Primary Pyrolysis Products of Thiokol Liquid Polysulfide

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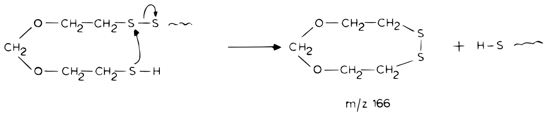
ABSTRACT: An analysis of the primary degradation products of the widely used commercial polysulfide polymer Thiokol LP-33 by direct pyrolysis−mass spectrometry (DP−MS) is reported. The mechanism of degradation is through a radical process involving the random cleavage of a formal C−O bond followed by backbiting to form the cyclic products.

Introduction

A plethora of information is available on the thermal degradation of polymers most often using DTA, DSC, or TG techniques and occasionally the flash pyrolysis−GC (Py−GC) method. The kinetic parameters derived from these studies generally do not provide information on primary bond breakage processes. Even Py−GC data lack this information due to various secondary reactions among primary products. Direct pyrolysis−mass spectrometry (DP−MS) is by far the most suited technique for gaining insight into the primary degradation products since pyrolysis is accomplished under high vacuum very close to the ion source and the primary products formed are rapidly removed from the hot zone and detected immediately.[1]

We report here DP−MS studies on Thiokol Liquid Polysulfide (Thiokol LP-33) polymer to investigate the nature of the primary degradation products. Thiokol LP is thiol-terminated liquid polysulfide polymer having the structure $H-(SCH_2CH_2OCH_2OCH_2CH_2S)_n-H$ and is extensively used for adhesives, sealants, insulators, etc.[2] Thiokol LP-33 has a molecular weight ($\bar{M}_n$) of 990, a viscosity (at 25 °C) of 19.9 P, and an −SH value of 5.24%. In spite of its commercial importance, only two reports are available on its thermal degradation, which are at variance with each other. A very early study using the distillation method[3] revealed the formation of a cyclic monomer only and was explained by an ionic mechanism involving the disulfide−thiol interchange process (eq 1). More recently, Py−GC−MS analysis on the same polymer revealed a large number of pyrolysis products in addition to the cyclic monomer, and this was explained by a radical mechanism.[4] To resolve the above discrepancy and to gain knowledge on the primary degradation products of polysulfide polymers, we have taken recourse to DP−MS analysis in our present investigation. Besides, we believe, it would also provide further input on the degradative behavior of weak-link polymers of group VIA elements.[5,6]



(1)

Experimental Section

Commercial Thiokol LP-33 was used without further purification.

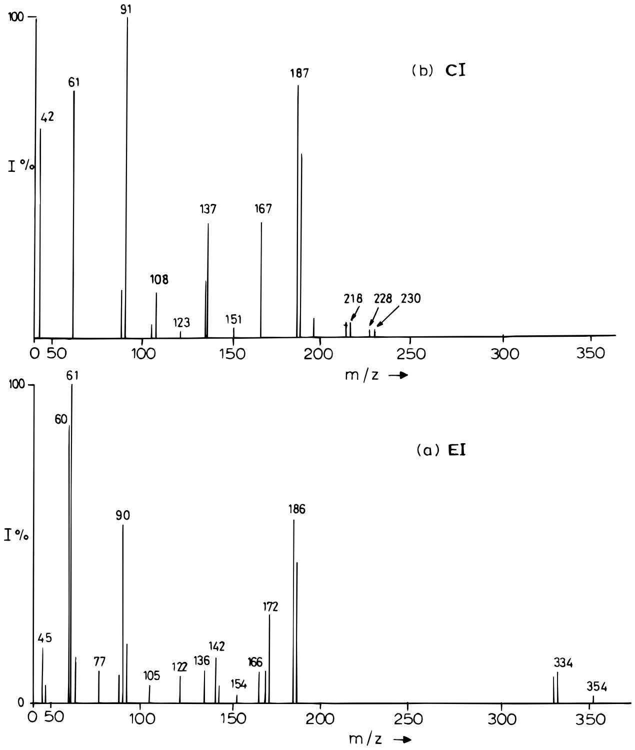


Figure 1. Mass spectra of Thiokol LP-33: (a) EI mass spectrum; (b) methane CI mass spectrum.

