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Pyrolysis Studies to Investigate Effects of Polymerization Techniques on Structure and Thermal Behavior of Poly(1,2-Epoxy-4-epoxyethylcyclohexanes)

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PYROLYSIS STUDIES TO INVESTIGATE EFFECTS OF POLYMERIZATION TECHNIQUES ON STRUCTURE AND THERMAL BEHAVIOR OF POLY(1,2-EPOXY-4-EPOXYETHYLCYCLOHEXANES)

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Key Words: Pyrolysis; Diepoxides; Effect of initiation; Thermal behavior

ABSTRACT

Thermal behaviors of poly(1,2-epoxy-4-epoxyethylcyclohexanes) (poly-EECH), polymerized by electroinitiation, radiation, and catalytic action of $HClO_4$ and BF_3-etharate, have been studied by direct pyrolysis MS and evolved gas analyses by mass and FT-IR spectrometric techniques. Direct pyrolysis experiments indicated that electroinitiated and catalytic polymerization of EECH with the use of BF_3-etharate produced the least stable polymers thermally. High mass peaks were related to the presence of blocks propagated through the 1,2-epoxy group, especially in the polymer produced by catalytic action of BF_3-etharate. Crosslinked structures were also justified by thermal analysis. Production of low molecular weight compounds such as CO, CO_2, CH_3OH, ethylene oxide,

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methylpropionate, and cyclohexane was investigated by evolved gas analysis.

INTRODUCTION

During the last decades, thermal degradation of polymers has been studied extensively with the use of various techniques [1-4]. Today, it is known that not only are weak links present in a polymer sample, but also the initiation mechanism of polymerization, anionic, radicalic, and the particular initiator used in the case of radical polymerization play an important role in the initial rate and products of thermal degradation [5-9]. The initiation mechanism will be even more important if polymerization can propagate through different active centers.

Epoxides have found various applications in plastics, coatings, adhesives, glass fiber reinforced plastics, and electrical encapsulation technologies. However, common epoxy resins have certain limitations such as degradation on exposure to sunlight, high viscosity, and low thermal stability. These limitations can be reduced or even eliminated by using cycloaliphatic diepoxides which can propagate through the two different epoxy rings in the monomer and can be crosslinked to enhance stability. Although cycloaliphatic diepoxides have gained interest in epoxy resin technology and in plastic and coating industries, there have been only few publications on the thermal stability and degradation products of epoxides in the literature [10-16].

Polymerization of 1,2-epoxy-4-epoxyethylcyclohexane (EECH) by different initiation mechanisms, such as electroinitiation, radiation-induced, and catalytic polymerization, with $HClO_4$ and BF_3-etharate as the catalysts, has been studied in our laboratories [17]. It has been shown that polymerized EECH yields mainly crosslinked polymers. The selective opening of the epoxy rings cannot be kept under control. The common spectrometric techniques applied indicated very similar structures for all the polymers prepared by different initiation mechanisms. We now report the application of pyrolysis techniques to investigate the effect of the initiation mechanism, mainly electroinitiation, radiation-induced and catalytic polymerization, on the thermal stability and degradation products of poly-EECH. Pyrolysis analysis were carried out using both direct pyrolysis MS and evolved gas analysis, indirect pyrolysis, by mass and IR spectrometric methods, to determine the merits and limitations of the pyrolysis techniques used.

EXPERIMENTAL

Materials

Electroinitiated and radiation-induced polymerizations of EECH were reported in our earlier publication [17]. Polymerization of EECH by using $HClO_4$ as a catalyst was carried out according to the literature method [17] by increasing the temperature to 65°C stepwise for complete gelation. Catalytic polymerization of EECH by borontrifluoride-etharate was performed at -78°C under vacuum. All the polymers produced were insoluble in common organic solvents, thereby indicating a crosslinked structure.

Thermal Analysis

The experimental setups used for direct pyrolysis MS and evolved gas analysis by mass and IR spectrometric techniques were described in detail in our previous studies [16, 19, 20].

Direct pyrolysis MS equipment consists of a direct insertion pyrolysis probe and its control unit designed in our laboratories [16, 19], a Balzers QMG 311 quadruple mass spectrometer, and a personal computer for the control of the instrument and data acquisition and processing. The pyrolysis probe consists of a stainless steel tube Ag soldered to a copper sample holder assemble. The proble can be directly inserted into the mass spectrometer by using a valve that allows differential pumping of the probe inlet line. Fine powder polymer samples (0.1 mg) were heated to 120°C rapidly and then the heating rate was kept constant at 2°C/min during the direct pyrolysis experiments.

In the case of evolved gas analysis [20] by MS, the same system with a pyrolysis chamber instead of the pyrolysis probe was applied. It basically consists of a pyrolysis chamber and a furnace. A needle valve is used to control the flow of the evolved gases into the mass spectrometer. Evolved gas analysis was also carried out with a Nicolet-510 FTIR spectrometer equipped with a pyrolysis IR gas cell. Samples of 1.0 and 10 mg were used in evolved gas analysis by mass and IR spectrometric techniques, respectively.

