Thermal Degradation of Liquid Polysulfide Polymers: Pyrolysis–GC–MS and Thermogravimetric Studies

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Synopsis

The thermal decomposition of Thioped, a liquid polysulfide polymer based on dichloroethyl formal, was studied using pyrolysis–GC–MS. The nature and composition of the products of pyrolysis at 358 and 485°C are given. A striking feature of the product analysis is the presence of several disulfide compounds only at the higher decomposition temperature. The pyrolysis-GC of other liquid polysulfide polymers (LP-2, LP-32, LP-3, and LP-33) showed that molecular weight had only marginal effect on the product composition. Ionic and radical mechanisms were considered to account for the product formation. Isothermal and dynamic thermogravimetric studies were carried out to differentiate between the two mechanisms. The results were found to be in agreement with a free radical mechanism, with cleavage of the formal C—O linkage as the preferred mode of initiation. The overall activation energy for the decomposition was found to be 190 kJ mol^{-1}.

INTRODUCTION

Studies on thermal decomposition of polysulfide polymers $[(—RS_x—)_n]$ are of interest for three reasons. First, these polymers find extensive applications in adhesives, sealants, insulators, among others.[1,2] Consequently, the thermal stability of these systems has attracted considerable attention. Patric[3] observed that dry distillation of methylene or ethylene polysulfide polymers at 100–130°C resulted in the evolution of probably a cyclic disulfide. Davis and Kohut[4] and Berenbaum[5] established the cyclic nature of the volatile compounds formed in the steam distillation of these polymers. The thermal stability of the ethylene formal disulfide polymers was studied by Rosenthal and Berenbaum.[6] Evolution of gaseous products on pyrolysis of polysulfide polymers was reported by Honma and Kawasaki.[7] However, there is no systematic investigation on the nature and composition of the products obtained on thermal decomposition of polysulfides at elevated temperatures.

Second, commercially available polysulfide polymers (R = —CH$_2$CH$_2$ OCH$_2$OCH$_2$CH$_2$—, x = 2) contain heteroatoms in the backbone and can undergo homolytic cleavage of the C—X bonds, resulting in the formation of a host of free radicals and, therefore, lead to a complex mixture of products. It was reported[8] that the degradation of the polymer in air is due to the breakdown of the formal linkage rather than the disulfide linkage. A radical mechanism, initiated by the peroxidation of the formal group, was proposed. Yet, the mechanism of decomposition of these systems at high temperatures and in the absence of air is not well studied.

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Finally, it is known that neighboring groups or atoms greatly influence the activation energies of decomposition of adjacent bonds. For example, it was observed in the thermal decomposition of polyethylene sulfide[9] that the activation energy for the clevage of C—S bond is only 238 kJ mol^{-1} compared to 289 kJ mol^{-1} for diethylene sulfide. Similarly, the dissociation energy for the S—S bond in dimethyl tetra sulfide[10] is much lower (150 kJ mol^{-1}) than that of the disulfide linkage (292) kJ mol^{-1}). The polysulfide polymer offers a convenient system to study the mutual influence of S—S, C—O, C—S, and C—C linkages on their dissociation.

Hence, in the present study, the thermal decomposition of thiol-terminated liquid polysulfide polymers based on dichloroethyl formal is investigated at temperatures above 350°C using pyrolysis–GC–MS. The nature and composition of the pyrolyzates are reported, and the mechanism of decomposition is discussed. Thermogravimetric studies are carried out to support the proposed mechanism and to evaluate the kinetic parameters.

EXPERIMENTAL

Materials

The thiol-terminated liquid polysulfide polymers (LPs) used were commercial samples obtained from Thiokol Chemical Cor. The Thioped sample used in this study was of similar structure prepared in our laboratories. Some physical properties of the samples used are given in Table I.

Pyrolysis-GC-MS

The pyrolysis was done with a Curie-point pyrolyzer JHP-2 and the products were separated on a Jeol Gas Chromatograph, JGC-20 KP, using OV-101 capillary column (0.28 mm × 30 m, GSCOT). The Electron Impact and Chemical Ionization spectra were recorded on Jeol JMS-D300 having JMS-2000 Data Processing System. The column temperature was programmed from 60°C to 210°C at 6°C/min and the flow rate used was 1 mL/min.

Low Resolution Pyrolysis GC

A furnace pyrolyzer, Shimadzu PYR-2A was directly coupled to a Shimadzu GC-5A gas chromatograph. Samples of about 0.6–0.7 mg were taken in a platinum boat and introduced into the furnace using a sample intro-

TABLE I
Properties of Polysulfide Samples

Sample	Mol wt[a]	Viscosity at 25°C (P)	SH value (%)
LP-2	3970	450	1.17
LP-32	4580	465	1.25
LP-3	830	16.6	5.68
LP-33	990	19.9	5.24
Thioped	2250	172	2.25

[a] Mol wt determined by VPO using Toluene solvent.

duction rod, the thermocouple of which measured the furnace temperature. A stainless-steel column (3 mm $\phi \times$ 2 m) packed with 25% squalane on shimalite 60–80 mesh support was used. The experimental conditions used were: column temperature, 60–120°C at 15°C/min; injection port, 250°C; flow rate, 40 mL/min; detector, FID. Shimadzu Data Processor C-R1A was used for calculation of peak areas.

Thermogravimetric Studies

Isothermal and dynamic TG studies were carried out in dry nitrogen atmosphere using Dupont 990 thermal analyzer.

RESULTS AND DISCUSSION

Characterization of Products

The pyrolysis-GC-MS of thiol-terminated liquid polysulfide, Thioped, was carried out as 358 and 485°C. At the lowest temperature chosen, the decomposition of the polymer was found to be complete by TGA. The mass chromatograms obtained are shown in Figures 1 and 2. The structures of the pyrolyzates were arrived at from mass spectral fragmentation. The weight percentage composition of the products was obtained from the peak heights in the mass chromatogram. The results so obtained on the nature and composition of the pyrolyzates are given in Tables II and III. A striking feature of the nature of products formed is that several disulfide compounds other than the cyclic monomer are formed only at the higher decomposition temperature.