Table 1. Molecular Ions of the Primary Degradation Products and EI/CI Fragment Ions Observed in the DP−MS of Thiokol LP-33

STRUCTURE	M^+	MH^+	EI/CI fragments
CH_3-CHO		45	
$-(CH_2-CH_2-S)-$	60	61	
$-(CH_2-O-CH_2-CH_2-S)-$	90	91	
$-(CH_2-O-CH_2-CH_2-S-S)-$	122	123	
$-(CH_2-O-CH_2-CH_2-S-S-CH_2)-$	136	137	
$-(CH_2-O-CH_2-CH_2-S-S-CH_2-CH_2)-$		151	
$-(CH_2-O-CH_2-CH_2-S-S-CH_2-CH_2-O)-$	166	167	
$-(S-S-CH_2-O-CH_2-CH_2-S-S)-$	186	187	
$-(S-CH_2-O-CH_2-CH_2-S-S)-$			154
$-(S-S-CH_2-CH_2-O-CH_2-O-CH_2-CH_2-S-S)-$			230

Mass Spectrometry. Pyrolysis was carried out using the direct insertion probe of a JEOL D mass spectrometer, heated

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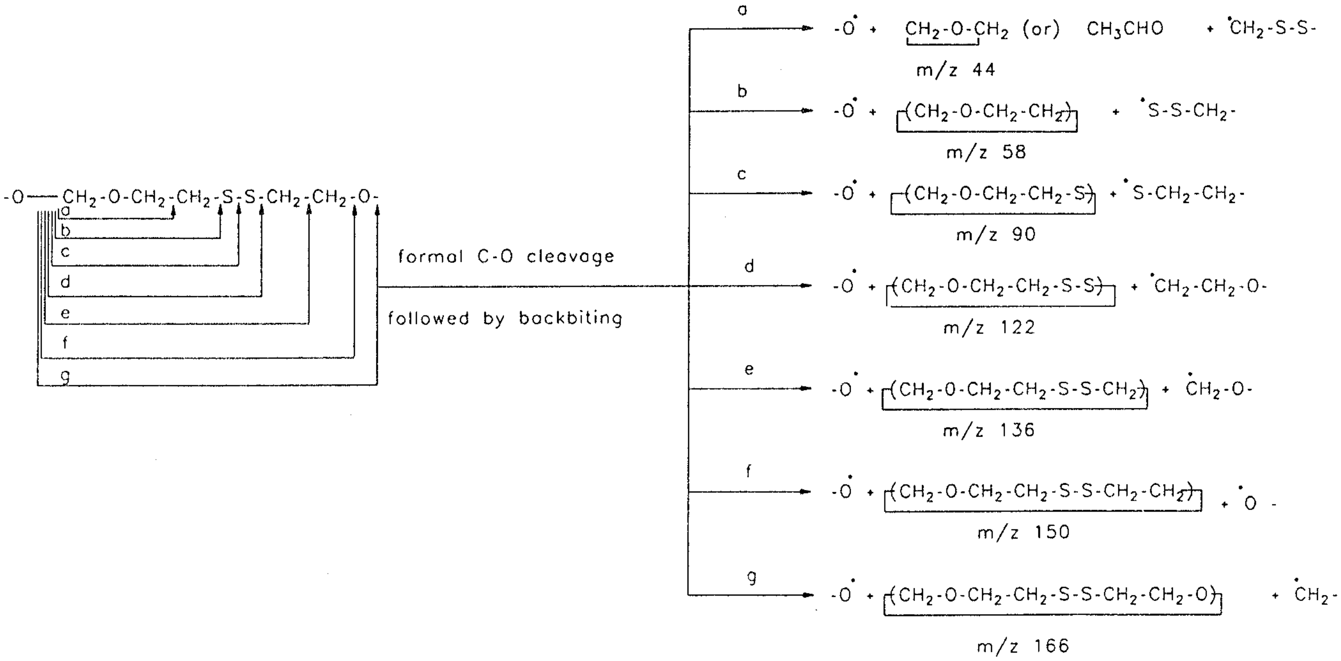
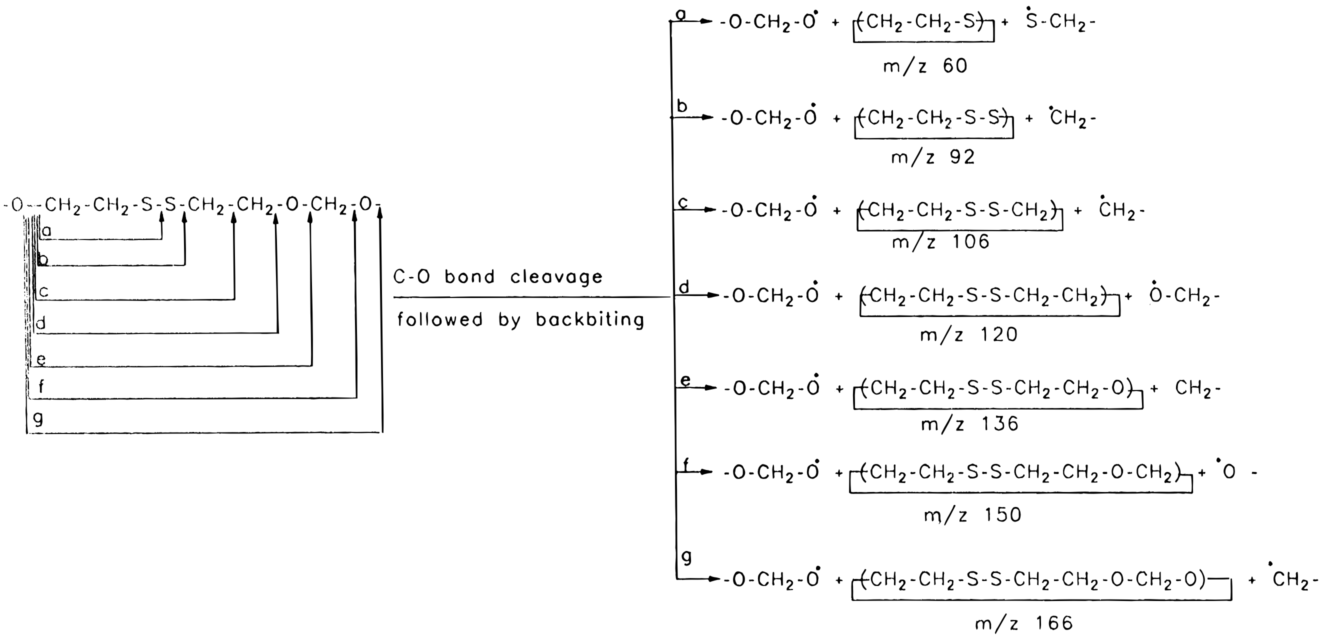
Scheme 1. Initiation of Degradation through Formal C–O Bond Cleavage



Scheme 2. Initiation of Degradation through Ether C–O Bond Cleavage



from 50 to 400 °C at a rate of 16 °C/min. Electron ionization (EI) was maintained at 18 eV, and chemical ionization (CI) (positive mode) was achieved using methane as the reagent gas.

