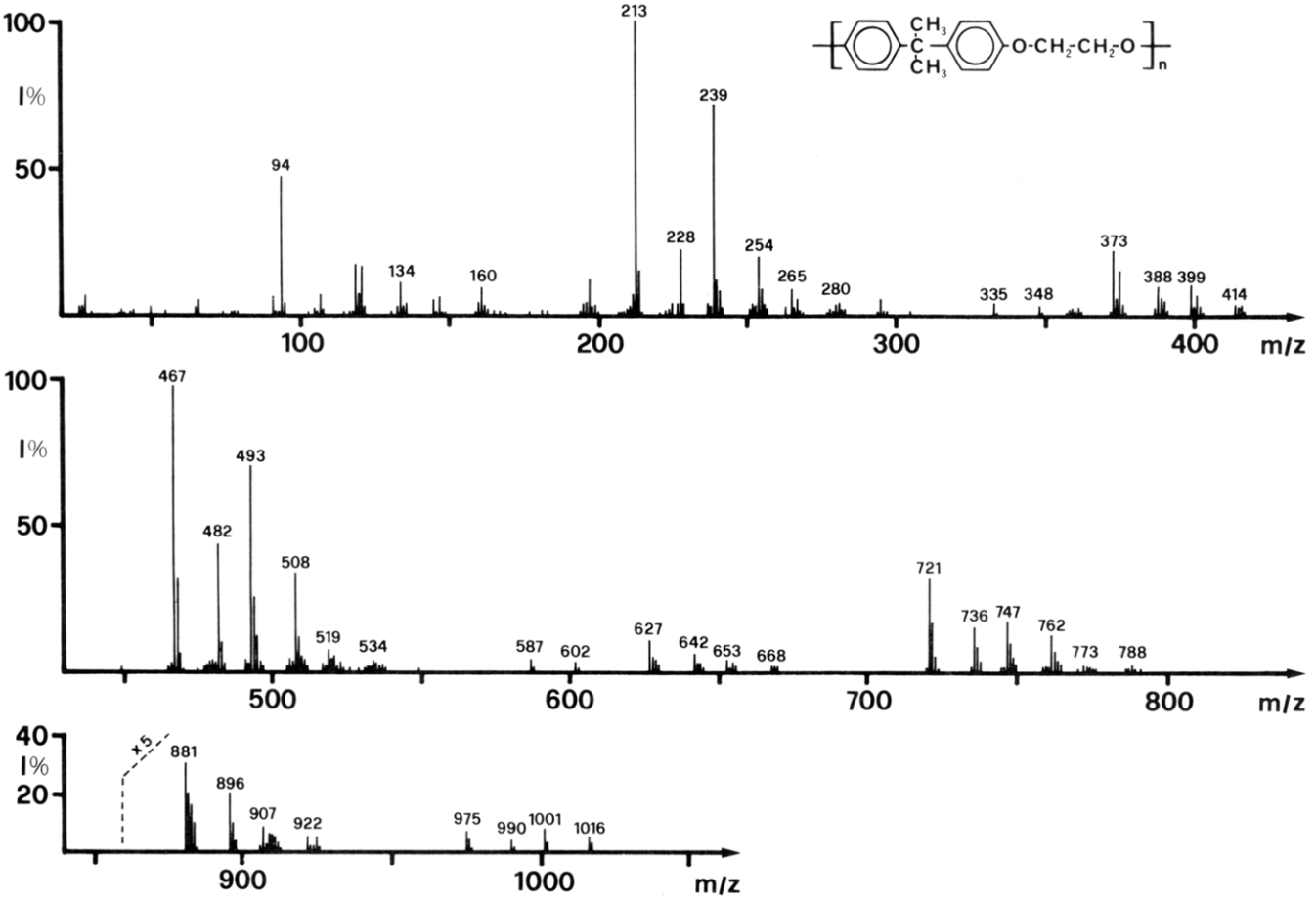
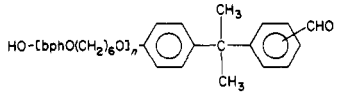
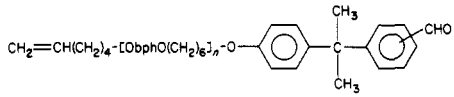
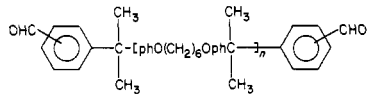