Effect of Molecular Weight

In order to obtain a better insight into the mechanism of decomposition, the effect of molecular weight on the nature and composition of the products was investigated. Low resolution pyrolysis GC was carried out on samples of different molecular weights (Thioped, LP-2, LP-32, LP-3, and LP-33) at two temperatures, 360 and 400°C. The chromatograms (Fig. 3) show essentially four major peaks. A comparison of the chromatogram of Thioped at 360°C with the mass chromatogram obtained at 358°C reveals that the predominant components of the four peaks are as follows: peak 1: 1,3-Oxathiolane (II); peak 2: 2-Mercaptomethyl oxirane (III); peak 3: 1,3-Dioxa-6-thiocane (V); peak 4: 1,3-Dioxa-6, 7-dithionane, the cyclic monomer (VI). The assignment of peak 4 was confirmed using an authentic sample and was found to contain essentially a single component. The results obtained for the different polysulfides are given in Table IV. An examination of the results shows that, at the decomposition temperature of 360°C, molecular weight and varying —SH concentration have only marginal effect on the products of decomposition; similar behavior is also observed at 400°C. Hence, it can be inferred that the decomposition is not end-initiated but is predominantly random.
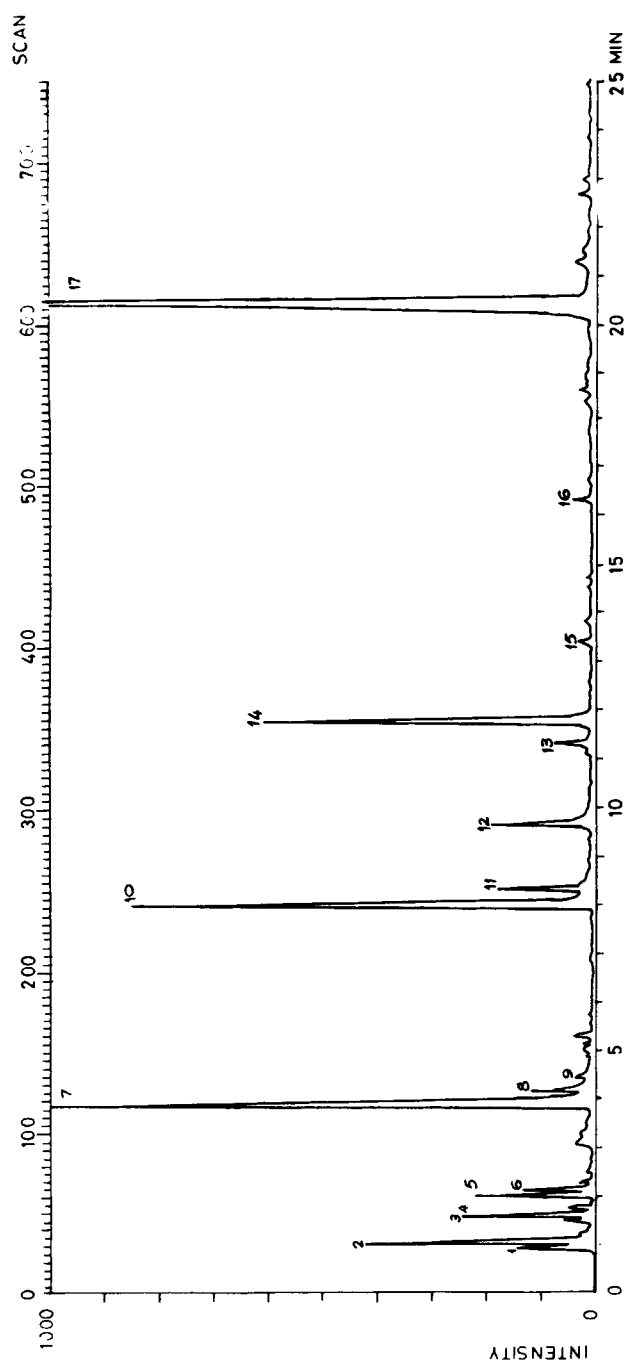
Fig. 1. Pyrolysis mass chromatogram of thioped at 358°C with OV-101 capillary column; column temp 60–210°C, 6°C/min; flow rate 1 mL/min.
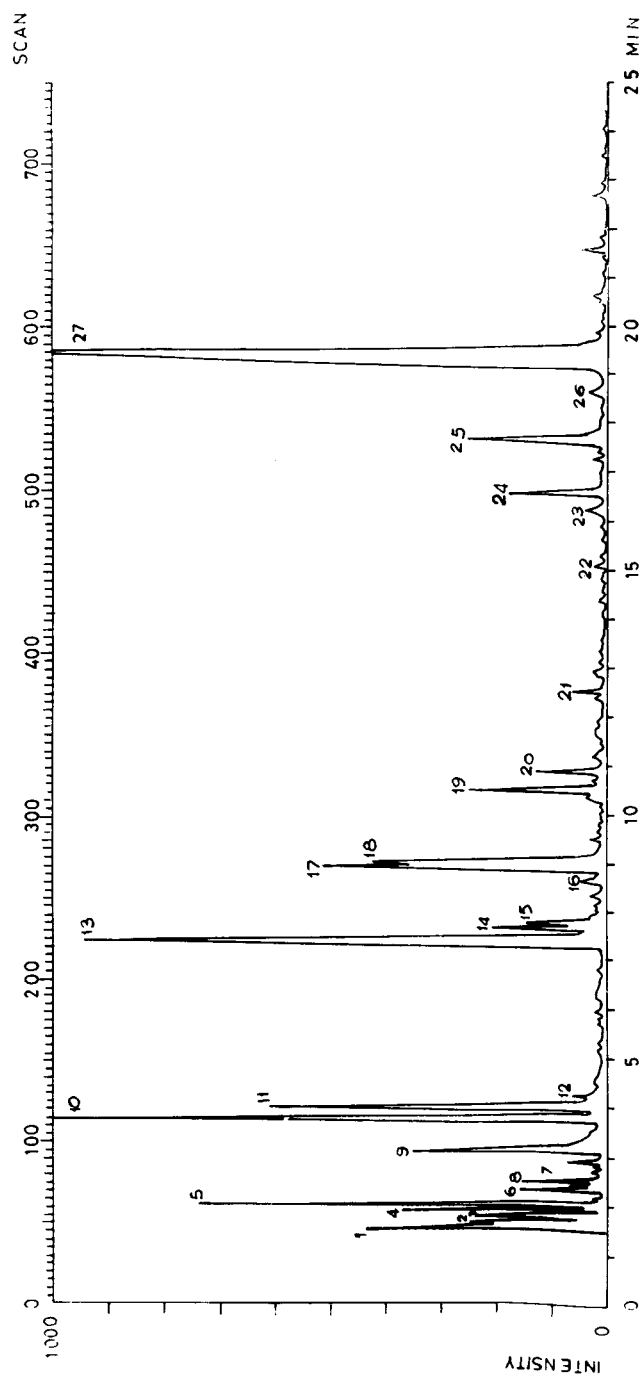
Fig. 2. Pyrolysis mass chromatogram of thioped at 485°C with OV-101 capillary column; column temp 60–210°C, 6°C/min; flow rate 1 mL/min.

Peak no.	M^+ (m/z)	Mol. formula	Compound	Wt%	Mol%
1	44	CO_2	Carbon dioxide	2.5	5.2
2	44	C_2H_4O	Acetaldehyde[a] (I)	7.5	15.7
3	76	CS_2	Carbon disulfide[b]	4.3	5.2
4	60	C_2H_4S	Thiirane[b] (VIII)	0.8	1.2
5	(70)	—	Not identified	3.9	5.1
6	102	$C_6H_{14}O$	Ethyl isobutyl ether[b] (VII)	2.3	2.1
7	90	C_3H_6OS	1,3-Oxathiolane[b] (II)	18.2	18.7
8	60	C_2H_4S	Vinyl mercaptan (IX)	2.0	3.1
9	104	C_4H_8OS	2-Methyl-1,3-oxathiolane[b] (X)	0.4	0.4
10	90	C_3H_6OS	2-Mercaptomethyl oxirane (III)	15.5	15.9
11	90	C_3H_6OS	2-Methoxythiirane (IV)	3.1	3.2
12	134	$C_5H_{10}O_2S$	4-Methyl-1,3-dioxa-5-thiepane (XI)	3.4	2.3
13	132	$C_5H_8O_2S$	—	1.2	0.8
14	134	$C_5H_{10}O_2S$	1,3-Dioxa-6-thiocane (V)	11.1	7.6
15	116	S_1 compound	—	0.4	0.3
16	130	S_1 compound	—	0.7	0.5
17	166	$C_5H_{10}O_2S_2$	1,3-Dioxa-6,7-dithionane (VI)	22.6	12.2

[a] *CRC Atlas of Spectral Data and Physical Constants for Organic Compounds*, 2nd ed., J. G., Grasselli and W. M. Ritehey, Eds., CRC Press, Cleveland, OH, 1975.
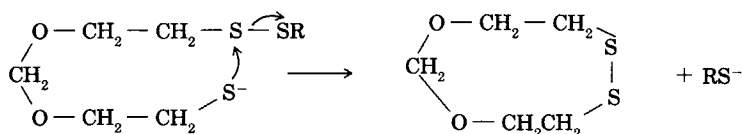
[b] *Registry of Mass Spectral Data*, E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Eds., Wiley-Interscience, New York, 1974.

