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PYROLYSIS MASS SPECTROMETRY OF HEXOLIC BASED POLYESTERS

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ABSTRACT

Polyesters based on hexolic anhydride, hexolic-ethylene glycol (H-EG) and hexolic-1,4-butanediol (H-BD), have been synthesized for the first time by melt condensation in vacuum. Pyrolysis mass spectrometric studies have been done on these two polyesters at 300°C. From the mass spectral data, a plausible mechanism of degradation is proposed. To explain the different fragment ions formed during pyrolysis–electron impact, β-scissions in esters, acyl–oxygen and alkyl–oxygen bond homolysis, carbon–carbon bond scissions in the alkyl part of the glycol unit, pericyclic type reaction, McLafferty type rearrangement, retro Diels–Alder reaction, etc., have been invoked. In both the polyesters HCl is found to be one of the major products of pyrolysis. Further, the present study provides clues for the presence of ether linkages in the H-EG polyester.

INTRODUCTION

Halogenated compounds [1–5], preferably chlorinated or brominated, are extensively used to impart flame retardancy in polymers. Hexachlorocyclopentadiene (HEX) and compounds containing a HEX moiety but devoid of any reactive functional groups are generally used as flame retardant additives. One of the easiest ways of obtaining flame retardant polyesters is to use halogenated diols or dicarboxylic acids/anhydrides as monomers or comonomers in the polyester synthesis.

1,4,5,6,7,7-Hexachloro-5-norbornene-2,3-dicarboxylic acid (HET-acid) is an attractive flame retardant comonomer in the field of polyesters. Detailed studies have been made about this material and polyesters based on this

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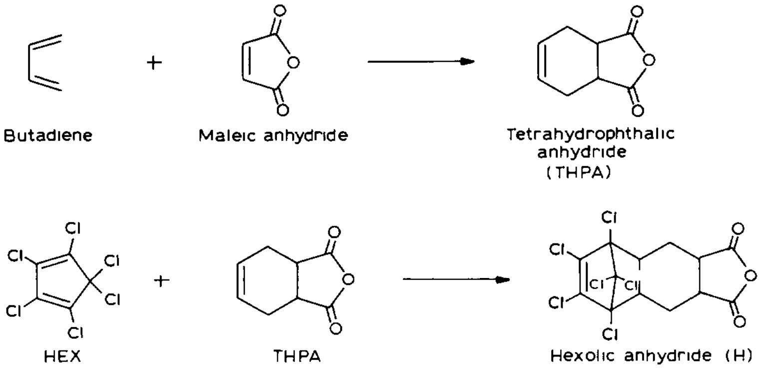
particular monomer [6–9]. Yet another interesting dicarboxylic acid anhydride containing the HEX unit is hexolic anhydride [10]. Research work on this particular compound is scarce.

Hexolic anhydride is synthesized by the well-known Diels–Alder reaction [11–13].



Herein we present the synthesis of polyesters based on hexolic anhydride, ethylene glycol and 1,4-butanediol. A preliminary study on the degradation behaviour of these polyesters is undertaken by pyrolysis–mass spectrometric techniques [14–17]. On the basis of the fragmentation ions formed during pyrolysis–electron impact, the mechanism of degradation is elucidated and presented in detail.

EXPERIMENTAL

Materials

Hexolic anhydride was supplied by Hooker Chemical Corporation, Belgium as a gift sample, and used as received without any further purification. Ethylene glycol (Merck) and 1,4-butanediol (Merck) were purified by vacuum distillation.

Methods

Synthesis of polyesters

Polyesters of hexolic anhydride with either ethylene glycol or 1,4-butanediol were synthesized by a melt condensation technique. The condensation was carried out at 170–180°C in vacuum (0.1 mm Hg) for 24 h. A clear, glassy product was obtained in both cases. The polyesters were purified by dissolving in acetone and reprecipitating in water. The precipitated product was filtered and dried in vacuo at 60°C.

Pyrolysis–mass spectrometry

Pyrolysis of H-EG and H-BD samples was performed by inserting the sample deposited on a platinum ribbon directly into the mass spectrometer.