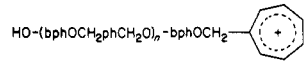
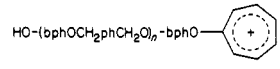
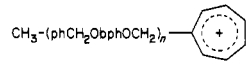
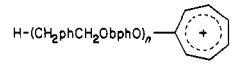
Figure 6. Mass spectrum of the thermal degradation products of polymer V at a probe temperature of 460 °C.

Table V
Thermal and EI Fragments of Polymer V[a]

thermal fragments	m/z (n)	EI fragments	m/z (n)
HO–[bphO$(CH_2)_6$O]$_n$–bphOH	228 (0), 538 (1), 848 (2)	CH_2=CH$(CH_2)_n^+$	41 (1), 55 (2), 69 (3), 83 (4)
HO–[bphO$(CH_2)_6$O]$_n$–bphO(CH_2)CH=CH_2	310 (0), 620 (1), 930 (2)	$CH_3(CH_2)_n^+$	29 (1), 43 (2), 57 (3), 71 (4), 85 (5)
CH_2=CH$(CH_2)_4$–[ObphO$(CH_2)_6$]$_n$–ObphO$(CH_2)_4$CH=CH_2	392 (0), 702 (1)	HO–[bphO$(CH_2)_6$O]$_m$–bphO$(CH_2)_n^+$	m = 0: 241 (1), 255 (2), 269 (3), 283 (4), 297 (5), 311 (6)
HO–[bphO$(CH_2)_6$O]$_n$–bphO$(CH_2)_4CH_3$	298 (0), 608 (1), 918 (2)		m = 1: 551 (1), 565 (2), 579 (3), 593 (4), 607 (5), 621 (6)
			m = 2: 861 (1), 875 (2), 889 (3), 903 (4), 917 (5), 931 (6)
$CH_3(CH_2)$–[ObphO$(CH_2)_6$]$_n$–ObphO$(CH_2)_4CH_3$	368 (0), 678 (1)		
		CH_2=CH$(CH_2)_4$–[ObphO$(CH_2)_6$]$_m$–ObphO$(CH_2)_n^+$	m = 0: 323 (1), 337 (2), 351 (3), 365 (4), 379 (5), 393 (6)
CH_2=CH$(CH_2)_4$–[ObphO$(CH_2)_6$]$_n$–ObphO$(CH_2)_4CH_3$	380 (0), 690 (1)		m = 1: 633 (1), 647 (2), 661 (3), 375 (4), 689 (5), 703 (6)
HO–[bphO$(CH_2)_6$O]$_n$–phH	94 (0), 404 (1), 714 (2)		
		$CH_3(CH_2)_4$–[ObphO-$(CH_2)_6$]$_m$–ObphO-$(CH_2)_n$	m = 0: 311 (1), 325 (2), 339 (3), 353 (4), 367 (5), 381 (6)
HO–[bphO$(CH_2)_6$O]$_n$–ph-C(CH_3)=CH_2	134 (0), 444 (1), 754 (2)		m = 1: 621 (1), 635 (2), 649 (3), 663 (4), 677 (5), 691 (6)
	240 (0), 550 (1), 860 (2)		
		HO–[bphO$(CH_2)_6$O]$_n$–phC$^+(CH_3)_2$	135 (0), 445 (1), 755 (2)
	322 (0), 632 (1)	CH_2=CH$(CH_2)_4$–[ObphO$(CH_2)_6$]$_n$–OphC$^+(CH_3)_2$	217 (0), 527 (1), 837 (2)
	252 (0), 562 (1), 872 (2)		

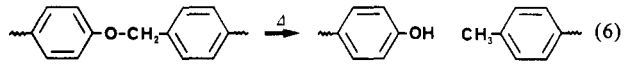
[a] bph = –C_6H_4-*p*-C$(CH_3)_2$-*p*-C_6H_4–; ph = 1,4-phenylene.

