

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.

References and Notes

- (1) Foti, S.; Montaudo, G. In "Analysis of Polymers Systems"; Bark, L. S., Allen, N. S., Eds.; Applied Science Publishers: London, 1982; Chapter 5, p 103.
- (2) Ballistreri, A.; Foti, S.; Montaudo, G.; Scamporrino, E. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1147, 3101; *Makromol. Chem.* **1979**, *180*, 2835, 2843; *Polymer* **1981**, *22*, 131.
- (3) Ballistreri, A.; Montaudo, G.; Puglisi, C.; Scamporrino, E.; Vitalini, D. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1397; *J. Appl. Polym. Sci.* **1982**, *27*, 3369.
- (4) Ballistreri, A.; Foti, S.; Maravigna, P.; Montaudo, G.; Scamporrino, E. *Makromol. Chem.* **1980**, *18*, 2161; *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1923; **1981**, *19*, 1679; **1983**, *21*, 1583; *Polym. Degrad. Stab.* **1982**, *4*, 287.
- (5) Montaudo, G.; Puglisi, C.; Scamporrino, E.; Vitalini, D. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3321; *Macromolecules* **1984**, *17*, 1605.
- (6) Foti, S.; Guiffreda, M.; Maravigna, P.; Montaudo, G. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1217.
- (7) Montaudo, G.; Przybylski, M.; Ringsdorf, H. *Makromol. Chem.* **1975**, *176*, 1763.
- (8) Hummel, D. O.; Düssel, H. J.; Rosen, H.; Rübenacker, K. *Makromol. Chem.* **1975**, *176*, 471.
- (9) Jachowicz, J.; Kryszewski, M.; Sobol, A. *Polymer* **1979**, *20*, 995.
- (10) Lee, A. K.; Sedgwick, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 685.
- (11) Brauman, S. K. *J. Fire Retard. Chem.* **1980**, *7*, 61.
- (12) Grassie, N.; Zulficar, M. In "Developments in Polymer Stabilization, Part 1"; Scott, G., Ed.; Applied Science: London, 1979; Chapter 6, p 197.
- (13) Williams, F. J.; Hay, A. S.; Relles, H. M.; Carnahan, J. C.; Loucks, G. R.; Boulette, B. M.; Donahue, P. E.; Johnson, D. S. In "New Monomers and Polymers"; Culberstone, B. M., Pittman, C. U., Jr., Eds.; Plenum Press: New York, 1984; p 67.
- (14) Wiley, R. H. *Macromolecules* **1971**, *4*, 254.
- (15) Ballistreri, A.; Montaudo, G.; Puglisi, C. *J. Therm. Anal.* **1984**, *29*, 237.
- (16) Schulten, H. R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984**, *3*, 231.
- (17) Foti, S.; Maravigna, P.; Montaudo, G.; Liguori, A. *Anal. Chem.* **1982**, *54*, 674.
- (18) Foti, S.; Maravigna, P.; Montaudo, G. *Macromolecules* **1982**, *15*, 883.
- (19) Montaudo, G.; Puglisi, C.; Scamporrino, E.; Vitalini, D. *Macromolecules*, following paper in this issue.
- (20) Alcock, H. R. *J. Macromol. Sci., Rev. Macromol. Chem.* **1970**, *C4*, 149.
- (21) Semlyen, J. A. *Adv. Polym. Sci.* **1976**, *21*, 41.
- (22) Goethals, E. J. *Adv. Polym. Sci.* **1977**, *23*, 103.
- (23) Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980; p 50.
- (24) Marty, R. A.; De Mayo, P. J. *Chem. Soc., Chem. Commun.* **1971**, 127.
- (25) Meuzelaar, H. L. C.; Haverkamp, J.; Hileman, F. D. In "Pyrolysis Mass Spectrometry of Recent and Fossil Biomaterials"; Elsevier: New York, 1982.

