# Characterization of Cured Polysulfide Polymers by Thermal Degradation: Pyrolysis-GC and Thermogravimetric Studies

T. S. RADHAKRISHNAN and M. RAMA RAO, *Chemicals Group, Vikram Sarabhai Space Centre, Trivandrum-695 022, India*

## Synopsis

Polymers prepared by curing thiol-terminated liquid polysulfide polymer [$HS(RS_2)_n RSH$, R = $—CH_2CH_2OCH_2OCH_2CH_2—$] with p-quinonedioxime, $PbO_2$, and $MnO_2$ were studied by pyrolysis-GC and thermogravimetry. Characteristic differences were observed in the composition of the pyrolyzates under flash pyrolysis at 420 and 470°C. The concentration of the cyclic monomer, 1,3-dioxa-6,7-dithionane, in the pyrolyzates was found to vary considerably from polymer to polymer. The change in mechanism with the extent of degradation and the corresponding overall activation energies were evaluated by thermogravimetry. The pyrolysis-GC and thermogravimetric data were shown to provide partial characterization of the substrates. Mn appears to be in a coordinated complex in the $MnO_2$-cured polymer.

## INTRODUCTION

The characterization of crosslinked and cured polymers is hindered by their intractability and insolubility, and, in recent years, examination of thermal degradation behavior of such polymers is widely recognized to provide characterizing information.[1,2] The nature and composition of the degradation species is a function of the chemical composition and molecular order in the substrate as well as the degradation conditions.

Thiol-terminated liquid polysulfide polymers of the general formula $HS(RS_2)_n RSH$ (R = $—CH_2CH_2OCH_2OCH_2CH_2—$) are employed as the base polymers in the formulations of adhesives and sealants widely used in aerospace industry.[3] The curing reaction in the formulations involves the oxidation of the mercaptan to a disulfide. Different oxidizing agents like lead dioxide, manganese dioxide, dichromates, etc., are employed as the oxidizing agents. The cured polymers are completely insoluble and are difficult to characterize. They contain metal ions in their reduced state and also may contain mercaptide bonds as is shown to be the case for $PbO_2$-cured polymer.[4] Also, the transition metal ions may form coordinated bonds with the heteroatoms in the polymer backbone. These factors are likely to affect the nature and composition of the thermal degradation products and may provide characterizing information. The mechanism and kinetics of thermal decomposition of liquid and ammonium dichromate cured polysulfide polymers from pyrolysis-GC and thermogravimetric studies are reported in our earlier papers.[5,6] This article describes the pyrolytic behavior of the polysulfide polymers obtained by curing the liquid polymer with three different types of

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curing agents; namely, an organic oxiding agent, *p*-quinone dioxime, an inorganic peroxide, $PbO_2$, and a transition metal peroxide, $MnO_2$. Pyrolysis-GC and dynamic thermogravimetric data are shown to provide partial characterization of the substrates. The overall activation energies for thermal decomposition of the cured polymers are evaluated.

## EXPERIMENTAL

### Materials

The liquid polysulfide polymer was prepared from dichlorodiethylformal with 2 mol % of 1,2,3-trichloropropane as the crosslinking agent according to known procedure.[3] The prepared polymer has a molecular weight of 3910 (by VPO); viscosity of 450 P at 25°C; and SH value of 1.23%. The oxidizing agents and other ingredients used were reagent grade commercial materials.

### Curing of Liquid Polysulfide

The composition of the cured polymers is given in Table I. The oxidizing agent and the other ingredients were mixed well. The liquid polymer was added and mixed thoroughly. The samples were cured for 24 h at room temperature and then at 70°C for 2 days. The mechanical properties were measured using an Instron 1121. Crosslink density was determined using the swollen compression method.[7] Indentation hardness (Shore A) was measured using a durometer type A following ASTM method.[8] The physical properties of the cured polymers are shown in Table II.

TABLE I
Composition of Cured Liquid Polysulfide Polymers

|  | Composition[a] | | |
|  | Polymer 1 | Polymer 2 | Polymer 3 |
|---|---|---|---|
| *p*-Quinone dioxime (PQD) | 4 | — | — |
| Lead dioxide | — | 8 | — |
| Manganese dioxide | — | — | 4 |
| Dimethyl formamide (DMF) | 10 | 10 | 10 |
| Diphenyl guanidine (DPG) | 2 | 2 | 2 |
| Zinc oxide | 0.5 | — | — |

[a] In parts by weight per 100 parts (phr) of liquid polymer.