Table VI
Thermal and EI Fragments of Polymer VII[a]

thermal fragments	m/z (n)	EI fragments	m/z (n)
HO–(bphOCH$_2$phCH$_2$O)$_n$–bphOH	228 (0), 558 (1)		331 (0), 661 (1)
HO–(bphOCH$_2$phCH$_2$O)$_n$–bphOCH$_2$phCH$_3$	332 (0), 662 (1)		317 (0), 647 (1)
HObphOCH$_2$phCH$_2$ObphH	542		105 (0), 435 (1)
CH$_3$–(phCH$_2$ObphOCH$_2$)$_n$–phCH$_3$	106 (0), 436 (1), 766 (2)		91 (0), 421 (1)
CH$_3$–(phCH$_2$ObphOCH$_2$)$_n$–phCH$_2$ObphH	316 (0), 646 (1)	CH$_3$–(phCH$_2$ObphOCH$_2$)$_n$–phCO$^+$	119 (0), 449 (1)
HbphOCH$_2$phCH$_2$ObphH	526		
HO–(bphOCH$_2$phCH$_2$O)$_n$–bphOCH$_2$phCHO	346 (0), 676 (1)		
CH$_3$–(phCH$_2$ObphOCH$_2$)$_n$–phCHO	120 (0), 450 (1)		
H–(bphOCH$_2$phCH$_2$O)$_n$–bphOCH$_2$phCHO	330 (0), 660 (1)		
Hph–(OCH$_2$phCH$_2$Obph)$_n$–OH	94 (0), 424 (1)		

[a] bph = –C_6H_4-*p*-C$(CH_3)_2$-*p*-C_6H_4–; ph = 1,4-phenylene.

The most intense peaks in the spectrum are due to thermal compounds arising from extensive hydrogen-transfer reactions (eq 6)

 (6)

The principal products generated by these reactions are xylene (m/z 105, M-1), bisphenol-A (m/z 228), and their higher homologues (Table VI). In the spectrum are also observed peaks corresponding to compounds having both methyl and hydroxy end groups at m/z 332 and m/z 662 (Table VI).