Effect of Temperature

The effect of temperature of pyrolysis on the composition of the products was studied using LP-2 in the temperature range 360–700°C. The results are given in Table V. As expected, the higher molecular weight components decrease in concentration with increase in temperature of pyrolysis. As it is reasonable to assume that the rates of formation of the products are proportional to their concentrations under flash pyrolysis conditions, a plot of the log of product concentration vs. $1/T$ should indicate whether the product is formed by a single mechanism or not.[11] This treatment was applied to the formation of the cyclic monomer (peak 4). The straight line plot obtained (Fig. 4) indicates that the cyclic monomer is formed essentially by a single mechanism.

Classification of Products of Pyrolysis

From an examination of the products given in Tables II and III, the pyrolyzates can be classified, for the purpose of discussion, into three groups. Group I consists of products which predominate (ca. 85 wt %) at a lower temperature of decomposition (358°C) and whose concentration decreases (ca. 42%) at higher temperature (485°C) of pyrolysis. Group II consists of products which are formed in minor amounts (ca. 8%) at 358°C and whose concentration increases at 485°C (ca. 25%). Group III comprises products

which are formed only at 485°C (ca. 28%). The structures of identified products of the three groups are shown in Chart I (classification of pyrolysis products of Thioped).

$$CH_3CHO$$

I

$$\begin{array}{c} S \\ H_2C \quad CH_2 \\ | \qquad | \\ H_2C - O \end{array}$$

II

$$\begin{array}{c} CH_2 - CH - CH_2SH \\ \diagdown \; O \; \diagup \end{array}$$

III

$$\begin{array}{c} CH_2 - CH - OCH_3 \\ \diagdown \; S \; \diagup \end{array}$$

IV

Group I

$$\begin{array}{c} CH_2 - CH_2 - O \\ S \diagup \qquad\qquad\quad \diagdown CH_2 \\ CH_2 - CH_2 - O \end{array}$$

V

$$\begin{array}{c} \quad CH_2 - CH_2 - O \\ S \diagup \qquad\qquad\quad \diagdown CH_2 \\ S \diagdown \\ \quad CH_2 - CH_2 - O \end{array}$$

VI

$$\begin{array}{c} CH_3 \\ \diagdown \\ CH - CH_2 - OCH_2CH \\ \diagup \\ CH_3 \end{array}$$

VII

$$\begin{array}{c} CH_2 - CH_2 \\ \diagdown S \diagup \end{array}$$

VIII

$$CH_2 = CH - SH$$

IX

$$\begin{array}{c} S \\ CH_2 \quad CH - CH_3 \\ | \qquad | \\ CH_2 - O \end{array}$$

X

$$\begin{array}{c} CH_2 - CH_2 - O \\ S \diagup \qquad\qquad\quad \diagdown CH_2 \\ CH - O \\ | \\ CH_3 \end{array}$$

XI

Group II

COS   CH_3SH

XII   XIII

$$\begin{array}{c} CH - CH \\ \| \qquad \| \\ HC \qquad CH \\ \diagdown S \diagup \end{array}$$

XIV

$$HOCH_2CH_2SH$$

XV

$$\begin{array}{c} S \\ CH_2 \quad CH - O - CH = CH_2 \\ | \qquad | \\ CH_2 - O \end{array}$$

XVI

$$\begin{array}{c} CH_2 \\ S \diagup \quad \diagdown CH_2 \\ | \qquad\qquad | \\ S \qquad\qquad O \\ \diagdown CH_2 \diagup \end{array}$$

XVII

$$\begin{array}{c} CH_2 \\ S \diagup \quad \diagdown CHOH \\ | \qquad\qquad | \\ S - - CH_2 \end{array}$$

XVIII

$$\begin{array}{c} CH_2 - CH_2 - O \\ S \diagup \qquad\qquad\quad \diagdown CH_2 \\ | \qquad\qquad\qquad \diagup \\ S - CH - O \\ | \\ CH_3 \end{array}$$

XIX

Group III

Chart I

Mechanism of Decomposition

Ionic Mechanism. As pointed out earlier, the thiol-therminated liquid polysulfides undergo cyclodepolymerization on dry or steam distillation. This was attributed to the facile interchange of mercaptide groups with the polymer disulfide bonds. The reaction could be initiated by ionic impurities or mercaptide groups present in the polymer. This "tail-biting" backbone depolymerization[5] was represented as

$$O-CH_2-CH_2-S \overset{\frown}{\longrightarrow} SR \qquad \begin{array}{c} O-CH_2-CH_2 \\ \diagup \qquad \qquad \searrow S \\ CH_2 \qquad \qquad \mid \\ \diagdown \qquad \qquad \diagup S \\ O-CH_2CH_2 \end{array} \quad + \; RS^-$$

Thus, at a relatively low temperature ($\not> 130°C$), only the cyclic monomer was observed. However, it might be argued that, at the high temperatures used in the present investigation, the mercaptide ion could attack other electrophilic centers available along the backbone of the polymer resulting in the formation of additional products as shown in Scheme I (ionic mechanism for degradation of Thioped).