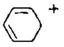
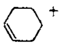
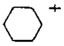
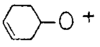
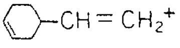
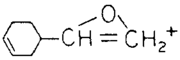
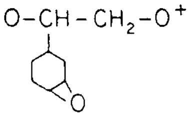
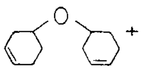
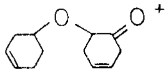
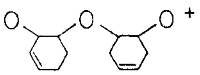
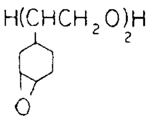
RESULTS AND DISCUSSION

Direct Pyrolysis

Thermal degradation products of poly-EECH prepared by electroinitiated, radiation-induced, and catalytic polymerization were studied by recording mass spectra as a function of temperature. Identical peaks were observed during the pyrolysis of the four polymer samples. Yet, both the relative intensities of the common peaks and the temperature ranges at which decomposition occurred changed considerably depending upon the initiation mechanism of the polymerization. Maximum product yields were observed at 254 and 262°C during pyrolysis of electroinitiated and radiation-induced polymer samples, respectively. In the case of the pyrolysis of the samples prepared by catalytic actions of $HClO_4$ and BF_3-etharate, maximum yields were detected at 257 and 250°C, respectively. In general, low mass peaks were more intense from all the samples under investigation and they started to appear at early stages of the thermal degradation. The base peak was at 28 amu, assigned to both CO^+ and $C_2H_4^+$ in all spectra from all four polymer samples. $C_2H_3O^+$ at 43 amu and $C_2H_4O^+$ and CO_2 at 44 amu were among the intense ions. On the basis of these results, it can be concluded that production of volatile compounds did not depend on the initiation mechanism of polymerization. Nevertheless, as high mass peaks are more diagnostic for thermal analysis, more emphasis will be given to fragments above 50 amu. In Table 1 the most intense and/or characteristic peaks observed at temperatures corresponding to maximum product yield are collected. Relative intensities are given with respect to the most abundant ion above 50 amu.

The mass spectra recorded during pyrolysis of poly-EECH prepared by electroinitiated and radiation-induced polymerization were quire similar. The base peak

TABLE 1. Relative Intensities and the Assigned Chemical Formulas of the Most Intense and Characteristic Ions Observed in Direct Pyrolysis Mass Spectra of Poly-EECH Prepared by Electroinitiation (EI), Radiation (Rad), Catalytic Action of $HClO_4$ (Cat_1) and BF_3-Etharate (Cat_2) at Temperatures Corresponding to Maximum Product Yield

	Relative intensity				
m/z	EI	Rad	Cat_1	Cat_2	Chemical formula
67	858	796	49	236	$C_5H_7^+$
77	483	574	80	684	$C_6H_5^+$
79	1000	1000	74	320	
81	732	726	63	249	
83	365	309	1000	742	
97	239	216	20	284	
107	111	110	19	222	
124	72	63	52	22	
140	31	33	25	< 1	Monomer
156	5	6	3	13	
178	2	1	< 1	49	
191	2	1	3	142	
207	2	< 1	1	1000	
282	5	< 1	< 1	529	

was at 79 amu due to $C_6H_7^+$ ion in both spectra, and the peaks above 130 amu were less than 5% of the base peak. In the case of the polymer sample produced by catalytic polymerization with the use of $HClO_4$, the base peak at 83 amu, due to $C_6H_{11}^+$, was the only abundant peak. The pyrolysis mass spectra of the fourth sample prepared by the catalytic action of BF_3-etharate were also noticeably different. The base peak was at 207 amu due to $C_{12}H_{15}O_3^+$, and the high mass peaks were relatively more intense.

To clarify the differences in degradation characteristics of the four polymers, the ion-temperature profiles, the variation of relative intensities of the peaks, mainly peaks at 79, 83, 140 (monomer peak), and 207 amu as a function of temperature, are plotted in Figs. 1, 2, 3, and 4.