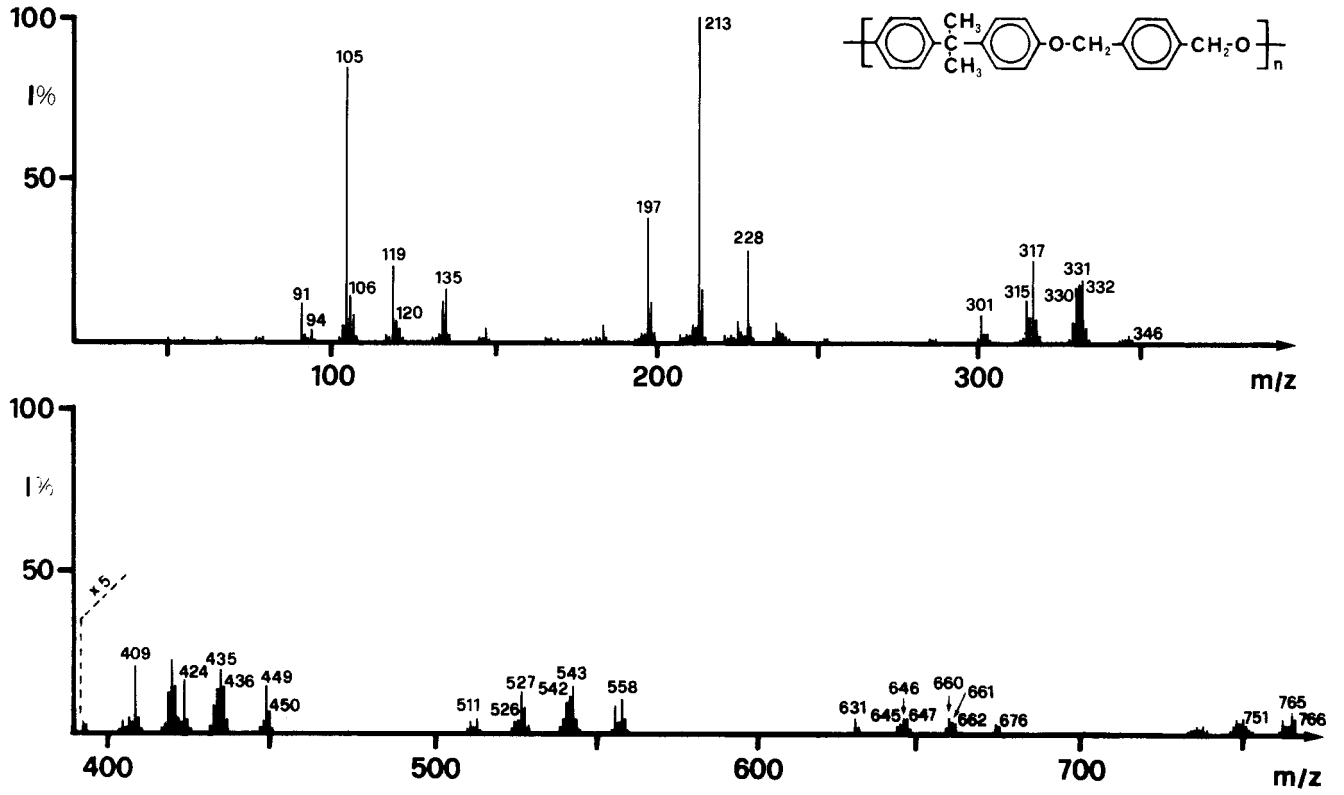


Figure 7. Mass spectrum of the thermal degradation products of polymer VII at a probe temperature of 350 °C.

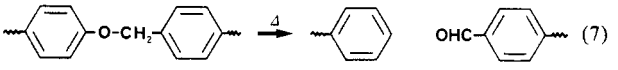
Table VII
Thermal and EI Fragment of Polymer VIII[a]

thermal fragments	m/z (n)	EI fragments	m/z (n)
HO-(phOCH$_2$phCH$_2$O)$_n$-phOH	110 (0), 322 (1), 534 (2)	HO-(phOCH$_2$phCH$_2$O)$_n$-phOCH$_2$	213 (0), 425 (1)
HO-(phOCH$_2$phCH$_2$O)$_n$-phOCH$_2$phCH$_3$	214 (0), 426 (1)	CH$_3$-(phCH$_2$OphOCH$_2$)$_n$	105 (0), 317 (1), 529 (2)
CH$_3$-(phCH$_2$OphOCH$_2$)$_n$-phCH$_3$	106 (0), 318 (1), 530 (2)	H-(CH$_2$phCH$_2$OphO)$_n$	91 (0), 303 (1), 515 (2)
CH$_3$-(phCH$_2$OphOCH$_2$)$_n$-phCH$_2$OphH	198 (0), 410 (1)	H-(phOCH$_2$phCH$_2$O)$_n$-phOCH$_2$	197 (0), 409 (1)
HO-(phOCH$_2$phCH$_2$O)$_n$-phOCH$_2$phCHO	228 (0), 440 (1)	CH$_3$-(phCH$_2$OphOCH$_2$)$_n$-phCO$^+$	119 (0), 331 (1), 543 (2)
CH$_3$-(phCH$_2$OphOCH$_2$)$_n$-phCHO	120 (0), 332 (1), 544 (2)	OHC-(phCH$_2$OphOCH$_2$)$_n$-phCO$^+$	133 (0), 345 (1), 557 (2)
H-(phOCH$_2$phCH$_2$O)$_n$-phOCH$_2$phCHO	212 (0), 424 (1)		
OHC-(phCH$_2$OphOCH$_2$)$_n$-phCHO	134 (0), 346 (1), 558 (2)		

[a] ph = 1,4-phenylene.