Thermal Degradation of Aromatic-Aliphatic Polyethers. 2.[†] Flash Pyrolysis-Gas Chromatography-Mass Spectrometry

G. Montaudo,*[‡] C. Puglisi,[§] E. Scamporrino,[‡] and D. Vitalini[§]

Dipartimento di Scienze Chimiche, Università di Catania, 95125 Catania, Italy, and Istituto per la Chimica e la Tecnologia dei Materiali Polimerici, Consiglio Nazionale delle Ricerche, Viale Andrea Doria, 6, 95125 Catania, Italy. Received June 11, 1985

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 paper¹ 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-

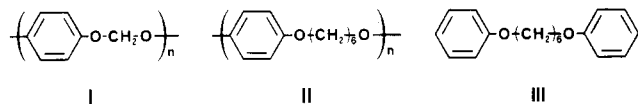
[†] For part 1, see ref 1.

[‡] Università di Catania.

[§] Consiglio Nazionale delle Ricerche.

sphere). Often, an extensive fragmentation of the polymer chain is occurring, and principally low molecular weight compounds are generated. Although high molecular weight compounds may also be formed, they may undergo further thermal degradation because of the relatively long residence time at high temperatures, and usually many high-mass pyrolyzates will not elute from the GC column. The pyrolysis products are separated by gas chromatography (GC) and analyzed by mass spectrometry (MS). As a consequence, time-resolved thermal degradation of polymers is not possible,^{1,3} compounds at high molecular weight are lost and the occurrence of secondary thermal degradation processes is observed.

In view of all this, it seemed interesting to perform Py-GCMS of two polyethers (I and II) investigated by DP-MS¹ and of a low molecular weight compound (III)



and to compare the results. The fact that Py-GCMS is a well-established method for polymer analysis,² while DP-MS is a relatively new technique, whose applications to polymers are still being explored,^{3,4} adds interest to this comparison.

Experimental Section

Materials. Poly(*p*-phenylenoxydimethylene ether) (polymer I) was synthesized from hydroquinone and dichloromethane according to the method already described.¹

Poly(*p*-phenylenoxyhexamethylene ether) (polymer II) was synthesized from hydroquinone and 1,6-dichlorohexane using tetrabutylammonium bromide (TBAB) as phase-transfer catalyst, as reported elsewhere.¹

1,6-Diphenoxyhexane was synthesized from phenol and 1,6-dichlorohexane, using TBAB as phase-transfer catalyst. Thus 0.2 mol of phenol, 0.1 mol of 1,6-dichlorohexane, 0.01 mol of TBAB, and 50 mL of toluene were placed into a three-necked flask, equipped with a magnetic stirrer and reflux condenser, under nitrogen flow. Then, 0.4 mol of NaOH pellets were added, and the dispersion was heated in an oil bath at 75 °C for 20 h. After cooling, the organic phase was separated and dried in a rotary evaporator. The solid residue was crystallized from toluene to obtain a white compound with mp 81–83 °C.

Flash Pyrolysis-Gas Chromatography-Mass Spectrometry. Flash pyrolysis experiments were carried out on a Pyroprobe Model 150 pyrolyzer from Chemical Data Systems, using a platinum coil at 950 °C (pyrolysis temperature set on the dial) per 5 s, a heating rate of 70 °C/ms, under helium. The weight of the samples was 0.5 mg.

Analyses of the pyrolysis products were performed on a Carlo Erba 4200 gas chromatograph combined with a Kratos MS 50 S double-focusing mass spectrometer. Gas chromatographic separation was accomplished on a WCOT silica capillary column (30 m × 0.22 mm i.d.), coated with an apolar stationary phase (CP-Sil 5 CB). The gas chromatographic separation of the products generated from the pyrolysis of 1,6-diphenoxyhexane was performed on a WCOT silica capillary column (30 m × 0.22 mm i.d.) coated with a polar stationary phase (Superox). The oven temperature program was as follows: 40 °C; initial time 5 min.; heating rate 10 °C/min.; final temperature 320 °C. Helium was used as carrier gas.