TABLE II
Physical Properties of Cured Liquid Polysulfide Polymers

|  | Tensile strength $(kg/cm^2)$ | Elongation (%) | Stress at 100% elongation $(kg/cm^2)$ | Shore A hardness | Crosslink density (mol/cc) | Mol wt between crosslinks |
|---|---|---|---|---|---|---|
| Polymer 1 | 9.9 | 205 | 6.5 | 41 | $1.1 \times 10^{-4}$ | 11,910 |
| Polymer 2 | 6.8 | 695 | 2.7 | 51 | $1.55 \times 10^{-5}$ | 91,610 |
| Polymer 3 | 8.4 | 142 | 6.9 | 58 | $6.35 \times 10^{-5}$ | 20,945 |

## Pyrolysis Gas Chromatography

Pyrolysis-GC experiments were carried out using a furnace pyrolyzer, Shimadzu PYR-2A coupled to a Shimadzu GC-5A gas chromatograph equipped with a Shimadzu C-R1A data processor. The experimental details are as reported earlier.[5]

## Thermogravimetric Studies

Dynamic thermogravimetric experiments were done using a DuPont 990 Thermal Analyser in dry nitrogen atmosphere at a flow rate of 50 mL/min. Thermograms were recorded at different heating rates ($\beta$) of 2, 10, 20, and 50°C/min.

# RESULTS AND DISCUSSION

## Effect of Added Salts

The curing of thiol-terminated liquid polysulfide polymers involves the oxidation of the mercaptan to disulfide using higher valency metal oxides or p-quinonedioxime. Consequently, the cured polymers will contain reduced forms of the metal ions or p-phenylenediamine heterogeneously dispersed in them. These products may have an effect on the nature and composition of the thermal degradation products of the polymers. In addition, other reagents used in the curing formulations may also affect the product distribution. Hence, a systematic study on the effect of various salts on the thermal degradation of liquid polysulfide polymer was undertaken first.

Twenty percent (w/w) of the salt was mixed thoroughly with the liquid polymer, and the resultant mixture was pyrolyzed at 420°C. The nature and composition of the pyrolyzates obtained are given in Table III. As was shown in our earlier studies,[5] the major components of the four peaks are: peak 1: 1,3-oxathiolane (I); peak 2: 2-mercaptomethyl oxirane (II); peak 3: 1,3-dioxa-

TABLE III
Effect of Various Salts on the Composition of Major Pyrolyzates
of Liquid Polysulfide, Pyrolysis Temperature 420°C

| Sample no. | Salt added | Peaks (area %) | | | |
|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 |
| 1 | — | 42.6 | 11.4 | 7.2 | 18.7 |
| 2 | KCl | 42.4 | 11.3 | 7.3 | 18.1 |
| 3 | $K_2SO_4$ | 47.3 | 11.0 | 6.2 | 17.9 |
| 4 | $BaCl_2$ | 49.3 | 11.3 | 5.7 | 17.2 |
| 5 | $PbCl_2$ | 22.1 | 10.7 | 7.5 | 50.7 |
| 6 | $ZnSO_4$ | 29.7 | 9.9 | 7.9 | 44.0 |
| 7 | $MnSO_4$ | 29.1 | 11.2 | 5.2 | 41.6 |
| 8 | $K_2Cr_2(SO_4)_4$ | 33.1 | 12.0 | 4.4 | 32.8 |
| 9 | PPD | 42.3 | 11.6 | 7.0 | 18.4 |
| 10 | DPG | 45.7 | 10.6 | 9.4 | 17.2 |
| 11 | DMF | 46.8 | 10.5 | 8.1 | 17.1 |
| 12 | ZnO | 36.4 | 11.6 | 10.3 | 22.6 |

6-thiocane (III); and peak 4: 1,3-dioxa-6,7-dithionane (IV). These results show that salts like KCl, $K_2SO_4$, and $BaCl_2$ and components like DMF, DPG, PPD, etc., have no effect on the nature and composition of the pyrolyzates. Salts like $PbCl_2$, $MnSO_4$, $ZnSO_4$, and $K_2Cr_2(SO_4)_4$, which are likely to form mercaptide bonds, greatly influence the composition, but not the nature of the pyrolyzates. Thus in the presence of $PbCl_2$, the formation of the cyclic monomer (IV) is increased to as much as 50% compared to 19% when no salt is present (Fig. 1, Table III). This was further confirmed by the product analysis at varying concentrations of $MnSO_4$ from 1 to 30%. A plot of the percentage of IV vs. the salt content is given in Figure 2. The concentration of IV steadily increases with increase in salt content and finally reaches a limiting value.