The extensive hydrogen-transfer reactions account for the abundant char residue (about 40%) formed during the pyrolysis (Table I).

Another thermal degradation process occurring is the hydrogen transfer from the methylene group to the phenyl ring; this reaction produces compounds with aldehyde and/or phenyl end groups (eq 7, Table VI)



(7)

APP is unable to cause variations in the PDT value (Table I) and in the distribution of the thermal decomposition products. The peaks at m/z 330, 660, 346, 676, 120, and 450 (aldehydes, Table VI) are still present in the spectrum of the polymer VII/APP mixture.

Polymer VIII. In Figure 8 the mass spectrum of polymer VIII taken at a probe temperature of 290 °C is shown.

The thermal decomposition of this polymer follows very closely that of polymer VII. Therefore the most intense peaks in the spectrum are due to compounds having methyl, hydroxy, aldehyde, or phenyl end groups (Table VII) which are generated by the hydrogen-transfer reactions (eq 6 and 7), as in the case of polymer VII.

Also in this case APP results unable to produce variations on PDT value of polymer VIII and on its thermal degradation pathway.

Conclusions

The thermal degradation pathways of aromatic–aliphatic polyethers investigated here appear to be strongly influenced by the chemical structure of each polymer.

The principal mechanisms of thermal decomposition ascertained in our study are summarized in Scheme I.

Polyformals I–III undergo a cyclization reaction (Scheme Ia) by intramolecular exchange most likely initiated at the chain ends. Another reaction occurring in the pyrolysis of polyformals is the thermal rearrangement of the polymer chain, leading to the formation of compounds with al-