Using an acetone solution of the substance, a 0.2 mg sample was accurately deposited on the platinum ribbon of the Hewlett-Packard 18580A pyroprobe. Before inserting the ribbon probe into the mass spectrometer, the ribbon was repeatedly heated to 200°C so as to evaporate the major portion of the solvent. The sample holder was then inserted into the mass spectrometer (Balzers QMG 511) so that a distance of ca. 5 cm was achieved between the sample holder and the ion source (EI, Cross Beam). The temperature of the mass spectrometer was 120°C. After setting up the high vacuum, the background spectrum was recorded. The sample deposited on the platinum ribbon probe was heated to 300°C for 20 s and the mass spectrum scan was immediately initiated. The mass spectra were recorded by means of a UV recorder.

The following instrument settings were employed: mass range, 10–550 amu; scan rate, 30 ms u^{-1}; gain, 1×10^{-7}; SEM, 300; res, 48; UV recorder speed, 25 mm s^{-1}.

DISCUSSION

The pyrolysis mass spectra of the polyesters H-EG and H-BD are presented in Fig. 1. The *m/z* values, relative intensities and probable

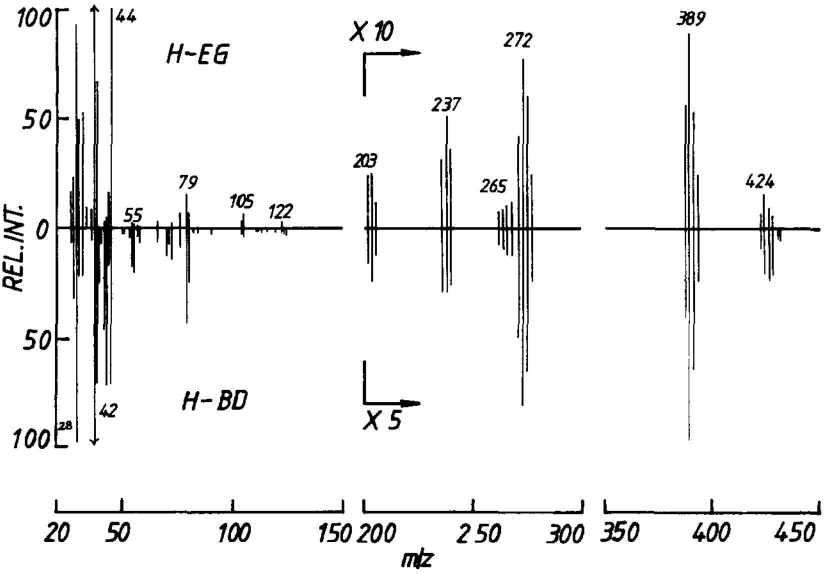
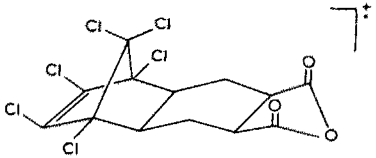
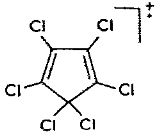
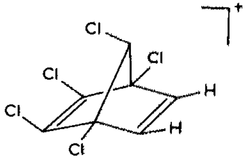
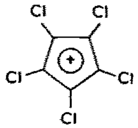


Fig. 1. Pyrolysis–mass spectra of H-EG (above) and H-BD (below) at 300°C.

TABLE 1

Pyrolysis–mass spectrometry studies on the polyesters H-EG and H-BD (pyrolysis temperature: 300°C)

Serial No.	m/z	Intensity (arbitrary units)		Probable structure of the ion
		H-EG	H-BD	
1	430	–	0.8	 hexolic $C_{13}H_8Cl_6O_3^{+\cdot}$
2	428	0.7	4.2	
3	426	1.0	4.8	
4	424	1.6	4.0	
5	422	0.8	1.8	
6	393	2.5	4.8	$[\text{hexolic-Cl}]^+$
7	391	5.4	12.9	
8	389	9.0	19.4	
9	387	5.7	8.1	
10	276	2.6	4.8	$C_5Cl_6^{+\cdot}$ → 
11	274	6.1	12.9	
12	272	7.9	16.1	
13	270	4.3	9.7	
14	267	1.3	2.4	$C_7H_2Cl_5^{+}$ → 
15	265	1.2	2.4	
16	263	0.8	1.8	
17	261	0.8	1.5	
18	239	3.6	5.2	$C_5Cl_5^{+}$ → 
19	237	5.3	5.7	
20	235	3.3	5.7	