These observations can be rationalized on the basis of ionic[5,9] and radical mechanism[5,10] proposed earlier, for the degradation of thiol-terminated liquid
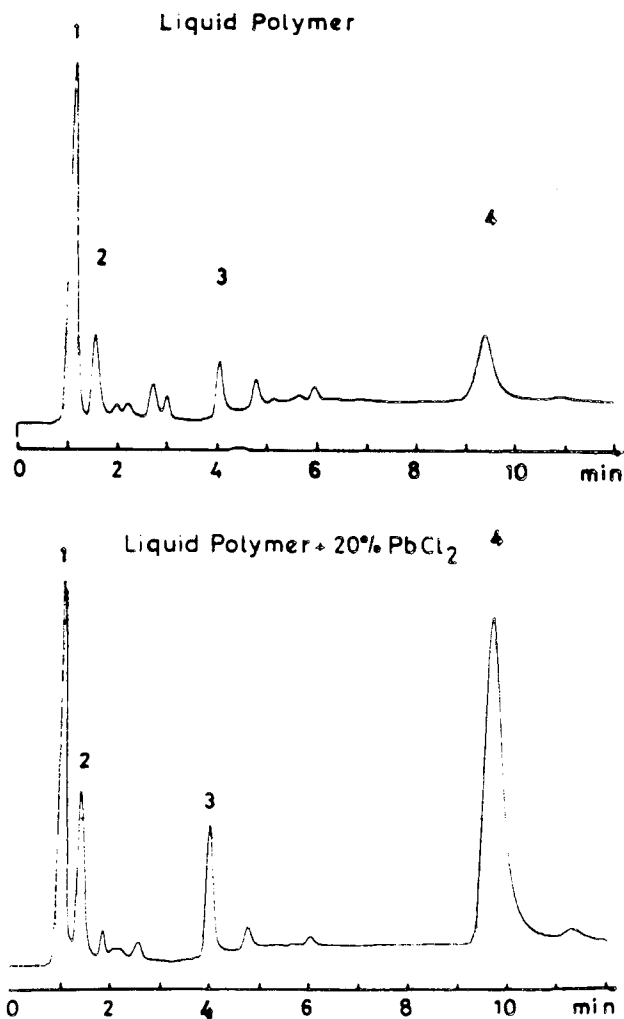


Fig. 1. Pyrograms of liquid polymer and liquid polymer mixed with 20% $PbCl_2$ at 420°C with a squalane column; column temp 60–120°C, 15°C/min; flow rate 40 mL/min.

Fig. 2. Plot of concentration of cyclic monomer, 1,3-dioxa-6,7-dithionane (IV) vs. amount of MnSO$_4$ added.

polysulfide polymers. The ionic mechanism involves the nucleophilic attack of the mercaptide ions on the disulfide (—SS—) bond leading to decyclopolymerization and formation of the cyclic monomer (IV):



The radical mechanism involves the preferential cleavage of the formal bond and formation of 1,3-oxathiolane (I), as well as the cyclic monomer (IV), as the main products:



In the presence of salts which are likely to increase the concentration of the mercaptide ions, the ionic mechanism dominates resulting in an increase in the concentration of IV and a decrease in the concentration of I. The concentration of IV goes on increasing till the mercaptide ion reaches an equilibrium-limiting value.