Mass spectra were acquired by Data General Eclipse/120 data system operating under Kratos DS 55 Software. The mass spectrometer was scanned repetitively from *m/z* 17 to *m/z* 500 at a scan rate of 0.7 s/decade; the ionizing conditions were 70 eV. The spectra were stored on a disk and manipulated by the data system in several ways, including display in real time. The analysis of GCMS data and the structural assignments of each compound were made by inspection of EI fragmentation pathways of the mass spectra.

Further assignments were confirmed by using the library search method provided with the Kratos DS 55 software. The latter uses

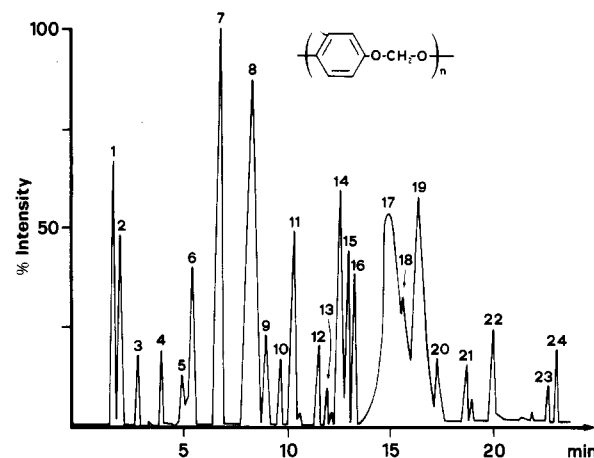


Figure 1. Total ion current chromatogram of the on-line flash pyrolysis-GCMS analysis of polyether I. The most important compounds have been numbered; the corresponding MS data have been compiled in Table I.

an algorithm comparing the mass spectrum of the unknown compound with library reference spectra to find the best matches.⁵

The library holds more than 38 000 entries, each containing a maximum of 20 peaks for mass spectrum. Each peak consists of integer (nominal) mass in the range 34–1024 amu, and its relative intensity in the mass spectrum is expressed in percentage of the base peak.

Score values accompanying computer best matching spectra, found in agreement with independent assignments, usually ranged between 90 and 100.

Results

Polyether I. Figure 1 shows the total ion current chromatogram of the on-line Py-GCMS of polyether I. The most significant peaks are numbered. The structural assignments of the pyrolysis products identified and the six most intense EI fragmentation ions, for each compound, are reported in Table I.

All the pyrolysis products identified can be classified in four groups: olefin and aromatic hydrocarbons, aldehydes, phenols, and ethers (Scheme I).

Given the wide range of compounds with different functional groups generated in the pyrolysis of polyethers and the use of an apolar stationary phase column, the phenolic and hydroquinone peaks in the GC tracing (Figures 1 and 2) were quite broad.

The most intense GC peaks in the chromatograms (Figure 1) are due to compounds containing hydroxy (phenol, hydroquinone) and aldehyde (benzaldehyde, benzenedicarboxaldehyde) groups. A series of aromatic hydrocarbons such as benzene, toluene, xylene, biphenyl, and dihydronaphthalene are also present with lower intensity. Methoxybenzene, methoxybenzaldehyde, phenoxyphenylmethane, and other ethers also appear among the pyrolysis products (Figure 1, Table I). The presence of GC peaks corresponding to 1,3-butadiene and 2,5-cyclohexadiene-1,4-dione, which are likely generated from benzene and hydroquinone, is also observed.

It can be noted that, among the pyrolysis products obtained by the Py-GCMS of polyether I (Table I), compounds reflecting the primary structure of the original polymer are not found. Although, higher molecular weight compounds containing the original structure of polymer I might be formed, they are not detected because either they undergo further thermal degradation or cannot be eluted.