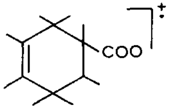
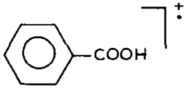
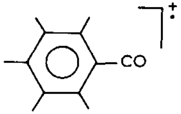
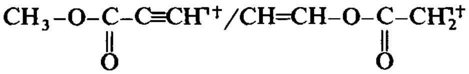
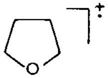
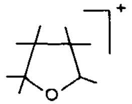
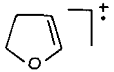
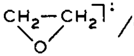
21	205	1.3	2.4	$C_5HCl_4^{\rceil +}$
22	203	2.6	4.5	
23	201	2.5	3.4	
24	124	–	3.2	
25	123	–	1.6	$[124\text{-}H]^+$
26	122	3.3	1.6	$C_7H_6O_2^{\rceil +\cdot} \rightarrow$ 
27	119	–	1.6	$C_3H_3O_5^{\rceil +}$
28	115	–	1.6	$C_3H_5Cl_2^{\rceil +}$
29	113	–	1.6	
30	111	–	1.6	
31	105	6.6	4.8	$C_7H_5O^{\rceil +} \rightarrow$ 
32	104	2.5	3.2	$C_7H_4O^{\rceil +\cdot}$
33	90	–	3.2	$HO\text{–}(CH_2)_4\text{–}OH^{\rceil +\cdot}$
34	84	–	1.6	 $CH_3\text{–}O\text{–}\underset{\overset{\Vert}{O}}{C}\text{–}C{\equiv}CH^{\rceil +\cdot}/CH{=}CH\text{–}O\text{–}\underset{\overset{\Vert}{O}}{C}\text{–}CH_2^{\rceil +\cdot}$
35	82	–	1.6	$O{=}C\text{–}CH{=}CH\text{–}C{\equiv}O^{\rceil +\cdot}$
36	80	8.2	25.8	$C_6H_8^{\rceil +\cdot}$
37	79	16.4	45.2	$C_6H_7^{\rceil +}$
38	76	6.6	9.7	$C_6H_4^{\rceil +\cdot}$
39	72	1.6	14.5	$CH_2CH_2\text{–}O\text{–}CH_2CH_2^{\rceil +\cdot}/$ 

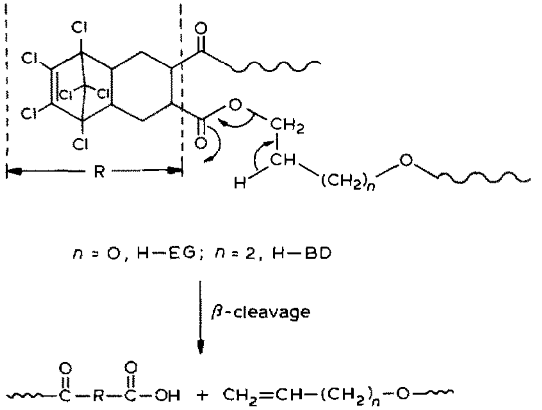
TABLE 1 (continued)

Serial No.	m/z	Intensity (arbitrary units)		Probable structure of the ion
		H-EG	H-BD	
40	71	–	8.1	$C_4H_7O^{\rceil +} \rightarrow$ 
41	70	–	12.9	$C_4H_6O^{\rceil +\cdot} \rightarrow$ 
42	66	3.3	6.5	$HC{\equiv}C{-}O{-}C{\equiv}CH^{\rceil +\cdot}/C_5H_6^{\rceil +\cdot}$
43	57	3.3	8.1	$CH_2{=}CH{-}O{-}CH_2^{\rceil +}/CH_3CH_2CH_2CH_2^{\rceil +}$
44	56	–	4.8	$CH{=}CH{-}O{-}CH_2^{\rceil +\cdot}/CH_2CH_2CH_2CH_2^{\rceil +\cdot}$
45	55	3.3	21.0	$CH{\equiv}C{-}O{-}CH_2^{\rceil +}/CH_2CH_2{-}CH{=}CH_2^{\rceil +}$
46	54	3.3	19.4	$C{\equiv}C{-}O{-}CH_2^{\rceil +\cdot}/CH_2{=}CH{-}CH{=}CH_2^{\rceil +\cdot}$
47	53	–	4.8	$CH_2{=}C{-}CH{=}CH_2^{\rceil +}$
48	51	–	3.2	$CH_2{=}C{-}C{\equiv}CH^{\rceil +}$
49	50	–	3.2	$HC{\equiv}C{-}C{\equiv}CH^{\rceil +\cdot}$