Results and Discussion

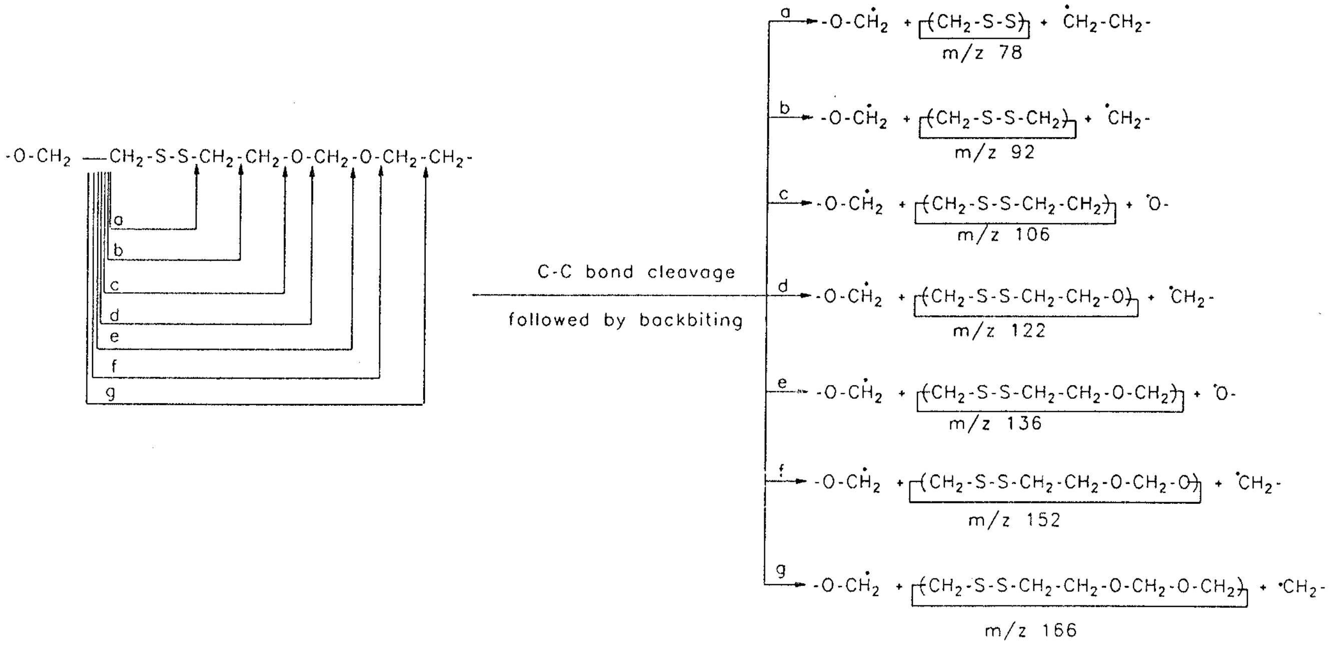
The EI and methane CI mass spectra of the pyrolysis products of Thiokol LP-33 are shown in parts a and b of Figure 1, respectively. The structural assignments of the molecular ion peaks appearing in both mass spectra are given in Table 1. The mechanism of the formation of pyrolysis products is discussed below.

Considering the structure of the polymer and various backbone cleavage reactions involving different bonds, the expected cyclic products formed by backbiting are reported in Schemes 1–5. Comparing the schemes with the observed primary products in Table 1 it clearly turns out that Scheme 1 matches in totality with the observed product distribution. Hence, the initiation of degradation through formal C–O bond cleavage seems to be the most plausible mechanism operative in Thiokol LP. It may also be noted that, although cyclic products of differing ring sizes are obtained, all of them follow the same basic mechanism, i.e., random formal C–O bond cleavage followed by cyclization.