The nature of the pyrolysis compounds cannot be easily accounted for without assuming the occurrence of a primary thermal process involving an intramolecular re-

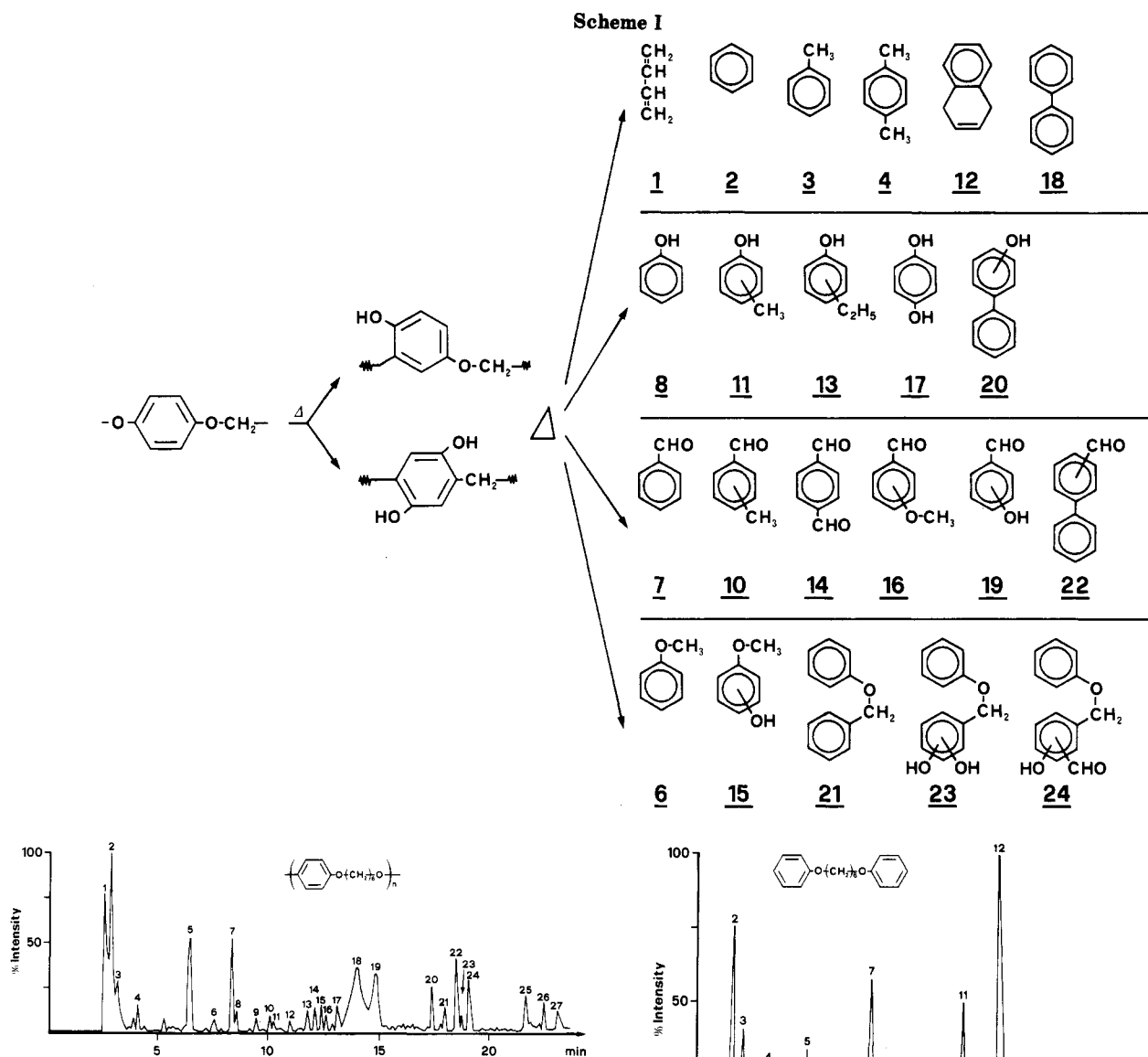


Figure 2. Total ion current chromatogram of the on-line flash pyrolysis-GCMS analysis of polyether II. The most important compounds have been numbered; the corresponding MS data have been compiled in Table II.

carboxaldehyde (Scheme I) may originate through recombination reactions.