TABLE III
GC-MS Analysis of Products of Pyrolysis at 485°C of Thioped

Peak no.	M^+ (m/z)	Mol. formula	Compound	Wt %	Mol %
1	60	COS	Carbonyl sulfide[b] (XII)	5.0	7.3
2	48	CH_4S	Methane.thiol[b] (XIII)	2.8	5.1
3	60	C_3H_8O	—	2.6	3.8
4	76	CS_2	Carbon disulfide[b]	4.2	4.9
5	60	C_2H_4S	Thiirane[b] (VIII)	8.5	12.5
6	(70)	—	Not identified	1.7	2.1
7	102	$C_6H_{14}O$	Ethyl isobutyl ether[b] (VII)	0.6	0.5
8	84	C_4H_4S	Thiophene[b] (XIV)	1.6	1.7
9	78	C_2H_6OS	Mercaptoethanol[a] (XV)	3.9	4.4
10	90	C_3H_6OS	1,3-Oxathiolane[b] (II)	11.5	11.2
11	60	C_2H_4S	Vinyl mercaptan (IX)	7.1	10.4
12	104	C_4H_8OS	2-Methyl-1,3-oxathiolane[b] (X)	0.6	0.5
13	90	C_3H_6OS	2-Mercaptomethyl oxirane (III)	10.9	10.7
14	90	C_3H_6OS	2-Methoxythiirane (IV)	2.3	2.3
15	132	$C_5H_8O_2S$	—	1.6	1.1
16	132	$C_5H_8O_2S$	2-Vinyloxy-1,3-Oxathiolane (XVI)	0.5	0.3
17	134	$C_5H_{10}O_2S$	4-Methyl-1,3-dioxa-5-thiepane (XI)	5.8	3.8
18	122	$C_3H_6OS_2$	4-Hydroxy-1,2-dithiolane (XVIII)	4.8	3.5
19	132	$C_5H_8O_2S$	—	2.8	1.9
20	134	$C_5H_{10}O_2S$	1,3-Dioxa-6-thiocane (V)	1.4	0.9
21	116	S_1 compound	—	0.6	0.5
22	130	S_1 compound	—	0.2	0.1
23	120	$C_3H_4OS_2$	—	0.3	0.2
24	122	$C_3H_6OS_2$	1-oxa-3,4-dithiane (XVII)	2.0	1.4
25	166	$C_5H_{10}O_2S_2$	4-Methyl-1, 3-dioxa-5,6-dithiocane (XIX)	2.8	1.5
26	134	$C_4H_6OS_2$	—	0.2	0.1
27	166	$C_5H_{10}O_2S_2$	1,3-Dioxa-6,7-dithionane (VI)	13.8	7.3

[a] *CRC Atlas of Spectral Data and Physical Constants for Organic Compounds,* 2nd ed. J. G. Grasselli and W. M. Ritehey, Eds., CRC Press, Cleveland, OH, 1975.
[b] *Registry of Mass Spectral Data,* E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Eds., Wiley-Interscience, New York, 1974.
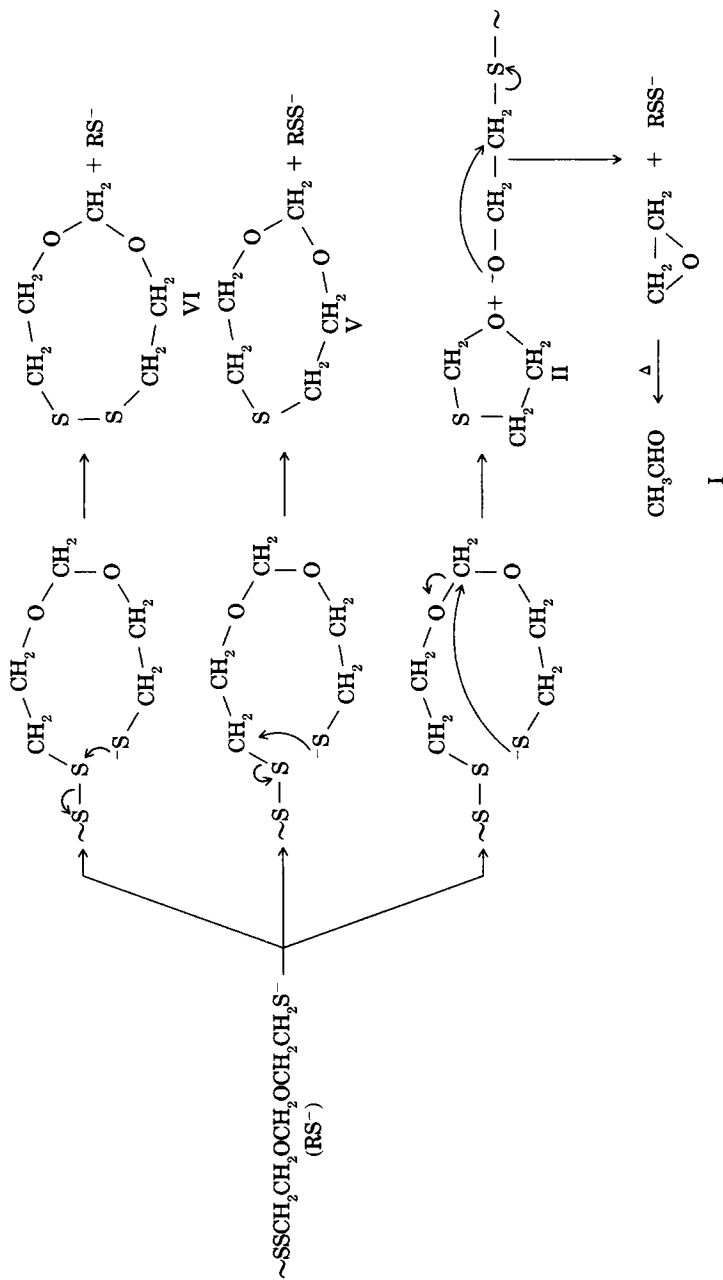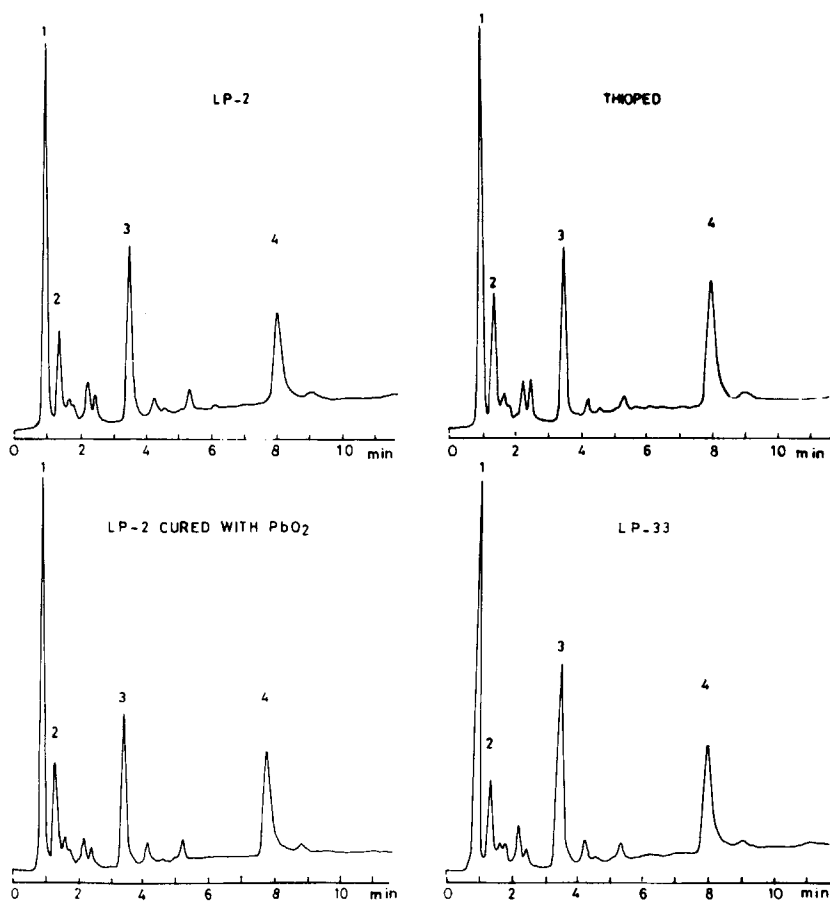
Scheme I.