TABLE IV
Composition of Major Pyrolyzates from Liquid and Cured Polysulfide Polymers

| Sample | Peaks (area %) | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Pyrolysis temperature 420°C | | | | |
| Liquid polymer | 42.6 | 11.4 | 7.2 | 18.7 |
| Polymer 1 | 29.2 | 11.2 | 9.8 | 36.8 |
| Polymer 2 | 34.6 | 13.8 | 9.0 | 22.8 |
| Polymer 3 | 45.6 | 10.1 | 15.4 | 9.8 |
| Polysulfide latex | 18.4 | 11.0 | 4.9 | 59.4 |
| Pyrolysis temperature 470°C | | | | |
| Liquid polymer | 53.4 | 9.6 | 4.3 | 10.2 |
| Polymer 1 | 54.0 | 12.8 | 2.6 | 15.9 |
| Polymer 2 | 55.7 | 12.5 | 3.8 | 11.4 |
| Polymer 3 | 60.7 | 10.5 | 6.8 | 5.0 |
| Polysulfide latex | 37.4 | 10.2 | 2.0 | 37.2 |

## Pyrolysis-GC Studies

The cured liquid polysulfide polymer samples 1, 2, and 3 obtained by curing the liquid polymer using PQD, $PbO_2$, and $MnO_2$, respectively, were pyrolyzed at 420 and 470°C. The product composition of the pyrolyzates is given in Table IV and the pyrograms are shown in Figure 3. Although the nature of the products formed are essentially the same in all cases, distinct differences are observed in their relative concentrations. Thus, polymer 1 gives the highest concentration of the cyclic monomer, IV, whereas polymer 3 gives the least amount of IV, but the highest amount of III. An interpretation of these results requires an understanding of the factors which influence the formation of the products.

The cyclic monomer, IV, is formed by cyclodepolymerization through both ionic and radical mechanisms, as pointed out earlier. The extent of depoly-merization, and consequently, the concentration of IV in the pyrolyzates, depend on the zip length, defined as the average number of monomer mole-cules formed between initiation and termination. A measure of zip length relative to chain length can be ascertained by pyrolyzing high molecular weight polymer. Hence, a polysulfide polymer latex from which the liquid polymer is obtained by degradation was subjected to pyrolysis, and the results are given in Table IV. It is seen that the concentration of IV in the pyrolyzates is about 60% compared to about 19% in the case of the liquid polymer. These results clearly show that the zip length is quite large, and depolymerization is limited by the chain length. The depolymerization process would continue till an impediment occurs along the chain. Such impediments occur either at the crosslinking points or due to the presence of mercaptide bonds ( ~ S—M—S ~ ). Hence, the crosslink densities of the polymers were measured, and the results are given in Table II. The presence   e mercaptide bonds can be inferred from the change in mechanism.   extent of degradation as was shown in our earlier studies.[5] Dynamic thermogravimetric experiments were carried out to obtain these data.
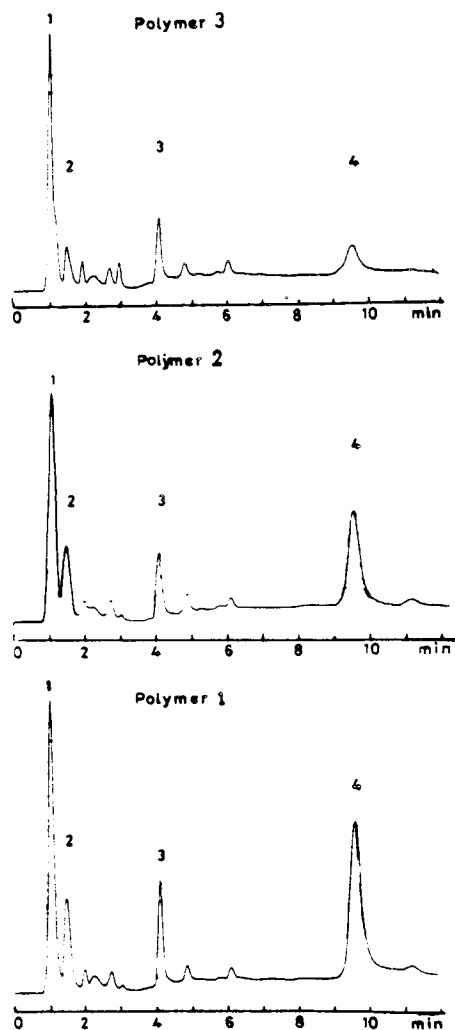
Fig. 3. Pyrograms of cured polysulfide polymers at 420°C with a squalane column; column temp 60–120°C, 15°C/min; flow rate 40 mL/min.