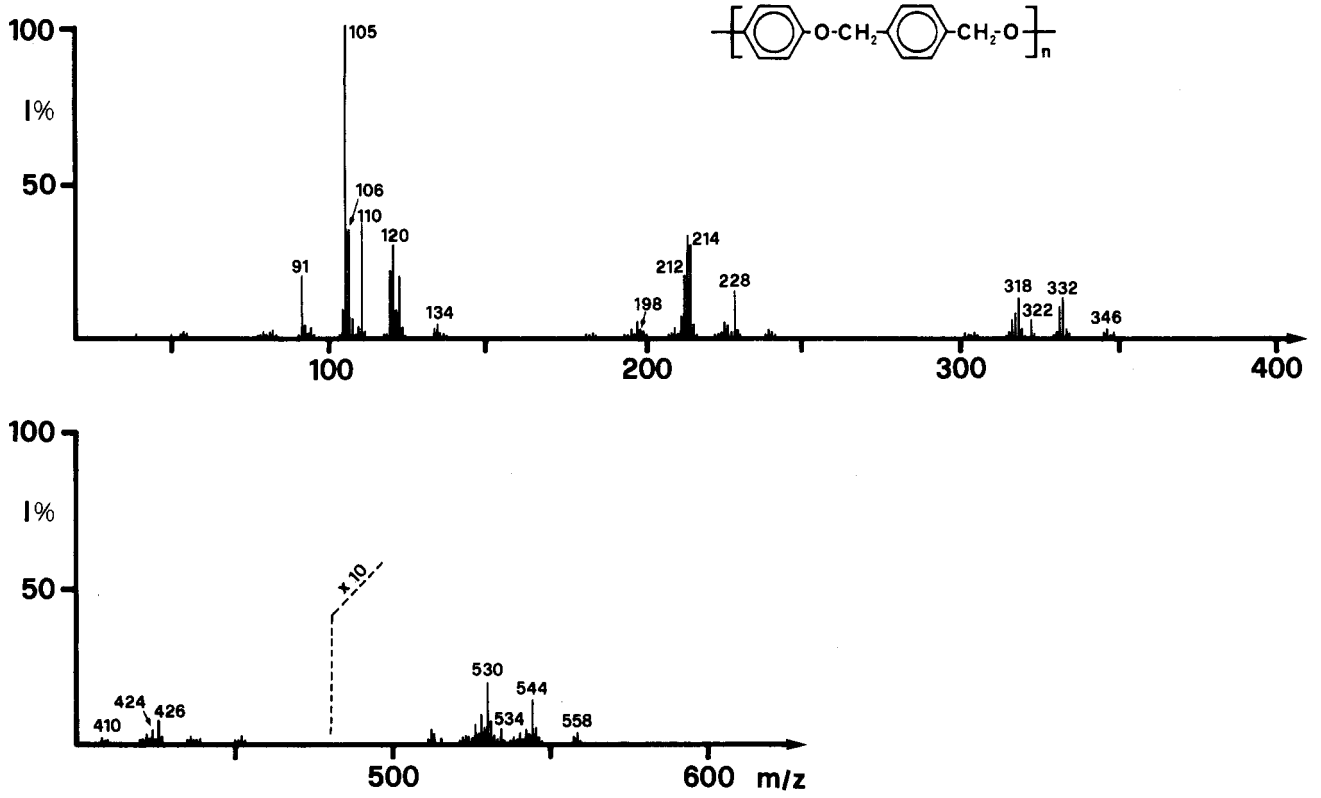
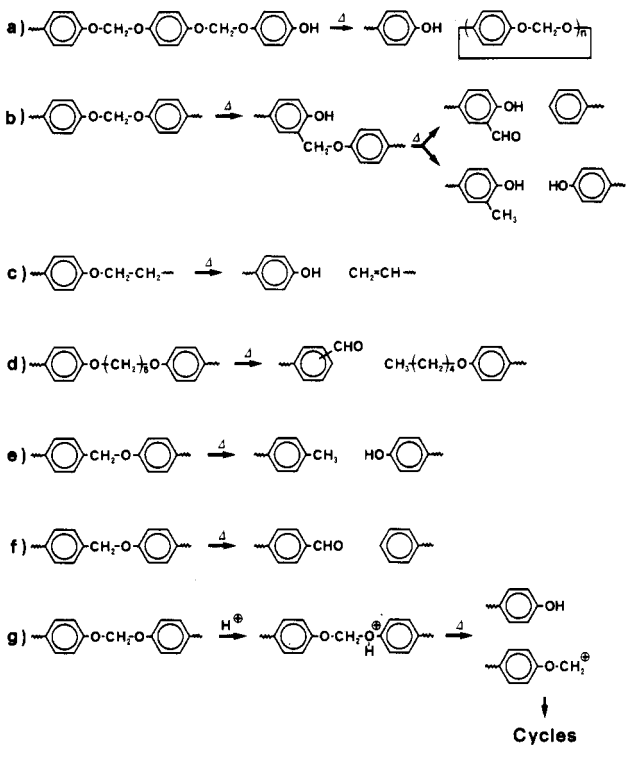


Figure 8. Mass spectrum of the thermal degradation products of polymer VIII at a probe temperature of 290 °C.

Scheme I



dehyde, hydroxy, methyl, and/or phenyl end groups (Scheme Ib).

The degradation process occurring in polyether IV involves a β-CH hydrogen transfer to the oxygen atom, producing compounds with hydroxy and olefin end groups (Scheme Ic).

Polymers V and VI follow the same degradation pathway of polymer IV (Scheme Ic); however, another thermal degradation mechanism involving a thermal rearrangement, leading to compounds with aldehyde and pentyl end groups, is also active (Scheme Id).

Polyethers VII and VIII decompose through two principal thermal processes: (i) an extensive hydrogen-transfer reaction leading to the formation of compounds with methyl and/or hydroxy end groups (Scheme Ie); (ii) a β-CH hydrogen transfer from the methylene group to the phenyl ring, resulting in the formation of compounds having aldehyde and/or phenyl end groups (Scheme If).

It appears therefore that, except for polyformals, which undergo cyclization, the aromatic-aliphatic polyethers investigated pyrolyze through hydrogen-transfer reactions leading to olefin, phenyl, hydroxy, aldehyde, and saturated aliphatic end groups, depending on the specific structure of the polyether.