Polyether II. Figure 2 shows the total ion current chromatogram of the on-line Py-GCMS of polyether II. The most significant peaks are numbered. Table II reports the structural assignments of the pyrolysis products identified and the six most intense EI fragmentation ions for each compound.

Pyrolysis products can be classified in five groups (Scheme II) according to their chemical structure. Thus, we find olefin and aromatic hydrocarbons, phenols, aldehydes, ethers, and quinones.

The most intense peaks (Figure 2) are due to phenols (phenol, hydroquinone), olefinic compounds (1,3-pentadiene, hexene) and 2,5-cyclohexadien-1,4-dione. Compounds with aldehyde functional groups show lower intensities, with the exception of the hydroxybenzaldehyde peak (Figure 2). Another series of peaks (21–27 in Figure 2) correspond to ethers having saturated or unsaturated aliphatic chains (Table II); benzofuran derivatives are also found (methylbenzofuran and dihydrobenzofuran).

Also in this case the nature of pyrolysis compounds can be accounted for by assuming a thermal rearrangement

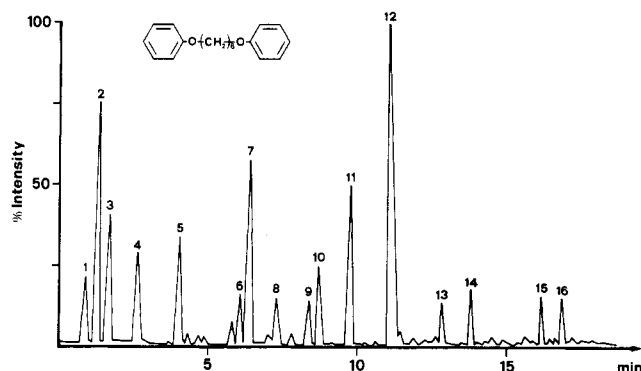
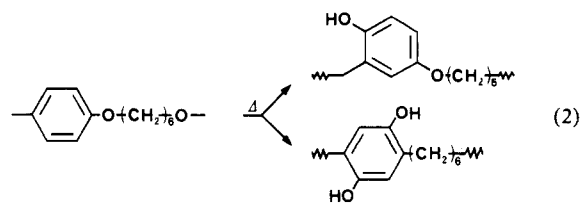


Figure 3. Total ion current chromatogram of the on-line flash pyrolysis-GCMS analysis of model compound III. The most important compounds have been numbered; the corresponding MS data have been compiled in Table III.

generating two main structures along the polymer chain (eq 2) through hydrogen-transfer, elimination, and/or re-