TABLE V
TGA Data for PQD Cured Polymer 1

| Conversion (%) | Temperature (K) for heating rate ($\beta$)(°C/min) | | | | Activation energy (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| | $\beta = 2$ | $\beta = 10$ | $\beta = 20$ | $\beta = 50$ | |
| 5 | 496 | 525 | 554 | 537 | 120.3 |
| 10 | 510 | 539 | 573 | 555 | 116.9 |
| 20 | 522.5 | 552 | 588 | 570 | 117.9 |
| 40 | 535 | 565 | 600 | 581 | 125.1 |
| 60 | 541 | 571 | 608 | 587.5 | 124.9 |
| 80 | 546 | 578 | 616 | 593.5 | 122.0 |
| 90 | 550 | 583.5 | 622 | 599 | 121.3 |

TABLE VI
TGA Data for $PbO_2$-Cured Polymer 2

| Conversion (%) | Temperature (K) for heating rate ($\beta$)(°C/min) | | | | Activation energy (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| | $\beta = 2$ | $\beta = 10$ | $\beta = 20$ | $\beta = 50$ | |
| 5 | 480.5 | 515 | 539 | 562.5 | 81.2 |
| 10 | 500 | 533 | 552.5 | 578 | 91.3 |
| 20 | 518 | 548 | 566 | 592 | 96.3 |
| 40 | 532 | 564 | 582 | 608.5 | 100.8 |
| 60 | 542 | 576 | 593 | 617.5 | 113.1 |
| 80 | 552 | 584 | 601 | 624 | 119.8 |
| 90 | 557 | 588 | 605.5 | 628.5 | 119.5 |

TABLE VII
TGA Data for $MnO_2$-Cured Polymer 3

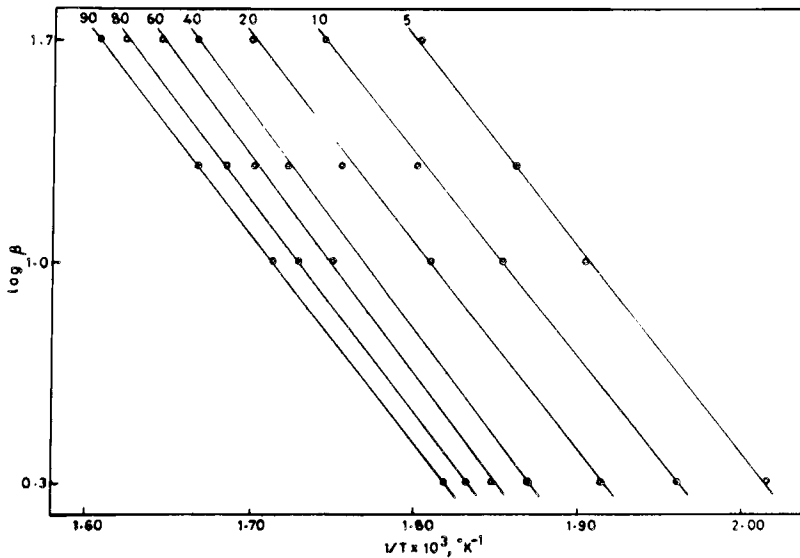| Conversion (%) | Temperature (K) for heating rate ($\beta$)(°C/min) | | | | Activation energy (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| | $\beta = 2$ | $\beta = 10$ | $\beta = 20$ | $\beta = 50$ | |
| 5 | 456.5 | 496 | 518.5 | 553 | 58.4 |
| 10 | 476.5 | 514.5 | 535 | 570.5 | 70.0 |
| 20 | 495 | 539 | 556 | 587 | 81.1 |
| 30 | 511 | 551 | 567.5 | 594 | 93.6 |
| 50 | 530 | 562.5 | 579 | 604.5 | 110.7 |
| 70 | 539.5 | 572.5 | 590 | 615 | 112.7 |
| 80 | 547 | 580 | 597.5 | 623 | 113.7 |
| 90 | 560 | 593 | 609 | 632.5 | 124.8 |
| 95 | 571 | 602.5 | 617.5 | 641 | 133.8 |