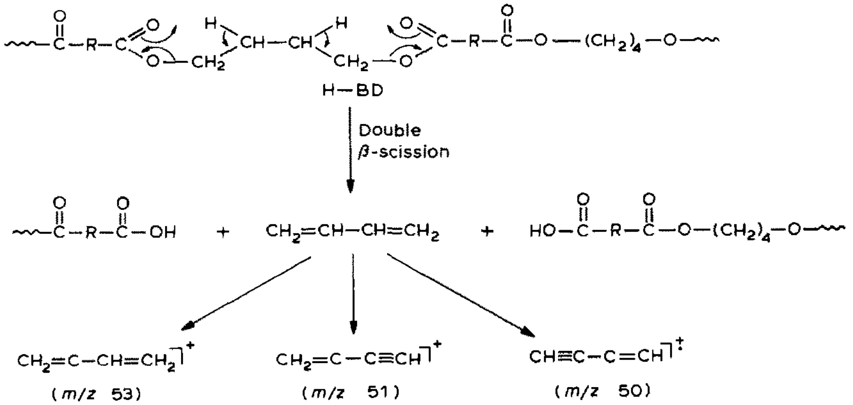
50	44	100.0	71.0	$CO_2^{\rceil+\cdot}$/  /$CH_3CHO^{\rceil+\cdot}$
51	43	14.8	17.7	$CH_3CO^{\rceil+}$/$CH_3-CH_2CH_2^{\rceil+}$
52	42	1.6	74.2	$CH_2CO^{\rceil+\cdot}$/$CH_3-CH{=}CH_2^{\rceil+\cdot}$
53	41	3.3	48.4	$C_2HO^{\rceil+}$/$CH_3-CH{=}CH^{\rceil+}$/$CH_2{=}CH-CH_2^{\rceil+}$
54	40	–	8.1	 /$CH\equiv C-CH_3^{+\cdot}$
55	39		25.8	 /$HC\equiv C-CH_2^{\rceil+}$
56	38	67.2	71.0	$HCl^{\rceil+\cdot}$
57	37	1.6	–	$Cl^{\rceil+}$
58	36	← off range →		$HCl^{\rceil+\cdot}$
59	35	8.2	6.5	$Cl^{\rceil+}$
60	33	9.6	–	$CH_3OH_2^{\rceil+}$
61	31	52.5	22.6	$CH_2OH^{\rceil+}$/$CH_3O^{\rceil+}$
62	29	49.2	22.6	$CH_3-CH_2^{\rceil+}$/$CHO^{\rceil+}$
63	28	91.8	100.0	$CH_2{=}CH_2^{\rceil+\cdot}$/$CO^{\rceil+\cdot}$
64	27	23.0	33.9	$CH_2{=}CH^{\rceil+}$
65	26	16.4	8.1	$CH\equiv CH^{\rceil+\cdot}$

structures of the ions are detailed in Table 1. Herein an elaborate discussion pertaining to the degradation mechanism of hexolic anhydride polyesters is presented.

It is well known that the main fragmentation route in polyesters is β-scission [14–16]. The transfer of a β-hydrogen from the methylene group present in the glycol part to the ester carbonyl oxygen through a six-membered cyclic transition state will lead to the production of a capped carboxylic acid end and vinyl- or but-1-enyl end capped units from H-EG and H-BD, respectively. This process is schematically represented below:

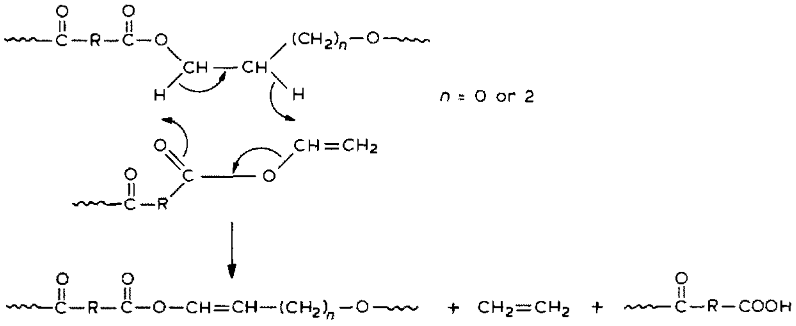


A double β-hydrogen transfer from the glycol unit to the ester carbonyl oxygens present on either side of the diol unit will lead to the formation of the carboxylic acid end capped units and acetylene or 1,3-butadiene from