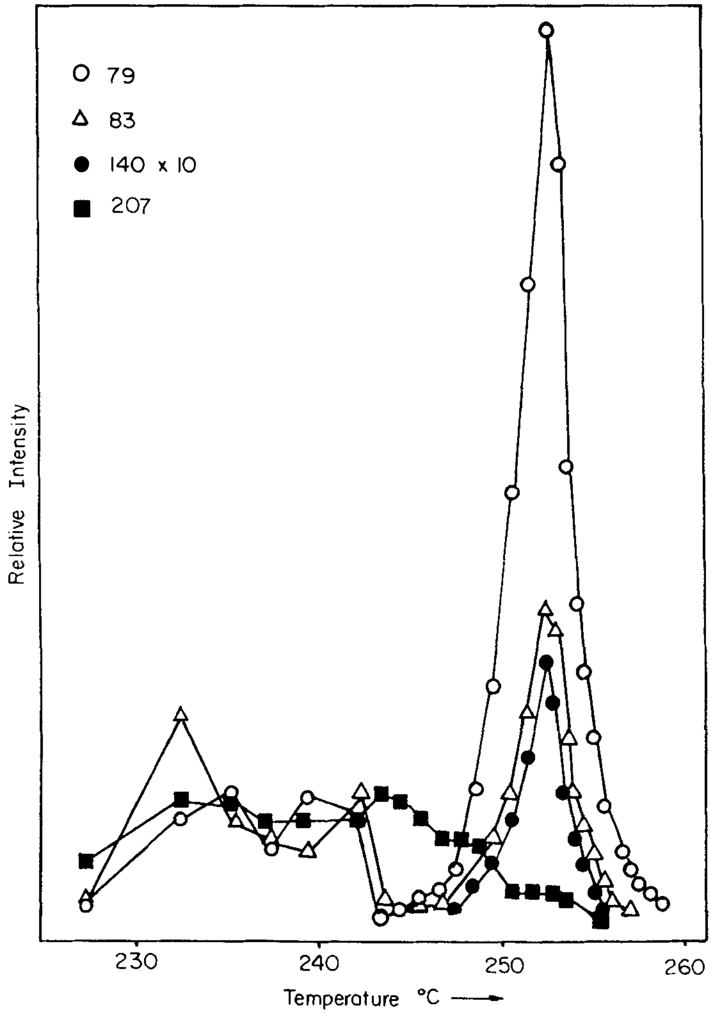


FIG. 1. Ion-temperature profiles of some characteristic peaks from electroinitiated poly-EECH.

It can be observed from Fig. 1 that electroinitiated poly-EECH degraded mainly in the temperature range of 220 to 270°C. Notice that three different degradation stages exist. Low mass ions observed at the initial stages disappeared around 245°C and then appeared again close to 250°C, above which product yield increased sharply. Monomer production was detected only at this last stage. This may indicate that low molecular weight, volatile products were produced at early stages of the thermal degradation process, while the main decomposition occurred above 260°C in a rather narrow temperature range. Note also that the ion-temperature profile of the peak at 207 amu was quite different. It was observed in a relatively broad temperature range of 220 to 265°C. Ion-temperature profiles of peaks at 191, 178, and 97 amu showed the same behavior. These different trends in ion-temperature profiles may be attributed to the presence of polymer blocks with different structures along the main chain.

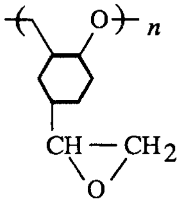
A three-stage degradation was also detected during the pyrolysis of poly-EECH produced by irradiation (Fig. 2). A peak at 207 amu was observed at initial stages of thermal degradation and disappeared totally above 255°C as in case of electroinitiated poly-EECH. Peaks at 79, 83, and 140 amu started to appear in the spectra only above 245°C, showing two maxima in ion-temperature profiles, with the second being the more intense. Again, main thermal decomposition occurred at the last stage. The production of 207 amu and related peaks, such as peaks at 191 and 178 amu, showed thermal characteristics similar to those produced from the electroinitiated sample, while other peaks shifted to higher temperatures.

Ion-temperature profiles of the same fragments from poly-EECH prepared by catalytic action of $HClO_4$ are given in Fig. 3. The base peak at 83 amu was observed in a broad temperature range of 245 to 265°C, with a maximum at 254°C. The production of 79 and 140 amu peaks took place mainly above 255°C. Contrary to the electroinitiated and radiation-induced poly-EECH pyrolysis results, peaks at 79 and 83 amu did not show an identical thermal behavior. The 207 amu and related peaks again showed up at earlier stages.

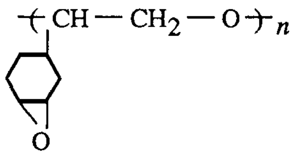
Decomposition of the polymer sample prepared by the catalytic action of BF_3-etharate occurred in the temperature range of 220 to 270°C. Around 250°C, total ion yield reached a maximum value (Fig. 4). The monomer peak at 140 amu could only be observed above 250°C, and it was less than 1% of the base peak.

The very weak monomer peak and the absence of a dimer or any intense high mass peak above 140 amu in any of the pyrolysis mass spectra of the four polymers except the polymer sample produced by catalytic action of BF_3-etharate may be attributed to a crosslinked structure.