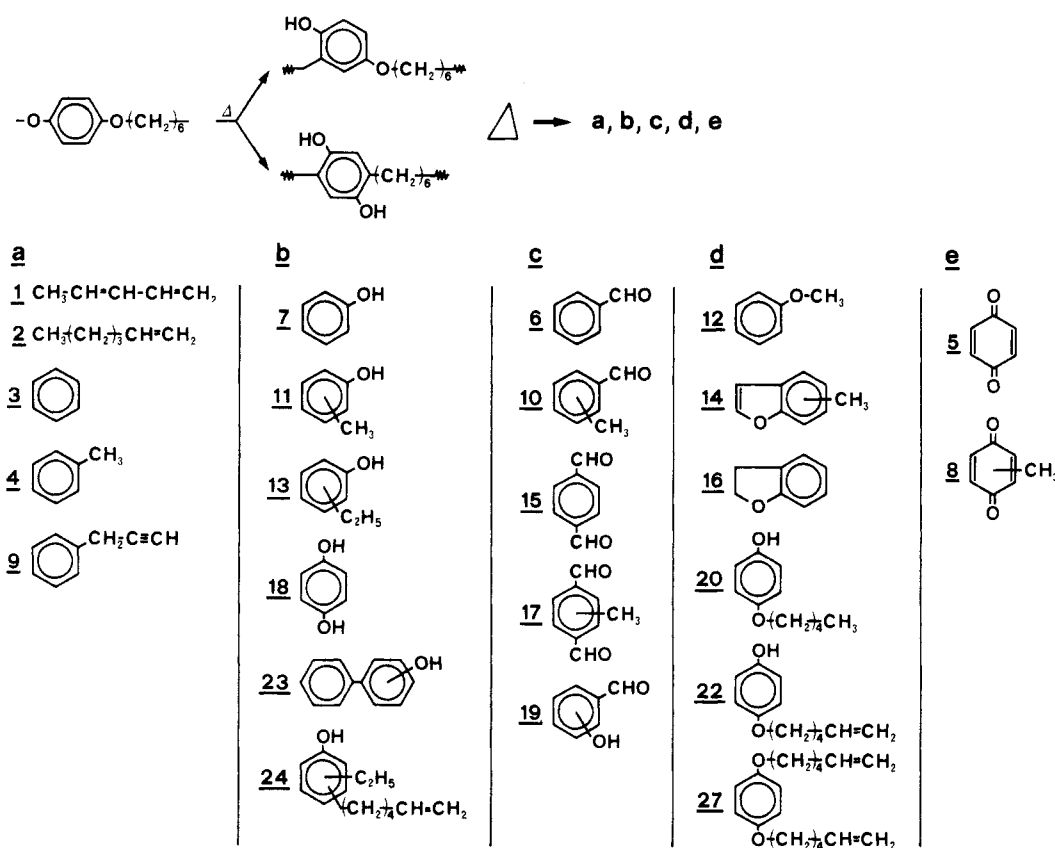


combination reactions to yield the pyrolysis products detected (Table II).

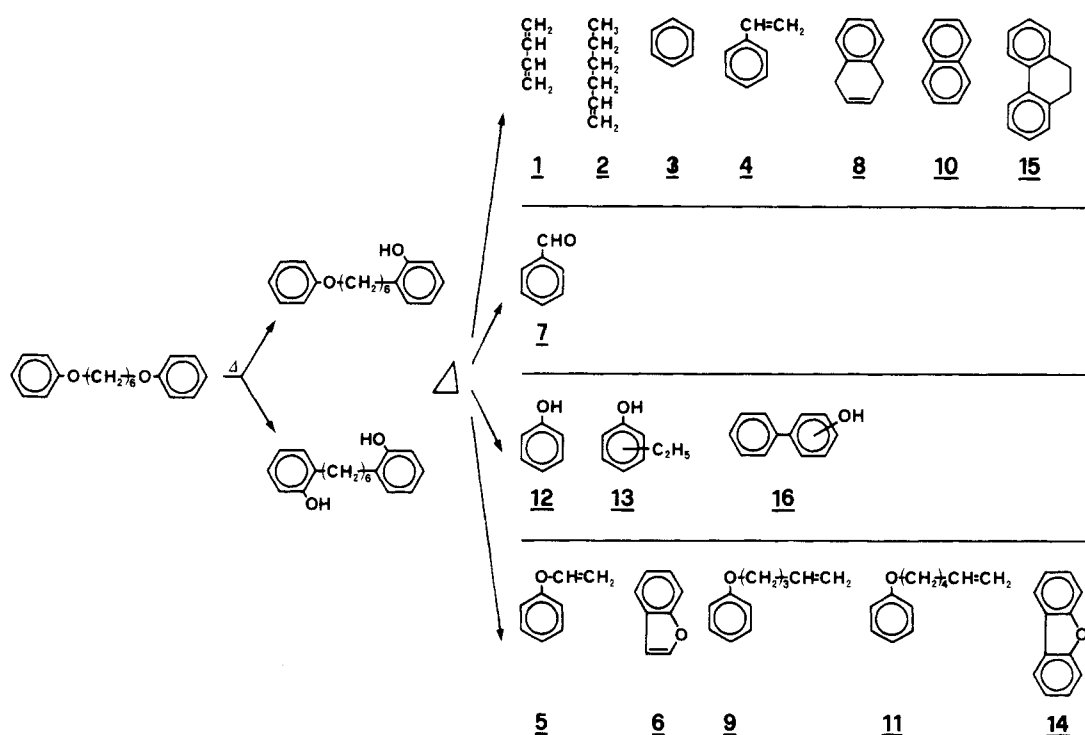
Compounds detected in the Py-GCMS of polyether II do not show the structural unit of the original polymer.