Fig. 4. Ozawa's plots of log $\beta$ vs. $1/T$ at constant values of percentage conversions for the degradation of polymer 1.
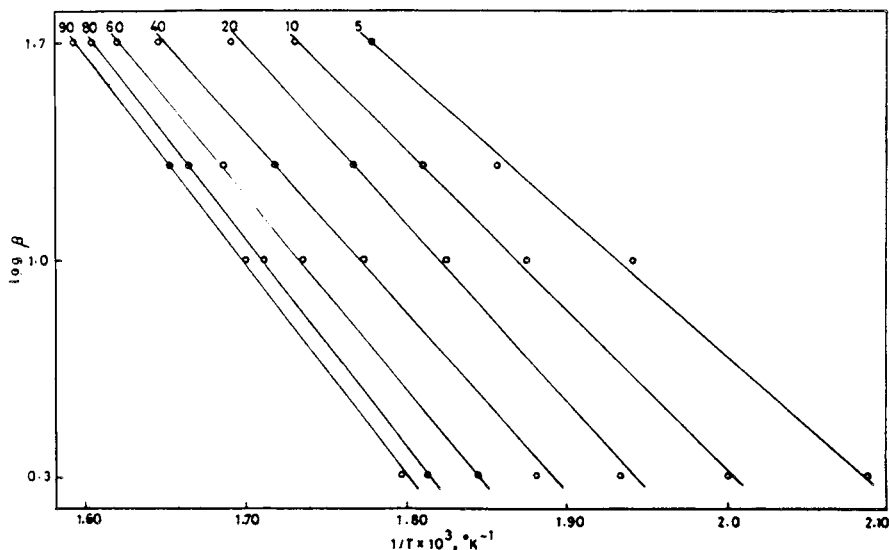
Fig. 5. Ozawa's plots of $\log \beta$ vs. $1/T$ at constant values of percentage conversions for the degradation of polymer 2.

## Thermogravimetric Studies

Thermograms for polymers 1, 2, and 3 were recorded at heating rates $(\beta)$ of 2, 10, 20, and 50°C/min, and, from the thermograms, the data in Tables V–VII were extracted. Following the treatment of Ozawa,[11] which is essentially the same as that of Flynn and Wall,[12] plots of $\log \beta$ vs. $1/T$ were constructed for constant values of conversion $(\alpha)$ $(\alpha$ is the fraction of active material decomposed). These isoconversional plots for polymers 1, 2, and 3 are
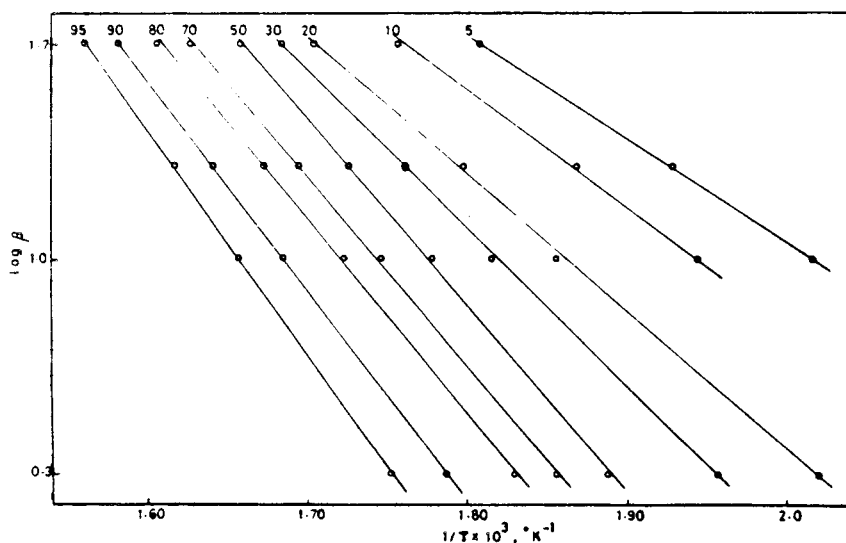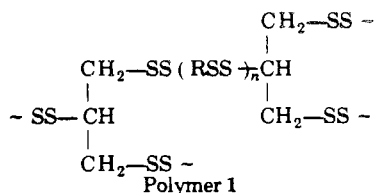


Fig. 6. Ozawa's plots of $\log \beta$ vs. $1/T$ at constant values of percentage conversions for the degradation of polymer 3.

shown in Figures 4, 5, and 6, respectively. The slope of such a line is given by $-0.4567\ E_d/R$, where $E_d$ is the overall activation energy for the decomposi-tion process. The calculated values of $E_d$ are also given in Tables V–VII. Change in activation energy with extent of conversion indicates a change in the mechanism of decomposition, and its magnitude suggests that the mecha-nism is ionic or radical.[5] These observations along with pyrolysis-GC data are used to characterize the cured polymers.