1,2-Epoxy-4-epoxyethylcyclohexane may polymerize by propagation through 1,2-epoxy or 4-epoxy ethyl groups to yield two different structures:



and



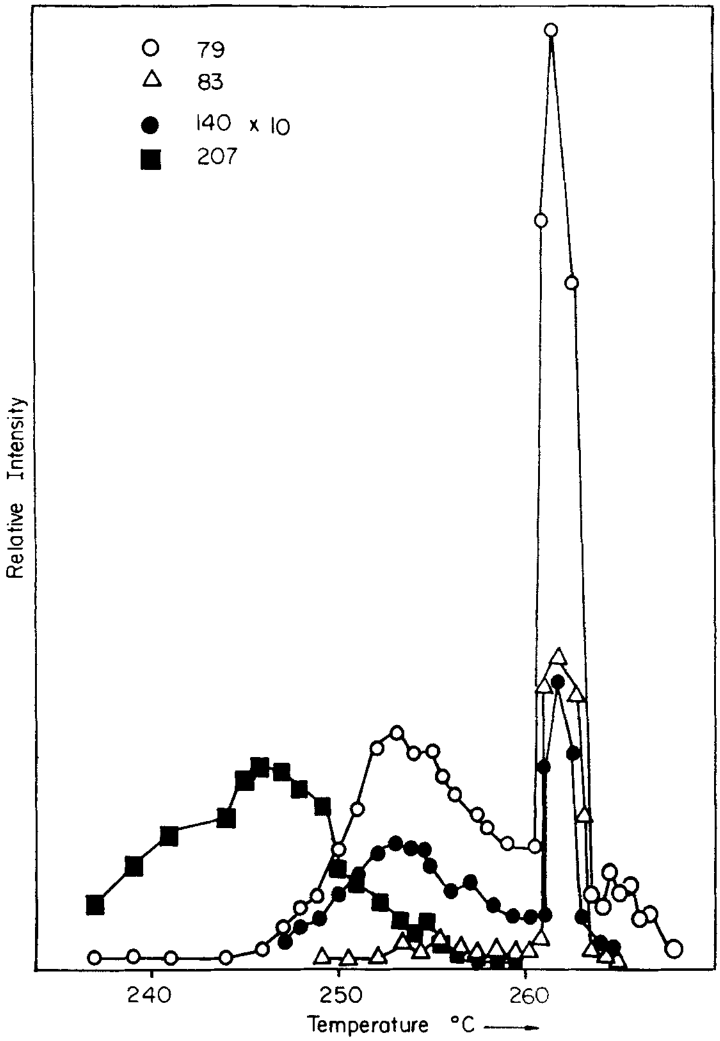


FIG. 2. Ion-temperature profiles of some characteristic peaks from radiation-induced poly-EECH.

However, selective opening of the epoxy rings could not be kept under control during the polymerization of EECH and crosslinked polymers were obtained as indicated by the insolubility of the samples in common organic solvents [17]. The relatively broad decomposition temperature ranges may also be a result of this crosslinking.

To make a better comparison, the ion-temperature profiles of the peak at 79 amu of all four poly-EECHs are replotted in Fig. 5. As the temperature at which main decomposition occurred is related to the thermal stability of the polymer in question, it may be concluded that radiation-induced and BF_3-etharate catalytic polymerization yielded more stable polymers. When analyzing the pyrolysis prod-

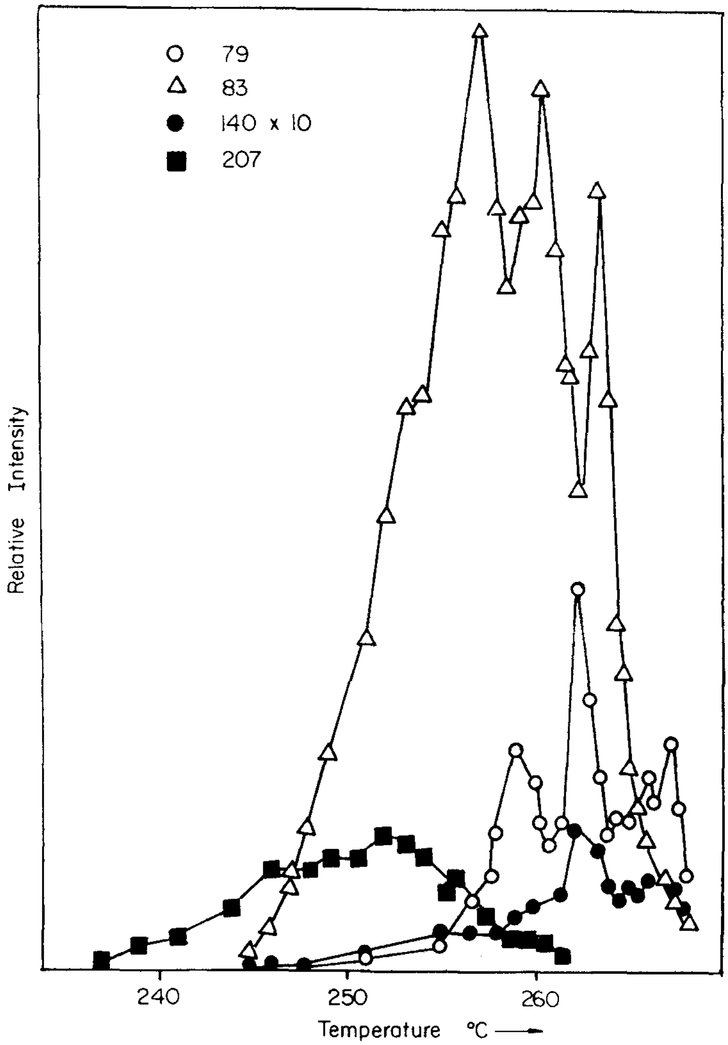


FIG. 3. Ion-temperature profiles of some characteristic peaks from poly-EECH prepared by catalytic action of $HClO_4$.