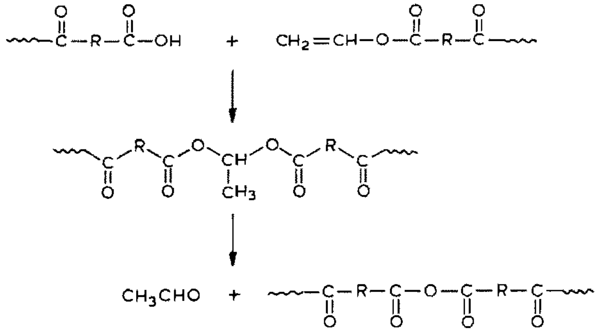


H-EG and H-BD, respectively. From Table 1 it is clear that acetylene is formed from both H-EG and H-BD whereas the ejection of butadiene is seen only in the case of H-BD.

The formation of ethylene during pyrolysis is seen to a considerable extent from both H-EG and H-BD. To explain this product formation it is necessary to invoke an intra-molecular and/or inter-chain hydrogen transfer to the vinyl end capped units formed by the *β*-scission process.

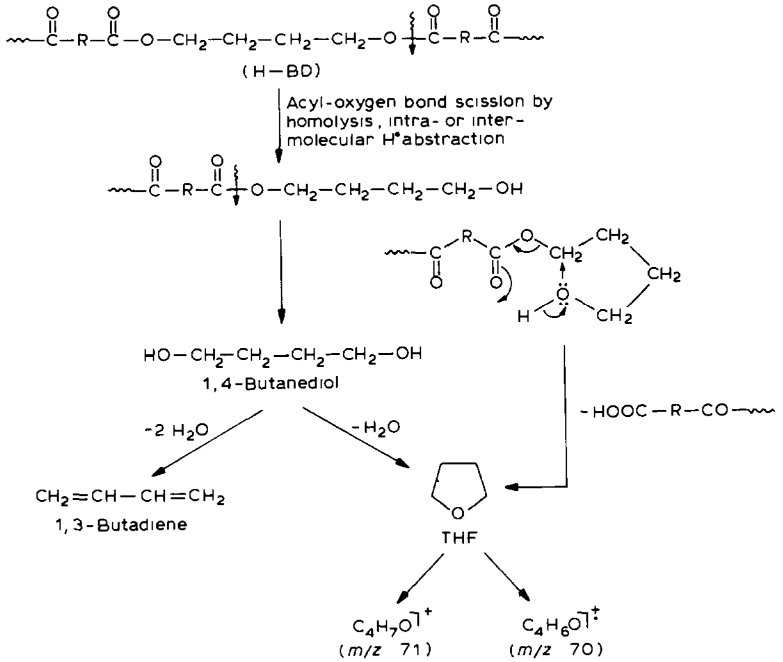


In any ethylene glycol containing polyesters, the chief degradation product is acetaldehyde [18]. The formation of acetaldehyde can be easily accounted for from the reaction product formed between the capped vinyl end and the terminated carboxylic acid units produced by *β*-scission.