Model Compound. The flash pyrolysis of a low molecular weight model compound was performed in order to confirm the thermal rearrangements observed in the case of polymer II.

Scheme II



Scheme III



The high resolution pyrogram of the on-line Py-GCMS of this model compound is shown in Figure 3. The structural assignments and the six most intense EI fragmentation ions for each pyrolysis compound are reported in Table III.

Also in this case it is possible to classify pyrolysis products in four groups (Scheme III): olefin and aromatic hydrocarbons, aldehydes, phenols, and ethers. Quinone compounds cannot be found in this case.

Although the chemical structure of the pyrolysis fragments is the same as that found for polyether II, the number of products is lower due to the simpler structure of the model compound. Consequently one finds, among the aldehydes, only benzaldehyde and among the phenols, only phenol, ethylphenol, and hydroxybiphenyl.

The most numerous peaks in the GC tracing (Figure 3) are due to ether, olefin, and aromatic compounds. Benzofuran and dibenzofuran are also present, among the

Table III
Mass Spectrometric Data of Model Compound as Obtained by Py-GCMS

peak ^a	molecular ion ^b	major EI fragments ^c	structural assignment ^d
1	54 (100)	39 (88), 53 (64), 50 (24), 51 (24), 52 (11), 49 (6)	1,3-butadiene
2	84 (32)	41 (100), 56 (88), 42 (64), 55 (60), 43 (52), 39 (49)	hexene
3	78 (100)	52 (32), 51 (32), 50 (32), 39 (29), 77 (18), 38 (11)	benzene
4	104 (100)	103 (40), 78 (32), 51 (28), 77 (23), 50 (12), 105 (12)	ethenylbenzene
5	120 (100)	91 (72), 94 (36), 77 (21), 51 (17), 119 (14), 39 (12)	(ethenyloxy)benzene
6	118 (100)	89 (36), 90 (36), 63 (20), 39 (14), 62 (12), 38 (8)	benzofuran
7	106 (92)	77 (100), 105 (92), 51 (36), 50 (18), 78 (13), 52 (9)	benzaldehyde
8	130 (100)	129 (72), 115 (44), 128 (40), 127 (21), 131 (11), 77 (8)	dihydronaphthalene
9	162 (22)	94 (100), 41 (58), 69 (26), 39 (24), 68 (23), 77 (23)	1-penten-5-phenoxy
10	128 (100)	51 (12), 129 (11), 64 (10), 127 (9), 63 (7), 102 (7)	naphthalene ^e
11	176 (70)	94 (100), 55 (87), 41 (83), 67 (76), 77 (75), 82 (60)	1-hexen-6-phenoxy
12	94 (100)	66 (24), 39 (24), 65 (20), 40 (14), 55 (9), 47 (6)	phenol ^e
13	122 (28)	107 (100), 77 (17), 39 (13), 108 (9), 51 (8), 53 (6)	ethylphenol
14	168 (100)	139 (23), 169 (12), 84 (10), 44 (5), 63 (5), 39 (4)	dibenzofuran
15	180 (100)	179 (60), 178 (36), 165 (25), 89 (18), 181 (13), 76 (13)	dihydrophenanthrene
16	170 (100)	169 (68), 141 (32), 115 (25), 168 (13), 171 (11), 142 (11)	hydroxybiphenyl

^a Peak numbers in Figure 1 and compound numbers in text.