ucts, one must take into account the further dissociation of pyrolysis products during the ionization in the mass spectrometer. Low mass peaks such as the peak at 79 amu may be thought to be produced during the ionization of the monomer or higher mass degradation products. However, although in general, the relative intensities of the monomer and high mass products were quite similar from all the samples under investigation, the relative intensity of the 79 peak was noticeably different; being the base peak from electroinitiated and radiation-induced polymers while being among the moderate peaks from the other samples. Thus it may be

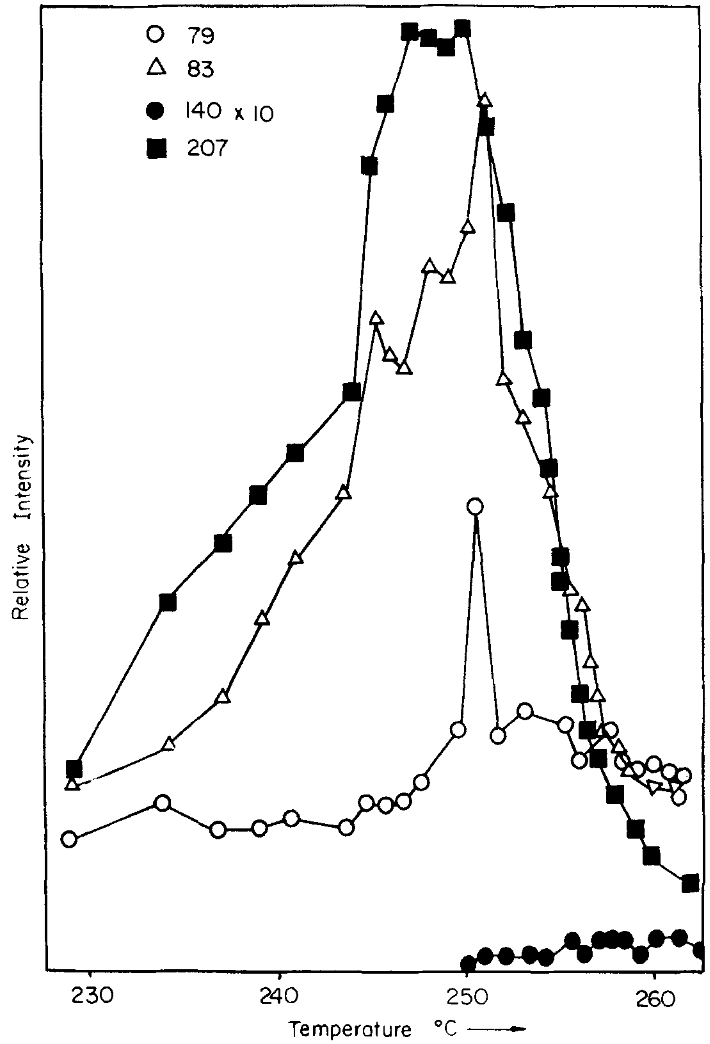
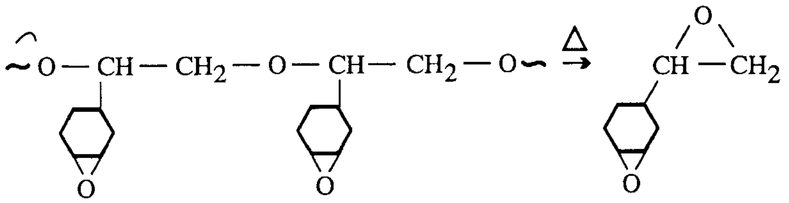
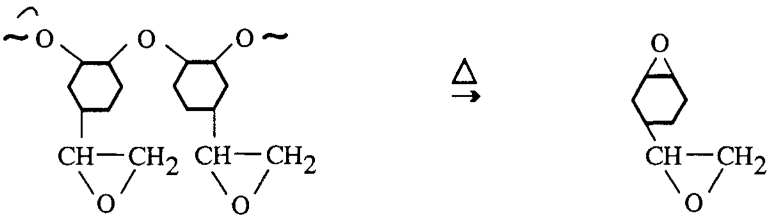


FIG. 4. Ion-temperature profiles of some characteristic peaks from poly-EECH prepared by catalytic action of BF_3-etharate.