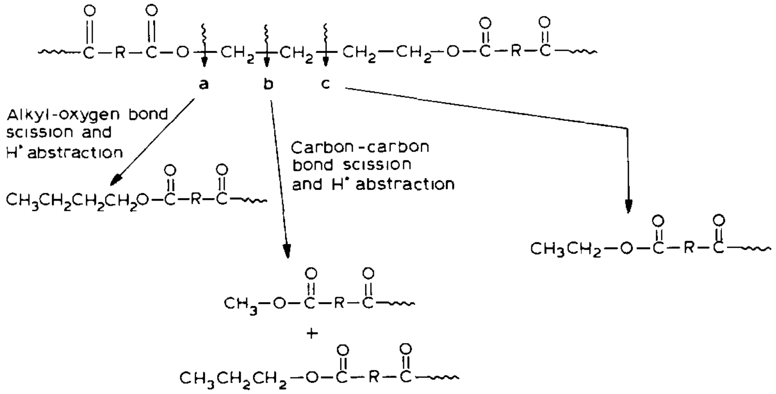


One of the major products in the degradation of the polyester H-BD is tetrahydrofuran (THF) (*m/z* 72). The formation of THF can be accounted for on the basis of two different mechanisms. The acyl–oxygen bond cleavage in the polyester chain by homolysis followed by an inter- or intra-molecular H˙ abstraction will lead to the formation of terminated alcohol units. This particular unit may further undergo a proton transfer through a bicyclo [4.3.0] type transition state and thus eject THF. The other possibility is that the terminated alcohol unit may further undergo a second homolysis at the acyl–oxygen bond followed by H˙ abstraction leading to the formation of a 1,4-butanediol molecule (*m/z* 90). This diol can give rise to either THF by the elimination of a water molecule or butadiene by the ejection of two water molecules.

Another degradation route in polyesters containing the aliphatic diols is the carbon–carbon bond scissions. The formation of $CH_3CH_2CH_2CH_2]^{+}$ (*m/z* 57), $CH_2CH_2CH_2CH_2]^{\cdot+}$ (*m/z* 56), $CH_3CH_2CH_2]^{+}$ (*m/z* 43) and $CH_3CH=CH_2]^{\cdot+}$ (*m/z* 42) species from H-BD clearly provides evidence for

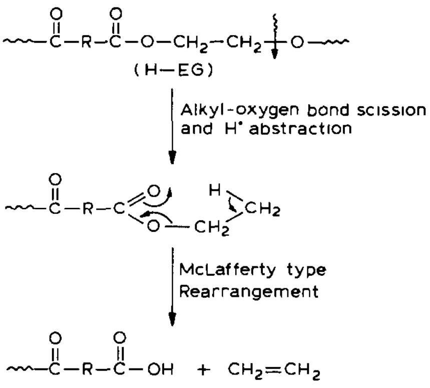


the occurrence of alkyl–oxygen and carbon–carbon bond scissions during the pyrolysis–electron impact process. Thus, alkyl–oxygen bond scission



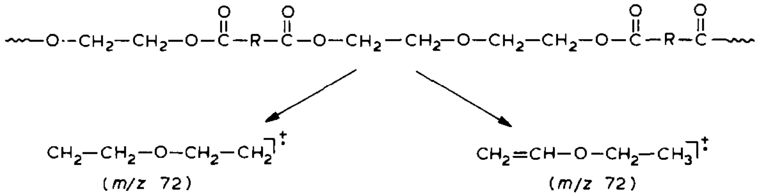
followed by H• abstraction will produce butyl ester units whereas carbon–carbon bond cleavages (**b** and **c**) will produce methyl-, propyl- and ethyl-esters.

Extension of the above arguments to the H-EG polyester system will lead to the production of methyl- and ethyl-esters. Though the possibility of ethylene formation in H-EG is accounted for on the basis of an eight-membered cyclic transition state, the ethyl esters produced by alkyl–oxygen bond scissions can easily undergo McLafferty type rearrangement to yield ethylene directly.

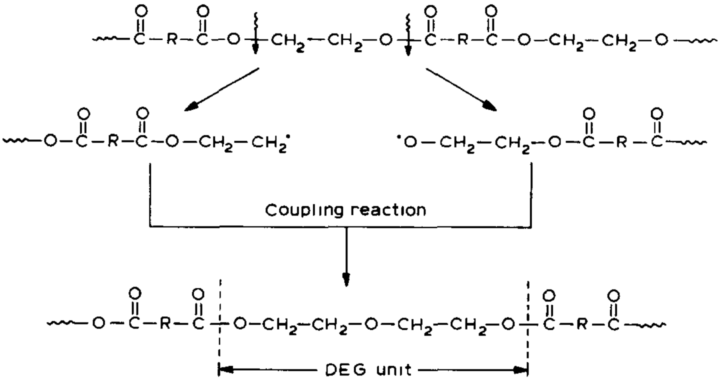


In order to explain the formation of the ion *m/z* 72 in the H-EG system, it is necessary to postulate the production of the ion of molecular formula $C_4H_8O]^{+\cdot}$, whose structure could be either $CH_3-CH_2-O-CH=CH_2]^{+\cdot}$ or $CH_2-CH_2-O-CH_2-CH_2]^{+\cdot}$. There are two possibilities by which the formation of *m/z* 72 can be explained.