Fig. 3.   Low resolution pyrograms of polysulfides at 400°C with squalane column; column temp 60–120°C, 15°C/min; flow rate 40 mL/min.

TABLE IV
Composition of the Major Pyrolyzates from Different Polysulfide Samples

	Peaks (area %)			
Sample	1	2	3	4
Pyrolysis temperature 360°C				
LP-2	27.1	12.7	21.8	27.8
LP-32	29.9	12.7	23.5	25.2
LP-3	21.5	11.1	17.4	39.3
LP-33	29.5	11.6	23.3	29.7
Thioped	24.5	13.9	16.9	32.6
LP-2 cured with PbO$_2$	24.2	12.8	21.7	30.8
Pyrolysis temperature 400°C				
LP-2	31.7	9.6	20.5	18.4
LP-32	32.1	9.7	20.1	18.8
LP-3	24.8	10.3	18.9	25.3
LP-33	31.9	8.5	22.9	20.2
Thioped	29.7	11.4	16.8	22.2
LP-2 cured with PbO$_2$	30.5	11.6	18.6	20.1

TABLE V
Effect of Temperature on Composition of Major Pyrolyzates from LP-2

Pyrolysis temperature (°C)	Peaks (area %)			
	1	2	3	4
360	27.1	12.7	21.8	27.8
400	31.7	9.6	20.5	18.4
500	66.7	7.2	2.1	4.9
600	78.8	1.6	0.3	2.0
700	84.7	0.2	0.1	1.1

Such a scheme would satisfactorily account for the formation of many of the group I products. However, this ionic mechanism suffers from the following limitations:

(i) This mechanism cannot explain the formation of group II and group III products.

(ii) If the ionic mechanism were operating, the concentration of the cyclic monomer (VI) is expected to be considerably higher relative to other products. But the experimental results given in Table II show that the major products (I, II, III, V, and VI) are formed in about equal amounts.

(iii) It is expected that complete curing with PbO_2 would decrease considerably the mercaptide ion concentration, which, in turn, should have an effect on the decomposition, if it is initiated by a mercaptide ion. But, it was observed that the nature and composition of the decomposition products of the PbO_2-cured and uncured samples remain essentially the same as shown in Table IV and Figure 3.

(iv) The thermogravimetric studies indicate a change in mechanism from low to high heating rates. The activation energy values suggest an ionic mechanism at low heating rates, as discussed later.

Free Radical Mechanism. The polymer backbone contains several het-
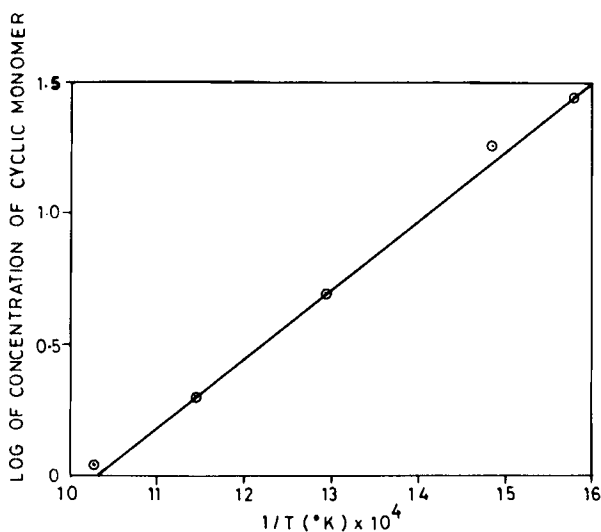
Fig. 4. Plot of log of concentration of cyclic monomer vs. $1/T$ (K).

eroatoms in its repeating unit ($-$S$-$CH$_2$$-CH_2$$-O-CH_2$$-O-CH_2$$-CH_2$$-$
S$-$) and the bond dissociation energies of the S$-$S, C$-$O (formal), and C$-$
S bonds are not much different.[12] Hence, initiation of the degradation could
be expectd by the homolytic cleavage of these C$-$X bonds. Such a free
radical mechanism can satisfactorily explain the formation of group I and
group II products as outlined in Scheme II (free radical mechanism for
degradation of Thioped).
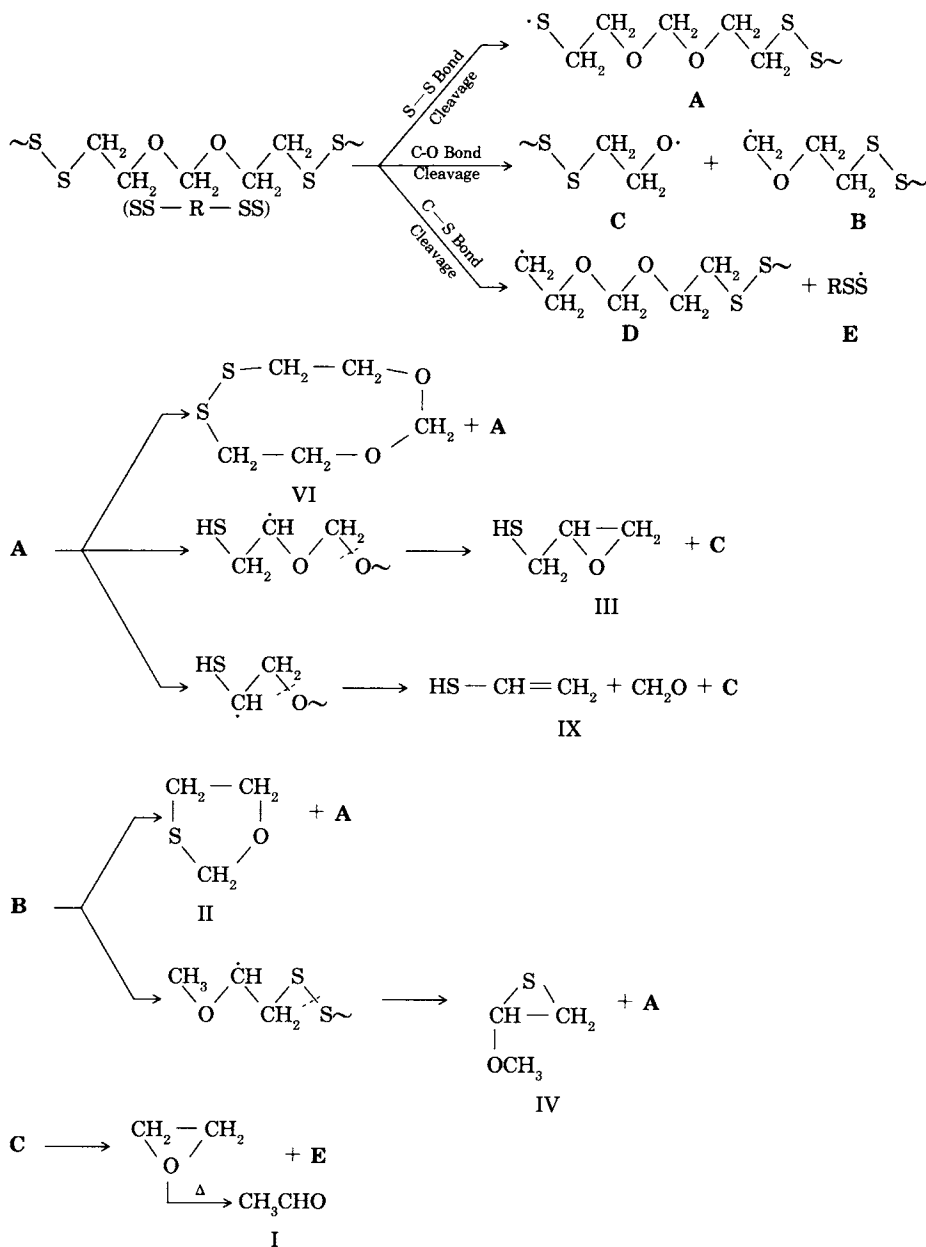
Scheme II.
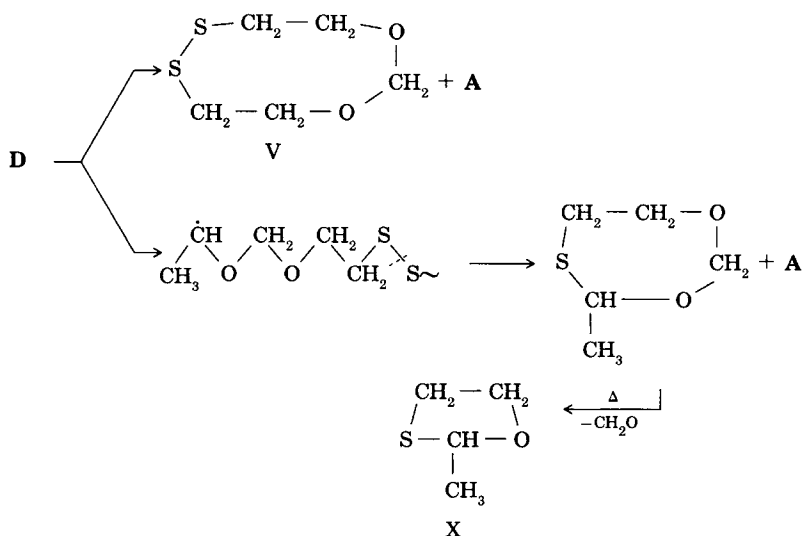
Scheme II—*Continued.*