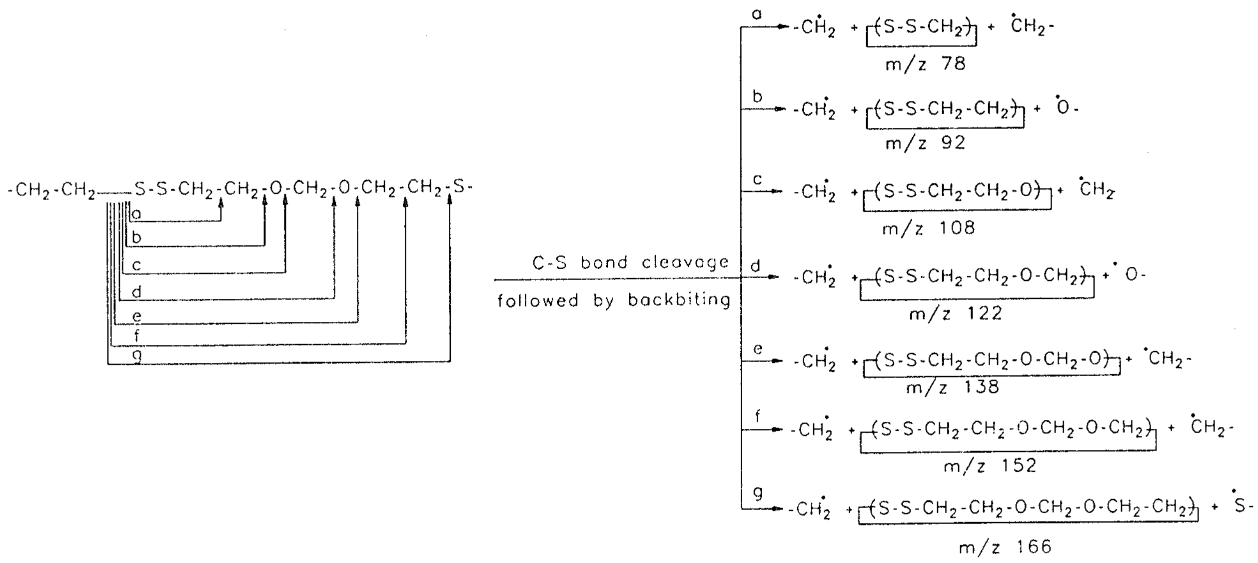
As to the formation of the cyclic monomer (*m/z* 166) by the thiol–disulfide interchange process, as proposed earlier (eq 1), it is most likely not the case since formation of this product can also be explained by formal C–O cleavage followed by cyclization (Scheme 1).

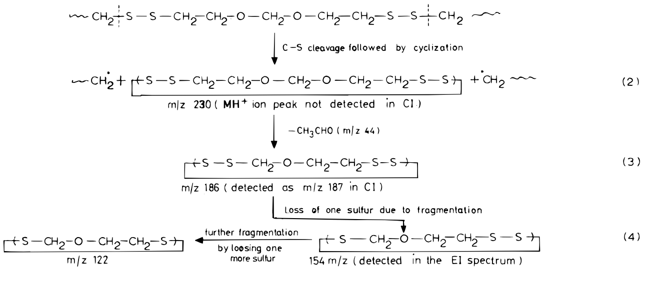
Schemes 1–5 do not explain the formation of the compound with *m/z* 186 (appearing at *m/z* 187 in the methane CI spectrum). We believe it could be a degradation product of the cyclic tetrasulfide (*m/z* 230) which may be formed from the breakage of C–S bonds followed by cyclization (eq 2). Although the correspond-