During the melt condensation of hexolic anhydride with ethylene glycol, two molecules of the glycol condense to yield diethylene glycol (DEG) by the removal of a water molecule. So there is a definite possibility for the incorporation of DEG units in the polyester chain. These DEG units may undergo alkyl–oxygen bond scission or *β*-hydrogen transfer followed by alkyl–oxygen bond cleavage with concomitant hydrogen radical abstraction to yield the ion *m/z* 72.

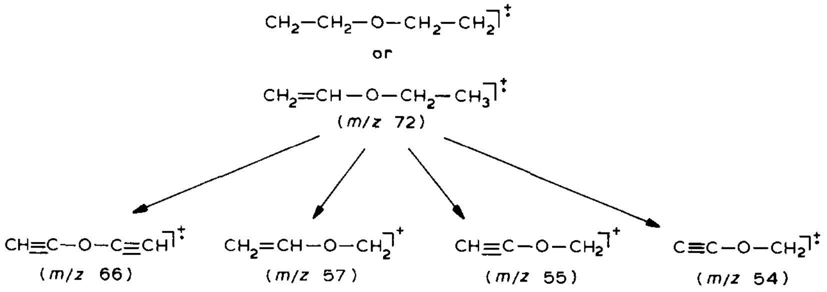


The other possibility is that the polyester H-EG, during pyrolysis, may produce alkoxy terminated and alkyl terminated free radicals by the homolysis of acyl–oxygen and alkyl–oxygen bonds, respectively. These two

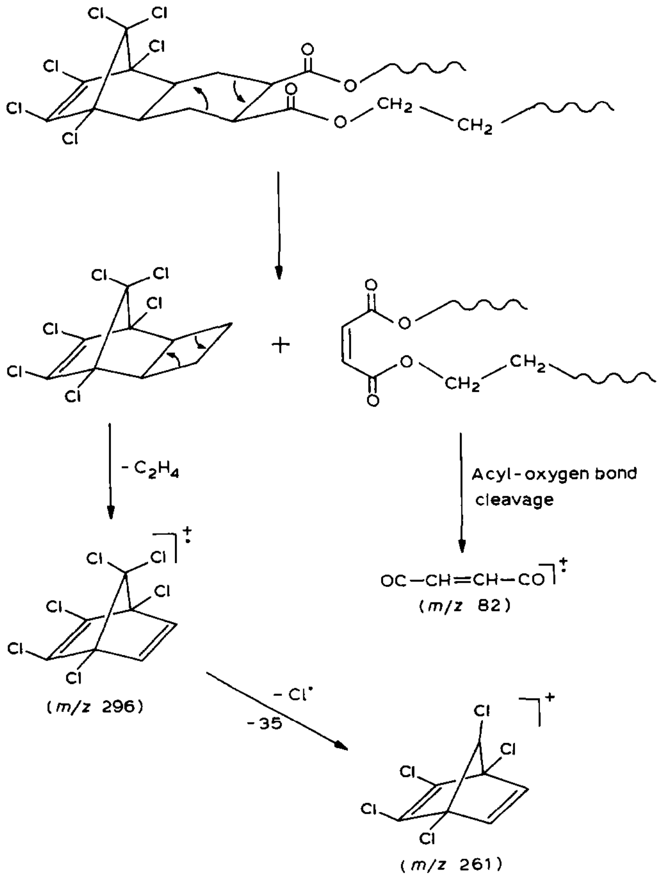


radicals can undergo a coupling reaction to yield the diethylene glycol unit, which may further degrade to yield the ion *m/z* 72.

The ions *m/z* 66, 57, 55 and 54 may be explained by subsequent fragmentation of the ion *m/z* 72 ($C_4H_8O^{\cdot+}$).