Thus, it is seen from Scheme II that the important reactions leading to product formation are: cyclization; β-hydrogen abstraction; radical attack on S—S bond; 1,2-hydrogen shift; radical rearrangements or combinations of these reactions. The high concentration of the cyclic products indicates that intramolecular cyclization is a preferred mode of the termination of a radical. For a RṠ radical, the β-hydrogen abstraction is at least equally preferred to the radical attack on a S—S bond. This is shown by the relative molar concentration of 2-mercaptomethyl oxirane (III—15.9%) and the cyclic monomer (VI—12.6%). The near equal concentrations of 1,3-oxathiolane (II—18.7%) and acetaldehyde (I—15.7%) is consistent with the view that they have a common origin as proposed in Scheme II. The radicals **B** and **C** are formed by the cleavage of the formal linkage and lead to the formation of the products II and I, respectively.

Further, the product composition should indicate the preferred mode of initiation. Products II and V can be formed through radicals resulting from the cleavage of the formal C—O and C—S linkages. The molar concentration of II (18.7%) and V (7.6%) suggest that the cleavage of the formal C—O bond is more facile than the C—S bond. The radical **A** formed by the cleavage of the S—S bond also results from the propagation steps of radicals **B** and **D**, and the observation that the major products formed (III and VI) from **A** are not in excess over II suggest that the S—S bond cleavage may be a less preferred mode of initiation. Overall, the cleavage of the formal C—O linkage seems to be the most preferred mode of initiation of decomposition. This is also observed to be the case when the decomposition takes place in air, as reported by Berenbaum.[8]

Thus, Scheme II satisfactorily explains the formation of group I products as due to primary radical reactions whereas group II products result from radical rearrangement reactions. These radical rearrangements are quite reasonable since the resulting radicals are stabilized by an adjacent heteroatom. The occurrence of the radical rearrangement reactions would in-

crease with increase in temperature. Consequently, the group II products are observed at higher concentrations with increase in pyrolysis temperature. The formation of group III products can be explained on the basis of secondary reactions and fragmentation of the primary products that are likely to take place at higher temperatures of decomposition. Also, the cleavage of additional bonds, like C—C, which require higher energy, can take place at higher temperatures. Thus, the formation of several disulfide compounds can be explained by the cleavage of the C—C bond. Scheme III outlines the formation of some of the group III products at elevated temperature.

Thermogravimetric Studies

The postulated ionic mechanism for the decomposition is catalytic in nature and is, therefore, expected to have a lower activation energy compared to the radical mechanism which involves bond cleavage. Hence, a determination of the activation energy for the decomposition process would give valuable information on the mechanism. With this in view, isothermal and dynamic thermogravimetric studies were carried out, and the kinetic parameters were evaluated.

Thermograms were recorded at five different heating rates (RH) (Fig. 5) and from the thermograms, the data in Table VI were extracted. Following the treatment of Ozawa,[13,14] plots of - log $[(RH)/T^2]$ vs. $1/T$ were constructed
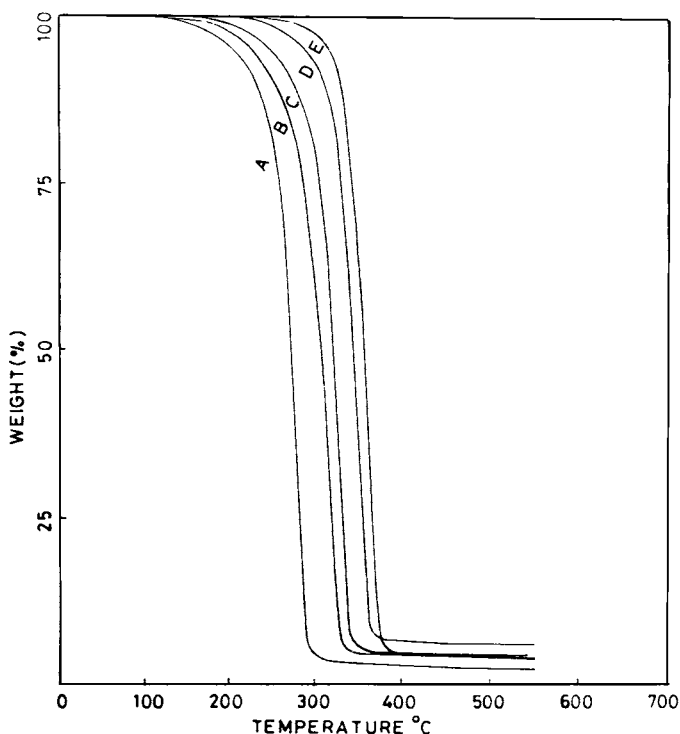