^b Molecular ion in the corresponding EI spectrum; the relative intensities are given in parentheses. ^c The relative abundances of the EI fragments are given in parentheses. ^d Structural assignments were confirmed by using the library search of the Kratos DS 55 software, except for peaks (e).

ethers, likely originated by cyclization reactions from vinyl phenyl ether and hydroxybiphenyl.

Discussion

Analytical pyrolysis methods are aimed at the characterization of the original sample through analysis of the pyrolysis products.

In the Py-GCMS, the pyrolysis compounds are separated and quantified, and the product distribution is used for the identification of the original sample. However, in this respect the Py-GCMS analysis of the two polyethers investigated here is elusive. In fact, from the inspection of the pyrolysis products detected, the identity of the original polymer cannot be recomposed or deduced.

The determination of polymer structure usually necessitates the identification (and quantification, when possible) of large pyrolytic fragments. In fact, higher molecular weight fragments yield information of the sequence arrangement of subunits, which is especially useful in the analysis of condensation polymers with large molecular weight repeating units, and of random, block, and sequential copolymers.

The thermal fragments detected in the pyrolysis of polyether I by DP-MS (cyclic formals, phenols, and aldehydes) show a range of molecular weight up to the pentamer stage and therefore contain the repeating unit of the original polymer I.

Pyrolysis products detected by Py-GCMS do not show compounds of molecular weight high enough to contain the repeating unit of the original polymer, so this information would have been lost. However, Py-GCMS has allowed the identification of lower molecular weight compounds (aldehydes and phenols, mainly) that match pretty well with those detected by DP-MS, permitting substantiation of the structural assignments and the mechanisms of the proposed thermal degradation.¹

An identical situation arises in the case of polyether II. Two mechanisms were found to be active by DP-MS:¹ a β -CH hydrogen transfer producing olefins and phenols and a rearrangement leading to compounds with aldehyde and pentyl end groups.¹

Pyrolysis fragments detected in the Py-GCMS of polyether II, although of low molecular weight, correspond to olefins, phenols, aldehydes and to a compound with pentyl end groups, substantiating the structural assignments and the mechanisms of the proposed thermal degradation.¹

It appears that the main value of Py-GCMS in the present study, in the elucidation of the mechanisms of thermal degradation of condensation polymers, lies in the identification of the structure and amount of the compounds generated in the pyrolysis.

In several instances, the chemical structure of the pyrolysis compounds detected by Py-GCMS is diagnostic and allows an assessment of the thermal decomposition pathways.²

However, only thermally stable low molecular weight compounds are eluted from the GC column, so Py-GCMS data often offer a partial view of the decomposition processes occurring.

Under this respect DP-MS suffers less limitation.

Acknowledgment. This work was carried out under financial support from the Italian Ministry of Public Education and Consiglio Nazionale delle Ricerche (Rome), Finalized Project of Fine and Secondary Chemistry.

Registry No. I, 93975-54-3; II, 99838-19-4; (hydroquinone)-(dichloromethane) (copolymer), 93975-21-4; (hydroquinone)-(1,6-dichlorohexane) (copolymer), 26374-78-7; 1,6-diphenoxyhexane, 10125-18-5; phenol, 108-95-2; 1,6-dichlorohexane, 2163-00-0.

References and Notes

- Montaudo, G.; Puglisi, C.; Scamporrino, E.; Vitalini, D. *Macromolecules*, preceding paper in this issue.
- Irwin, W. J. "Analytical Pyrolysis"; M. Dekker: New York, 1982 and references cited therein.
- Schulten, H. R.; Lattimer, R. P. *Mass Spectrom. Rev.* **1984**, *3*, 231.
- Foti, S.; Montaudo, G. In "Analysis of Polymers Systems"; Bark, L. S., Allen, N. S., Eds.; Applied Science: London, 1982; Chapter 5, p 103.
- Kratos Ds 55 Software User's Guide, library search application note.