### Characterization of Cured Polymers

Polymer 1, obtained by curing the liquid polysulfide polymer with PQD, represents a polymer with no added metal salts and serves as a reference sample. The data given in Table III indicate that the ingredients used in the curing formulation and the PPD which is formed during curing reaction have no catalytic effect on the decomposition, the product composition remaining essentially unaltered. Hence, it may be inferred that the composition of the pyrolyzates reflects only the structure of the cured polymer. Polymer 1 gives the highest concentration of the cyclic monomer IV (36.4%, Table IV) among all the cured polymers. Good mechanical properties and high crosslink density (Table II) of the polymer suggest almost complete curing. Ozawa's plots (Fig. 4) show no change in activation energy $E_d$ with the extent of degradation, $\alpha$ (Table V), indicating a single mechanism for the entire decomposition process. The value of 122 kJ mol$^{-1}$ for $E_d$ suggests a radical mechanism for decom-position and rules out the presence of any mercaptide bonds. Therefore, the structure of polymer 1 should be quite similar to the structure of the polymer latex and may be represented as

$$
\begin{array}{c}
\mathrm{CH_2{-}SS\ -} \\
| \\
\mathrm{CH_2{-}SS\,(\ RSS \,\overset{}{\rightarrow}_{\!n}CH} \\
| \qquad\qquad\qquad | \\
\mathrm{\sim SS{-}\,CH \qquad\qquad CH_2{-}SS\ \sim} \\
| \\
\mathrm{CH_2{-}SS\ \sim} \\
\text{Polymer 1}
\end{array}
$$

The molecular weight between crosslinks is about 10,000 giving an average value for $n$ of about 60 which agrees well with the expected theoretical value ($n = 50$) when 2 mol % crosslinking agent is used. The lower percentage of the cyclic monomer IV in the pyrolyzates relative to the polymer latex might be due to differing molecular weights and/or chain lengths. The structures of the other polymers are discussed in comparison with polymer 1.

Polymer 2, obtained by curing the liquid polymer with PbO$_2$, shows a smaller concentration of the cyclic monomer IV (22.8%, Table III) relative to polymer 1, indicating greater impediments along the chain either due to crosslinking points or presence of mercaptide ($\sim$ S—Pb—S $\sim$) bonds. How-ever, the measured crosslink density of polymer 2 is less than that of polymer 1 (Table II). Furthermore, thermogravimetric data indicate a change in the mechanism of decomposition with $\alpha$ (Fig. 5, Table VI) as evidenced by the change in the $E_d$ with $\alpha$. The lower value of $E_d$ ($< 100$ kJ mol$^{-1}$) in the initial stages of decomposition ($\alpha < 0.2$) clearly proves the simultaneous
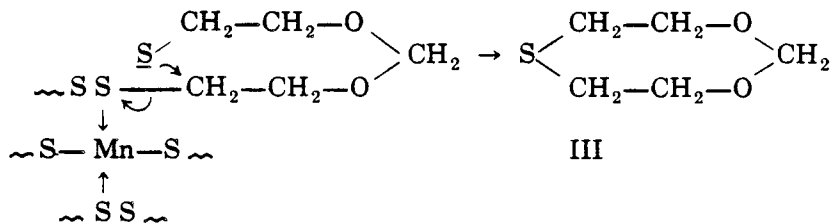
occurrence of ionic and radical mechanisms and, therefore, the presence of ∿S—Pb—S∿ bonds. Thus, the extent of curing of this polymer is incomplete. The inferior mechanical properties of polymer 2 compared to those of polymer 1 also support this conclusion. Based on these considerations, the structure of polymer 2 may be shown as

$$CH_2SS\sim$$
$$|$$
$$+S—Pb—SRSS+(RSS)_n—CH$$
$$|$$
$$CH_2SS\sim$$
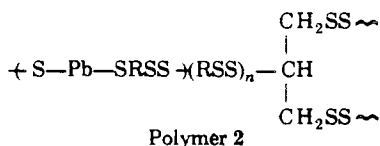
Polymer 2