Scheme III.
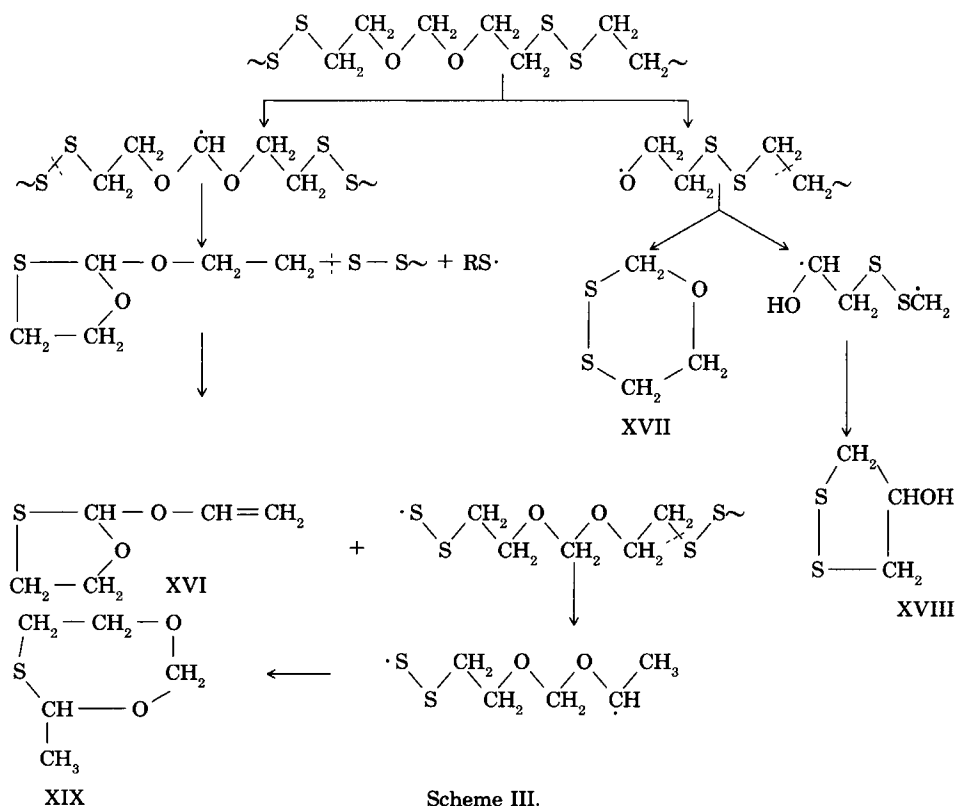
Fig. 5.   TGA of LP-2 at different heating rates (°C/min): (A) 2; (B) 10; (C) 20; (D) 50; (E) 100.

for constant values of conversions and are shown in Figure 6. The activation energies, obtained from the slopes of these plots, are found to be different at different conversions and these values are also indicated in Table VI. This clearly suggests a change in the degradation mechanism as the decomposition progresses. At 10% conversion, the activation energy is only 55 kJ mol^{-1}, suggesting the predominance of a low activation energy process, probably the ionic one. As the percent conversion increases, the activation energy increases and can be attributed to the predominance of a higher activation energy process, probably the radical one.

A complete evaluation of the kinetic parameters was carried out by solving the Coats and Redferns equation,[15] using a computer programme.[16] The

TABLE VI
TGA Data for Decomposition of LP-2

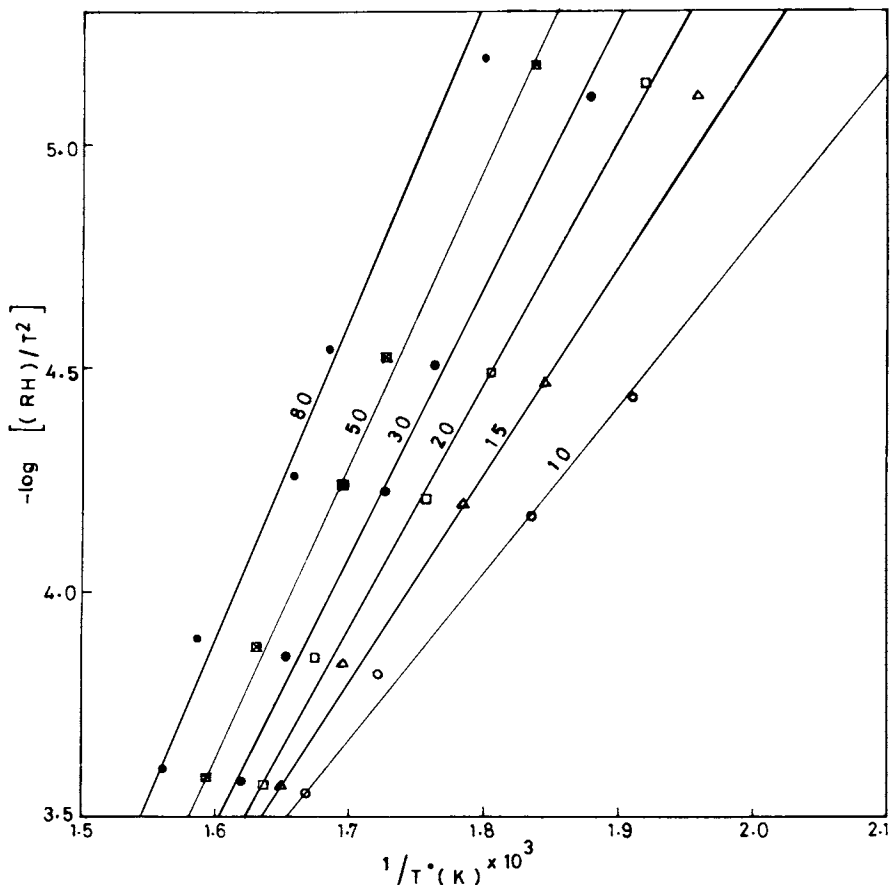| Conversion (%)	Temperature T (K) for (RH) (°C min^{-1})					Activation energy E (kJ mol^{-1})
	T for 2	T for 10	T for 20	T for 50	T for 100	
10	501	523	545	586	600	55.2
15	514	542	560	594	606	88.6
20	521	554	569	599	611	104.9
30	532	567	579	605	617	115.4
50	544	580	590	614	627	125.8
80	555	592	602	630	640	138.4

Fig. 6.   Plots of $-\log[(\text{RH})/T^2]$ vs. $1/T$ for LP-2 at various values of percentage conversion.

values of the parameters obtained from the thermograms at different heating rates are summarized in Table VII. Here, again, the results indicate that at high heating rates, the process requiring higher activation energy predominates. Under the flash pyrolysis conditions employed in the present study, the heating rate is very high (ca. 700°C/min), and hence the higher activation energy process should predominate. This observation, coupled with the product analysis, suggests the high activation energy process to be a free radical process.