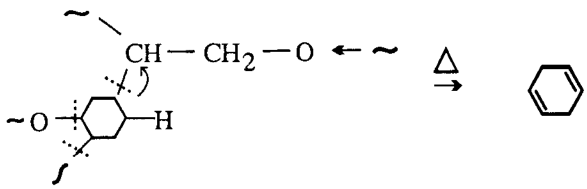
concluded that fragment 79 was produced mainly during thermal decomposition processes. Remember that the monomer peak, if present, also showed a very identical trend with this fragment. Thus it can be suggested that both fragments were produced by the same mechanism, most probably by bond scissions at random points. If the polymerization has occurred by propagation through only one epoxy group, then a higher monomer yield may be expected due to the direct cleavage of weakest C—O bonds as



and



whereas if the polymerization by propagation through both of the epoxy groups occurred, then each monomer unit may be bonded with up to four other monomer units, yielding a highly crosslinked structure which may mainly degrade to cyclohexadiene:



The two decomposition stages in the ion-temperature profiles of this fragment may be attributed to variations in the extent of crosslinking.

Ion-temperature profiles of both electroinitiated and radiation-induced poly-EECHs were quite similar, except for the shift to lower temperatures in the case of the electroinitiated sample. Consider also the very similar relative intensities of the fragments produced during thermal decomposition of these polymers: one may conclude that the two polymerization techniques yield polymers with essentially the same structure degrading through the same routes.

The polymer samples produced by the catalytic actions of $HClO_4$ and BF_3-etharate showed quite different thermal behaviors. The intensity of the fragment at 79 amu from poly-EECH prepared by the catalytic action of $HClO_4$ reached its maximum value close to 250°C as in the case of the radiation-induced sample, whereas the same fragment from the sample polymerized by the catalytic action of BF_3-etharate gave a maximum very close to the temperature corresponding to the maximum yield of the 79 amu fragment from the electroinitiated sample. However, remember that the pyrolysis mass spectra of the catalytically prepared samples were

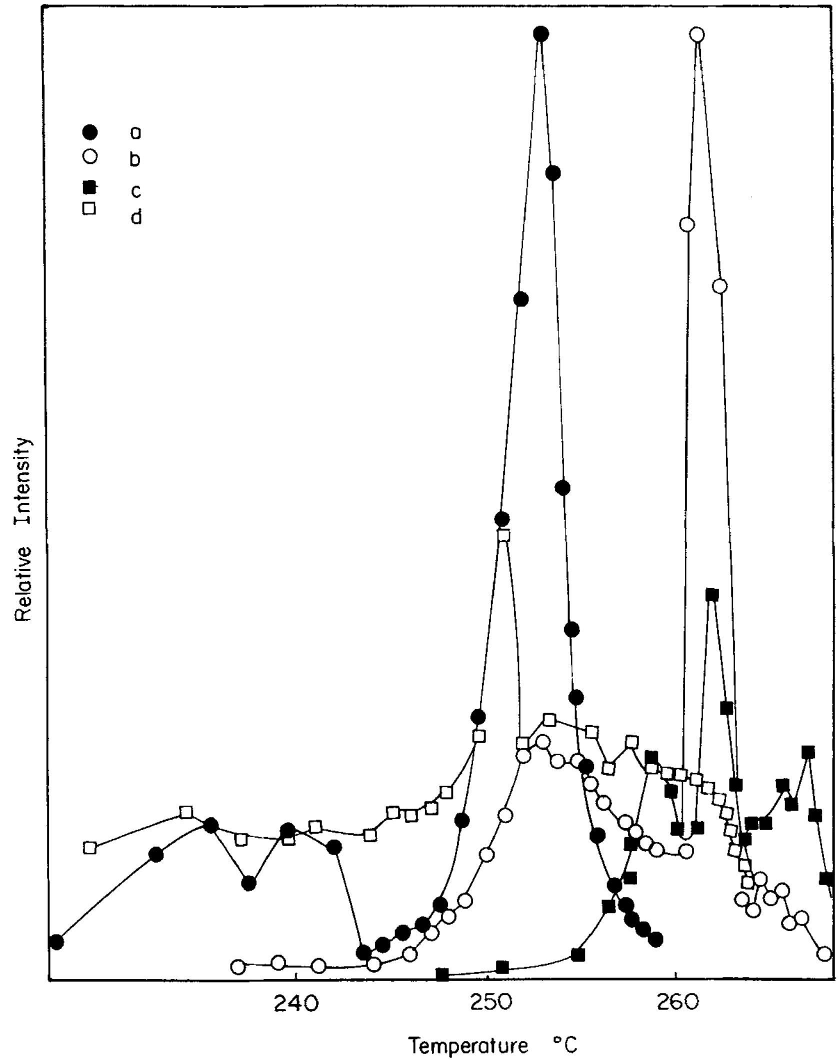
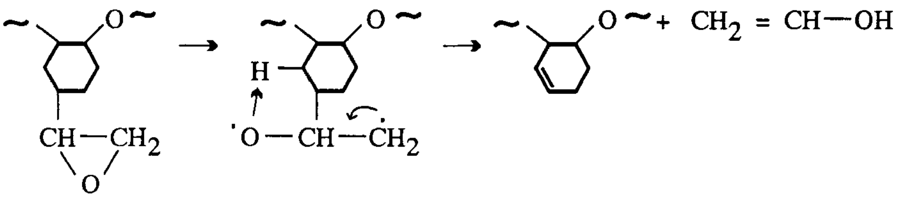


FIG. 5. Ion-temperature profiles of peak at 79 amu from poly-EECH prepared by (a) electroinitiation, (b) radiation, (c) catalytic action of $HClO_4$, and (d) catalytic action of BF_3-etharate.