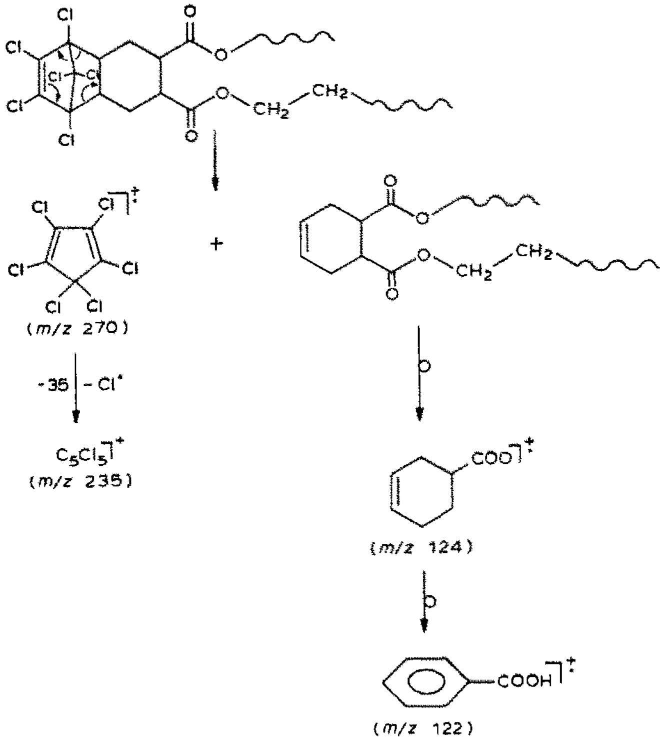


The formation of the ion *m/z* 82 is seen in the case of the H-BD system. The proposed structure for this ion is OC–CH=CH–CO$^{\cdot+}$. This particular species is formed by a pericyclic or electrocyclic type reorganization in the hexolic part of the polyester and thus gives rise to the polyester units



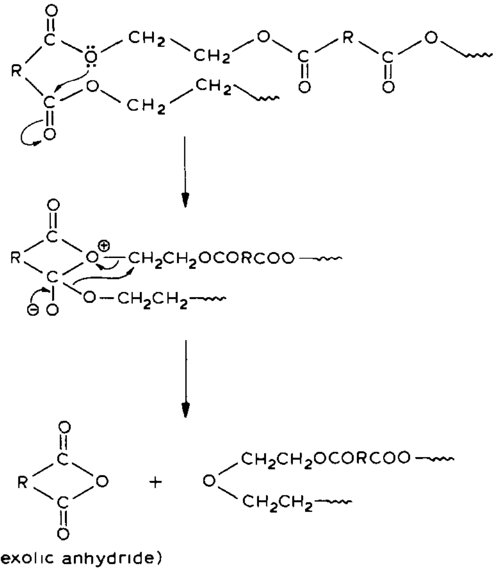
containing maleic acid fragments. Thus the $C_9H_6Cl_6$ formed can further undergo ejection of ethylene followed by loss of Cl$^\cdot$ leading to the formation of the ion $C_7H_2Cl_5^{\neg +}$ (*m/z* 261).

The formation of hexachlorocyclopentadiene (HEX) ($C_5Cl_6^{\neg \dot{+}}$; *m/z* 270) and benzoic acid (*m/z* 122) can be accounted for through the retro Diels–Alder reaction in the hexolic part of the polyester.



Since benzoic acid formation is noted, the ions *m/z* 105, 104, 80, 79, and 76 are expected due to fragmentation of the parent ion (*m/z* 122). For all the chlorinated products registered in the mass spectra, the structures are assigned on the basis of the isotopic intensities. As expected, the $HCl^{\neg \dot{+}}$ (*m/z* 36 and 38) species is formed in large amounts from both H-EG and H-BD.

Hexolic anhydride formation is seen in both H-EG and H-BD during pyrolysis since a well-defined group of peaks is present in the mass range 422–430. The formation of hexolic anhydride from the polyesters can be easily accounted for by the attack of the lone pair of electrons present in the ester oxygen on the carbonyl carbon through a five-membered cyclic transition state. The species formed, on concomitant electron reorganization will produce hexolic anhydride and polyalkylene oxide directly from the polyester chain. The polyalkylene oxide from H-EG and H-BD will act as the precursor for acetaldehyde and/or ethyleneoxide, $CH_2CH_2\text{–}O\text{–}CH_2CH_2^{]+}$ and THF, respectively.



It is very clear that the ejection of hexolic anhydride directly from the chain requires a highly strained conformation. The other plausible route for hexolic anhydride formation is the production of dicarboxylic acid through the well-known double β-scission in the polyester chain followed by dehydration.

ACKNOWLEDGEMENTS

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