The presence of APP affects the thermal decomposition of the polyethers, lowering the thermal stability of those having a PDT value higher than 400 °C and changing sometimes the nature of the pyrolysis products formed.

In polymers I and II the protonation of the oxygen atom by acid species leads to the formation of a carbenium ion that selectively promotes the generation of cyclic compounds (Scheme Ig), lowers their PDT values, and prevents the occurrence of other reactions like those reported in Scheme Ib.

APP affects the thermal degradation of polymers IV–VI lowering the PDT values and enhancing the abundance of the compounds arising from the β-CH hydrogen-transfer reactions.

The thermal stability and the composition of volatile pyrolytic products of polyethers VII and VIII are not influenced by the presence of APP.

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Registry No. I, 66983-33-3; II, 93975-54-3; III, 89883-46-5; IV, 69941-80-6; V, 73102-14-4; VI, 99838-19-4; VII, 33635-42-6; VIII, 34514-23-3; (bisphenol A)·(methylene chloride) (copolymer),

66987-35-7; (hydroquinone)·(methylene chloride) (copolymer), 93975-21-4; (resorcinol)·(methylene chloride) (copolymer), 89905-54-4; (bisphenol A)·(1,2-dichloroethane) (copolymer), 99838-16-1; (bisphenol A)·(1,6-dichlorohexane) (copolymer), 99838-17-2; (hydroquinone)·(1,6-dichlorohexane) (copolymer), 26374-78-7; (bisphenol A)·(*p*-xylene dibromide) (copolymer), 95983-88-3; (hydroquinone)·(*p*-xylene dibromide) (copolymer), 99838-18-3; catechol, 120-80-9; dichloromethane, 75-09-2; IX, 71247-65-9; X, 72004-84-3; XI, 263-29-6.

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Thermal Degradation of Aromatic–Aliphatic Polyethers. 2.† Flash Pyrolysis–Gas Chromatography–Mass Spectrometry

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ABSTRACT: The flash pyrolysis–gas chromatography–mass spectrometry (Py–GCMS) of two polyethers and of a low molecular weight model compound (1,6-diphenoxyhexane) has been performed. The pyrolysis products, generated through thermal rearrangement of polymer chains and subsequent thermal decomposition of thermal rearranged polymers, have been identified also with the help of a mass spectra library search system. Among the pyrolysis products detected, aldehydes, phenols, ethers, and aliphatic and aromatic hydrocarbons are the most abundant. The Py–GCMS profile is characteristic of each sample analyzed, in the appearance of unique components and in the distribution of the pyrolysis products. The Py–GCMS results are compared with those obtained by direct pyrolysis mass spectrometry of the same polyethers.

Introduction

In the accompanying paper[1] we have investigated the thermal decomposition of several polyethers by direct pyrolysis–mass spectrometry (DP–MS). The results indicate that those polymers undergo thermal degradation through hydrogen-transfer reactions leading to compounds with olefin, phenyl, hydroxy, aldehyde, and saturated aliphatic end groups. An intramolecular-exchange reaction, which produces cyclic formals as primary thermal fragments, it has been observed only in the case of polyformals.[1]

The identification of such a variety of pyrolysis products by DP-MS was sometimes difficult. In fact, the mass spectrum of a polymer is a multicomponent mixture produced by thermal degradation and, furthermore, the molecular ions of the thermally formed compounds appear mixed with the fragment ions formed by electron-impact reactions.[1]

Among analytical pyrolysis techniques, flash pyrolysis–gas chromatography–mass spectrometry (Py–GCMS) is capable of yielding precise information about the nature of the compounds generated by thermal degradation of polymers.[2,3] The small amount of sample required, the high resolution analysis, and the qualitative and quantitative information available from this technique have made Py–GCMS an essential tool in polymer analysis.[2,3] Furthermore the mechanistic information that may be obtained on the thermal fragmentation processes occurring in polymers also makes this technique very attractive.[2,3]

Py–GCMS differs from DP–MS for the pyrolysis conditions (heating rate up to 100 °C/ms, under inert atmo-

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