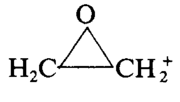
considerably different. Only the fragment at 83 amu was intense in the pyrolysis mass spectra of the sample polymerized by the catalytic action of $HClO_4$. This may indicate that some hydrogenation reactions occurred during pyrolysis of the sample, which predominantly increased the yield of the fragment at 83 amu. The base peak in the mass spectra of the polymer prepared by catalytic action of BF_3-etharate was at 207 amu. The presence of peaks at 207, 191, and 178 amu may be attributed to the presence of polymer blocks propagated through the 1,2-epoxy group without crosslinking. These peaks showed very identical trends as a function of temperature during pyrolysis of all four polymer samples under investigation. They were produced more readily at lower temperatures, indicating that the thermal stabilities of these blocks were low. The relative intensities of these peaks were weak except when produced during pyrolysis of the poly-EECH prepared by the catalytic action of BF_3-etharate.

Thermal degradation probably started by opening of the 4-epoxyethyl group, followed by a McLafferty-type rearrangement reaction abstraction of hydrogen at the γ-position, followed by elimination of $CH_2{=}CH{-}OH$:



Then decomposition occurred at random points along the polymer chain. The weak carbon—oxygen bonds were undoubtedly dissociated to yield the observed fragments. The lower degradation temperature and the considerably different relative intensities of the decomposition products of the sample prepared by the catalytic action of BF_3-etharate indicated that the extent of crosslinking was lower compared to other polymer samples, and that polymerization through the 1,2-epoxy group was the main route for this sample.

TABLE 2. The Most Intense and/or Characteristic Ions Observed during the Indirect Pyrolysis Mass Spectrometric Analysis of Poly-EECH

m/z	Chemical assignment
28	CO^+, $C_2H_4^+$
30	H_2CO^+
31	CH_3O^+
32	CH_3OH^+
43	CH_3CO^+
44	CO_2^+, 
57	$CH_3CH_2CO^+$
59	CH_3COO^+
68	$C_4H_4O^+$
72	$CH_3CH_2COCH_3^+$
73	$CH_3CH_2COO^+$
84	C_6H_{12}
88	$CH_3CH_2COOCH_3^+$

Duplicate experiments indicated high reproducibility for the thermal decomposition processes in all four polymer samples.

Evolved Gas Analysis by MS

The mass data obtained during evolved gas analysis, indirect pyrolysis of the poly-EECH samples prepared by four different initiation techniques were quite similar. No peak above 100 amu was observed from any of the polymer sample at