TABLE VII
Kinetic Parameters for the Decomposition of LP-2

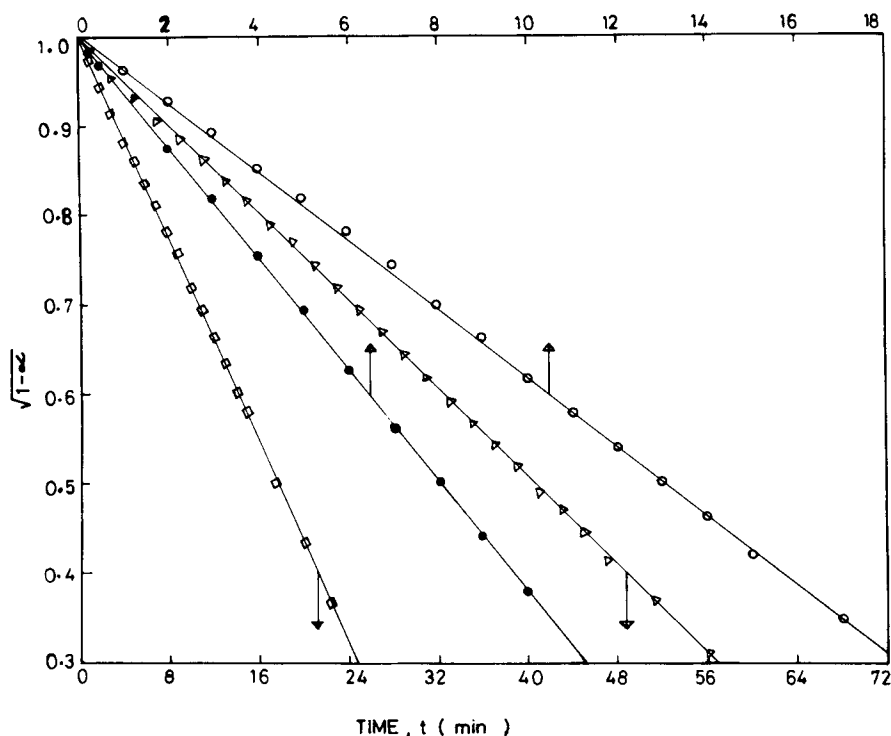| Sample no.	Heating rate (°C/min)	n	E (kJ mol^{-1})	A	Correlation coefficient
1	2	0	71.1	2.4×10^2	0.990
2	10	0	61.0	6.4×10^2	0.985
3	20	0	78.2	2.2×10^4	0.986
4	50	0.35	152.6	7.2×10^{10}	0.997
5	100	0.75	194.8	3.4×10^{14}	1.000
6	Isothermal	0.5	186.7	9.2×10^{14}	—

Fig. 7.   Plots of $\sqrt{1-\alpha}$ vs. time from isothermal TG curves for LP-2: ($\triangle$) 250°C; ($\square$) 260°C; ($\bigcirc$) 265°C; ($\bullet$) 270°C.

Further, the results from isothermal kinetics are also in agreement with the above observations. Isotherms were recorded at 250, 260, 265, and 270°C. The zero- and first-order kinetic expressions could not be fitted with the observed data. However, the data could be interpreted by a contracting interface mechanism[17] with reaction order equal to ½. The plots of $\sqrt{1-\alpha}$ (where α = fraction decomposed) vs. time are linear over the entire reaction periods, as shown in Figure 7. The corresponding Arrhenius plot (Fig. 8) gives a value of 186.7 kJ mol^{-1} for the activation energy, in good agreement with the value obtained from dynamic TG analysis at the high heating rate of 100°C/min.

Thus, the product analysis by GC–MS, the isothermal and dynamic TG studies suggest that the data on the thermal decomposition of the polysulfide polymers can be correlated if it is assumed that the ionic and free radical processes occur simultaneously and their relative importance depends on the temperature, the radical process becoming more important at higher temperatures. It is to be stressed here that the ionic process can either lead to only the cyclic monomer (VI) by cyclodepolymerization or to other additional products, as outlined in Scheme I.

Comparison with Polyoxymethylene

As discussed earlier, the preferred mode of initiation for the polysulfide polymers is the cleavage of the formal bond, and hence it is instructive to
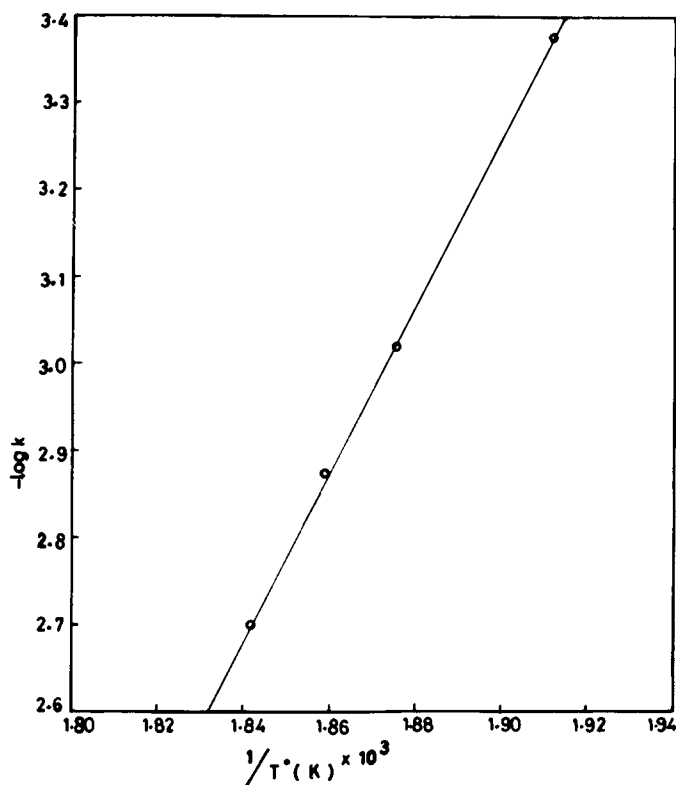
Fig. 8. Arrhenius plot for isothermal kinetics for LP-2; $E = 186.7$ kJ mol^{-1}; $k_{523\,K} = 4.2 \times 10^{-4}$ s^{-1}; $k_{533\,K} = 9.6 \times 10^{-4}$ s^{-1}; $k_{538\,K} = 1.3 \times 10^{-3}$ s^{-1}; $k_{543\,K} = 2.0 \times 10^{-3}$ s^{-1}.

compare this polymer with those polymers having a formal bond along their backbone. The thermal decomposition of polyoxymethylene (POM) was studied by several workers.[18-21] Grassie and Roche[20] reported that the activation energy for the decomposition of POM changes with percent conversion. Polysulfides also show very similar behavior. They considered molecular, ionic, and radical mechanisms for the decomposition. Molecular mechanism was preferred because of the absence of cross products expected from the radical mechanism. When the decomposition is base catalyzed, the mechanism is decidedly anionic, a process quite analogous to the ionic cyclodepolymerization of the polysulfides.

Further, Wilson and Hamaker[21] identified two distinct temperature dependent processes for the decomposition of POM. The first one, a low temperature process occurs in the region 145–303°C and has an activation energy of 92 kJ mol^{-1}. The second one is a high temperature process and prevails in the region, 303–412°C, with an activation energy of 192 kJ mol^{-1}. These values of the activation energy are quite similar to the values obtained for polysulfides at low and high heating rates, i.e., 70 and 190 kJ mol^{-1}. This analogous behavior of POM and polysulfide polymers is in accord with the conclusions arrived at earlier, namely, that the polysulfides decompose according to the ionic or free radical process, depending upon the temperature, and the preferred mode of initiation is the cleavage of the formal linkage.

CONCLUSIONS

The important conclusions that can be drawn from the present study are: (1) The thermal decomposition of thiol-terminated liquid polysulfides gives rise to a complex mixture of products. The product formation can be explained by a free radical mechanism. (2) The most preferred mode of initiation is the cleavage of the formal C—O linkage. (3) At low heating rates, the mechanism of decomposition changes with extent of conversion and at high heating rates a single mechanism prevails. (4) The activation energy for the isothermal or high heating rate decomposition is about 190 $kJ \cdot mol^{-1}$.

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