Scheme 3. Initiation of Degradation through C−C Bond Cleavage



Scheme 4. Initiation of Degradation through C−S Bond Cleavage





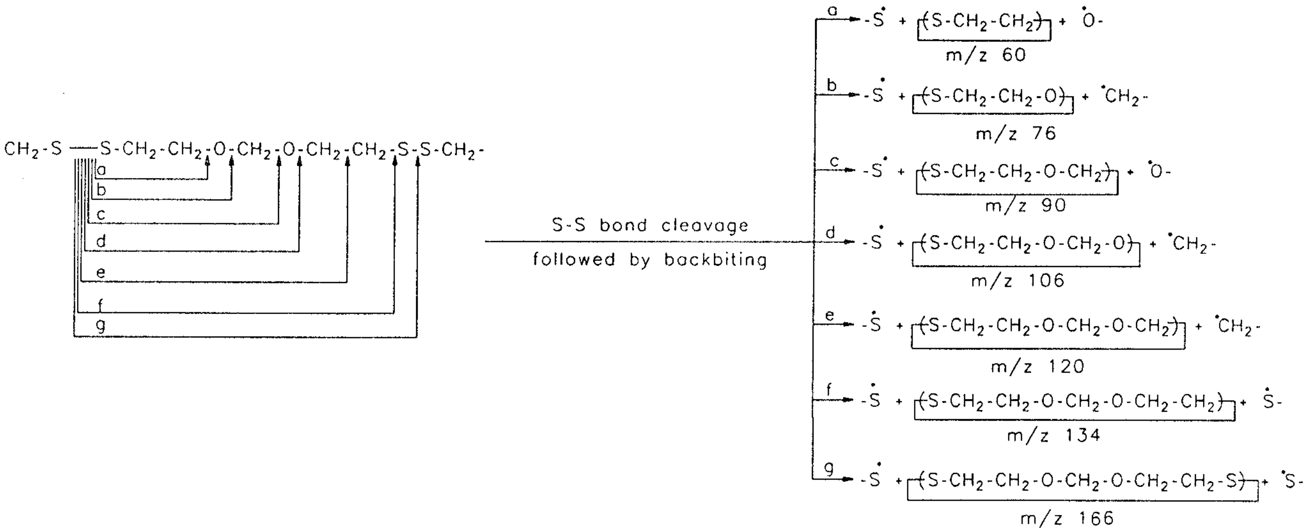
ing MH^+ ion peak is missing in the methane CI spectrum, the *m/z* 230 peak is present in the CI spectrum. This cyclic tetrasulfide (*m/z* 230) then undergoes decomposition with the loss of acetaldehyde (*m/z* 44), forming the cyclic tetrasulfide of *m/z* 186 (eq 3). Loss of one sulfur from this compound, due to fragmentation, leads to a cyclic trisulfide of *m/z* 154 (eq 4). The presence of a peak at *m/z* 154 in the EI spectrum is due to this fragmentation reaction. Subsequent loss of one more sulfur results in the cyclic disulfide of *m/z* 122 (eq 5).

Comparison between Ionic and Radical Mechanisms. In contrast to the single product observed in the distillation method[3] and the large number of products in the Py−GC−MS method[4] reported earlier, in the present work we obtain only eight products. We believe the discrepancy in the earlier reports is mostly due to the separation and the analysis of products; the distillation method seems to be crude. The large number of pyrolysis products observed in the Py−GC−MS analysis, as compared to the present work, is attributed to the secondary reactions of the primary pyrolysis products.

Conclusions

From the primary degradation products of Thiokol LP-33, it has been found that the degradation proceeds through a radical mechanism involving random cleavage of the formal C−O bond followed by backbiting to form the cyclic products.

Scheme 5. Initiation of Degradation through S−S Bond Cleavage



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References and Notes

(1) Foti, S.; Montaudo, G. In *Analysis of Polymer Systems*; Bark, L. S., Allen, N. S., Eds.; Applied Science: London, 1982; p 103 and references therein.

(2) Kishore, K.; Ganesh, K. *Adv. Polym. Sci.* **1995**, *121*, 81.

(3) Davis, F. O. U.S. Patent 2715635, 1955.

(4) Rama Rao, M.; Radhakrishnan, T. S. *J. Appl. Polym. Sci.* **1985**, *30*, 855.

(5) Kishore, K.; Ganesh, K. *Macromolecules* **1993**, *26*, 4700.

(6) Kishore, K.; Murthy, K. S. In *The Polymeric Materials Encyclopedia. Synthesis, Properties, and Applications*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, in press.

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