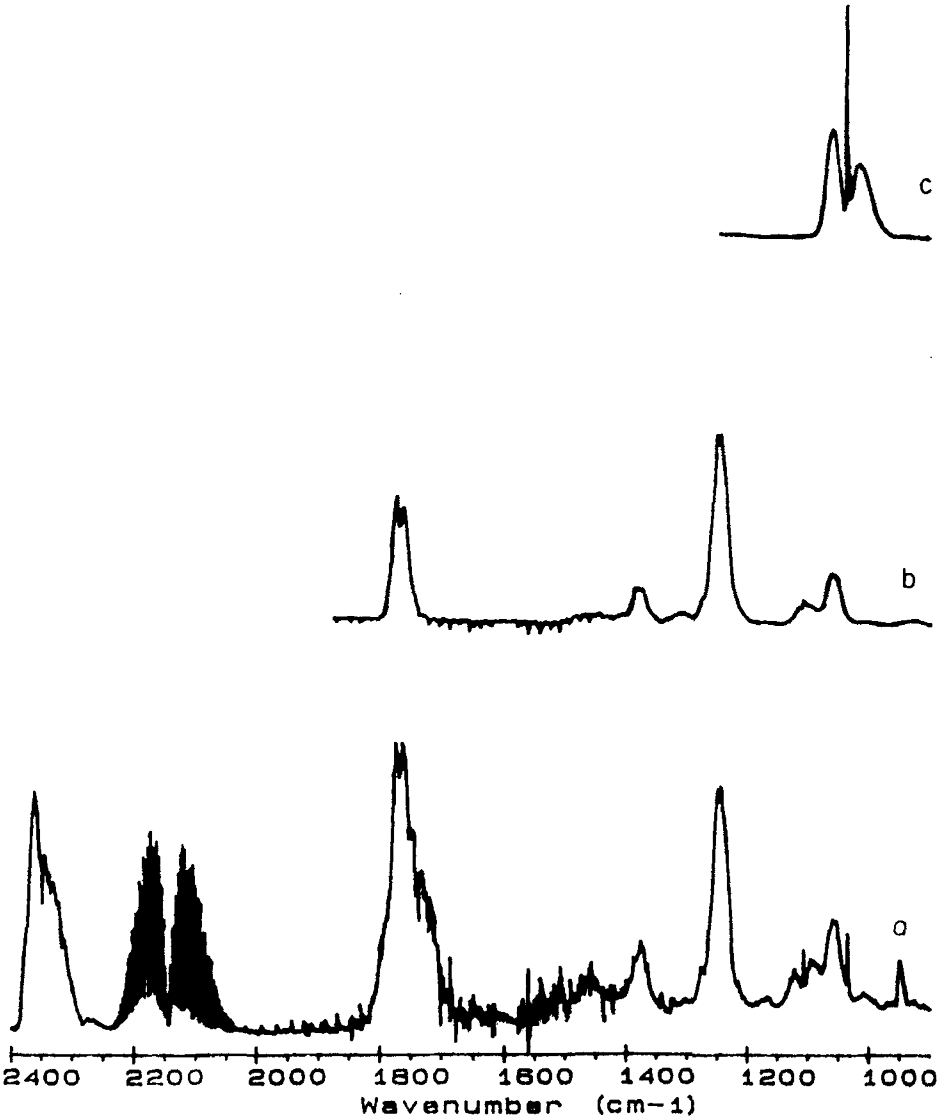


FIG. 6. FT-IR spectra of (a) gases evolved during pyrolysis of PEECH, (b) ethyl acetate, and (c) methanol.

any temperature during evolved gas analyses. Product peaks started to appear at 150°C, and maximum yield was detected around 290°C. The base peak was at 28 amu due to both CO and C_2H_4. Other intense peaks at 44 and 84 amu can be attributed to CO_2 and cyclohexane, respectively. The peak at 44 amu may also be associated with ethylene oxide. The peaks at 88, 73, 59, 57, and 31 amu indicated formation of $CH_3CH_2COOCH_3$, and those at 72, 57, and 43 may be due to CH_3CH_2-$COCH_3$. The most intense and/or characteristic peaks present in the spectra at 290°C are summarized in Table 2.

Thus with the use of present results it can be concluded that only low molecular weight volatile degradation products could reach the mass spectrometer from the pyrolysis chamber. The absence of peaks above 100 amu may be also related with the crosslinked structure of the polymers under investigation. Contrary to direct pyrolysis results, very similar mass spectra were recorded during evolved gas analysis of the four poly-EECH samples produced by different initiation mechanisms. Therefore, it may be concluded that the evolved gas analysis, indirect pyrolysis, MS technique is not a suitable method to be applied for determination of the effect of the initiation mechanism on the thermal stability of poly-EECH samples.

Evolved Gas Analysis by FT-IR

Very identical spectra were recorded during evolved gas analysis of all four polymer samples by FT-IR spectrometry as in the case of mass spectrometric analysis. Intense CO and CO_2 absorptions at 2145 and 2350 cm^{-1} were detected above 130°C. A sharp peak at 950 cm^{-1} indicated C_2H_4 formation. Strong peaks in the 1270–1000 and 1800–1700 cm^{-1} regions confirmed the presence of molecules having C=O and C—O—C functional groups. Absorptions around 1450 and 860 cm^{-1} may be associated with the presence of cyclohexane. Furthermore, bands around 1250 cm^{-1} and in the 840–750 cm^{-1} region may be attributed to epoxy absorptions. Nevertheless, as many other functional groups also absorb in these regions, it is hard to reach any definitive conclusion for the production of cyclohexane and ethyleneoxide.

Taking into account mass data, FT-IR spectra were compared with those of pure methylpropionate, methanol, and cyclohexane. The pyrolysis FT-IR spectrum of poly-EECHs and the gas-phase FT-IR spectra of CH_3OH and $C_2H_5COOCH_3$ are given in Fig. 6. On the basis of similarities observed the presence of CH_3OH and $C_2H_5COOCH_3$ was confirmed.

CONCLUSION

Thermal analysis by direct pyrolysis MS of poly(1,2-epoxy-4-epoxyethylcyclohexanes) indicated that not only structure but also thermal stability depends upon the polymerization technique applied. It has been observed that polymer samples produced by electroinitiation and the catalytic action of BF_3-etharate were the least stable. With the use of evolved gas analysis by mass and FT-IR spectrometric methods, similar volatile products, such as CO, C_2H_4, CO_2 CH_3OH, and C_2H_5.$COOCH_3$, were detected, pointing out that the volatile thermal decomposition products did not depend upon the initiation mechanism when thermal analyses were carried out in a closed reactor in a medium where the occurrence of secondary reactions was possible. Although ethylene oxide and cyclohexane formation indicated by mass data could not be supported by IR results, it is worth noting that for a reliable evolved gas analysis, mass and infrared analyses should be employed together because neither techniques can differentiate the molecules in a mixture with high certainty, but only give a response for a functional group or characteristic fragment that may be present in many similar molecules. The present results indicate that evolved gas analysis cannot be applied to determine the effect of initiation mechanism on thermal stability and structure. It has also been noted that direct pyrolysis MS gives more information on the extent of crosslinking compared to other common spectroscopic techniques such as IR and NMR.

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