Polymer 3, obtained by curing with $MnO_2$, shows the least concentration of IV indicating larger number of crosslinking points and greater extent of curing than polymers 1 and 2. However, the observed crosslink density of polymer 3 is less than that of polymer 1. In addition, thermogravimetric data indicate the presence of mercaptide (∿S—Mn—S∿) bonds as shown by the change in mechanism with $\alpha$ (Fig. 6) and low values of $E_d$ (Table VII). These apparently contradicting results can be reconciled if it is assumed that Mn is in the form of a coordinated complex in the cured polymer with S acting as electron pair donors. A plausible structure for the coordinated complex may be represented as

$$\sim S \quad \sim SS\sim$$
$$\diagdown \quad \nearrow$$
$$Mn$$
$$\nearrow \quad \diagdown$$
$$\sim SS\sim \quad S\sim$$
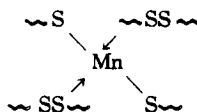
The proposed structure would show a high crosslink density but still contain mercaptide bonds, and show good mechanical properties (Table II) as well. This structure can also satisfactorily explain the least concentration of the cyclic monomer because of the greater number of impediments along the chain due to both ionic and coordinate bonds. Further, the highest concentration of III observed in the pyrolyzates of polymer 3 compared to polymers 1 and 2 can also be rationalized by such a coordinate structure. When the metal ion is absent in the polymer chain, the nucleophilic attack of $R\bar{S}$ on ∿SS∿ bond is favored and leads to the formation of IV as given earlier. In the presence of a coordinated metal ion, the $CH_2$—S bond adjacent to the S donor atom becomes polarized and the nucleophilic attack takes place on the C—S bond in preference to the S—S bond involved in coordination. This leads to the formation of III in larger quantities:

$$CH_2—CH_2—O \qquad\qquad CH_2—CH_2—O$$
$$S \diagup \qquad\qquad\qquad\qquad S \diagup \qquad\qquad\qquad CH_2$$
$$\qquad\qquad\qquad\diagdown CH_2 \rightarrow \qquad\qquad\qquad\qquad\diagup$$
$$\sim SS —— CH_2—CH_2—O \qquad\qquad CH_2—CH_2—O$$
$$\downarrow$$
$$\sim S— Mn—S \sim \qquad\qquad\qquad\qquad\qquad III$$
$$\uparrow$$
$$\sim SS \sim$$

These results were further confirmed by the pyrolysis of polymer samples prepared by curing the liquid polysulfide with different concentrations of

TABLE VIII
Composition of Major Pyrolyzates from Polysulfide Samples
Cured with Various Amounts of $MnO_2$, Pyrolysis Temperature 390°C

| Sample | Peaks (area %) | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| Liquid polymer | 36.4 | 11.2 | 18.6 | 20.6 |
| Liquid polymer–$MnO_2$ | | | | |
| 1 phr[a] | 36.1 | 11.8 | 22.8 | 12.7 |
| 2 phr | 36.8 | 12.3 | 26.6 | 12.0 |
| 3 phr | 33.5 | 9.8 | 31.8 | 12.1 |
| 4 phr | 32.6 | 10.2 | 32.8 | 11.5 |
| 5 phr | 33.2 | 10.1 | 32.6 | 11.8 |

[a] Parts by weight per 100 parts liquid polymer.

$MnO_2$ ranging from 1 to 5 parts per hundred gram resin (phr). The pyrolysis-GC results are given in Table VIII. A steady increase in the concentration of III is observed with increasing amounts of Mn, reaching a imiting value around 5 phr of $MnO_2$. This direct correlation between concentration of III and the amount of the curing agent is consistent with the proposed structure for the $MnO_2$-cured polymer.

## CONCLUSION

The important conclusions that can be drawn from the present study are: (i) the concentration of the cyclic monomer (IV) formed in the flash pyrolysis of cured polysulfide polymers reflects the structure of the cured polymer; (ii) thermogravimetric data could be used to find the presence of mercaptide bonds in the cured polymers; (iii) pyrolysis-GC and thermogravimetric techniques can be used to characterize insoluble polymers, which is clearly brought out in the case of $MnO_2$-cured polymer.

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