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Degradation Kinetics and Mechanisms of Polymers Using Thermal Spectrometric Techniques

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ABSTRACT

Techniques utilizing mass spectrometry, thermogravimetry, and gas chromatography in combination to study polymer degradation kinetics and mechanisms are described. The ability to observe volatile species generated under controlled thermal and environmental conditions and the simultaneous accumulation of weight loss data enables acquisition of both kinetic and mechanistic parameters in single run experiments. Polymer degradation mechanisms are best understood when initial oxidative sites can be established. Consequently, data points obtained with these techniques in conjunction with bulk phase analyses provide powerful tools for determining the primary reactions occurring during polymer oxidations.

INTRODUCTION

On-line monitoring of thermogravimetric analyzer effluents by mass spectrometry and gas chromatography provides a means for the

continuous analysis of polymer degradation products. Through identification of the volatiles generated and their order of evolution, mechanistic and kinetic data can be readily obtained. In conjunction with bulk phase analyses of the nonvolatile products, the degradation process can be elucidated. Three polymer systems, polymethylene sulfide, polystyrene, and poly-4-methylpentene, serve to illustrate how the technique can be applied.

EXPERIMENTAL

The thermogravimetric-mass spectrometric (TGA-MS) and thermogravimetric-gas chromatographic-mass spectrometric (TGA-GC-MS) analyses were run using procedures and instrumentation described previously [1-7]. All IR spectra were recorded with the Perkin-Elmer 521 grating spectrophotometer on compression molded films of from 2 to 5 mils thickness.

RESULTS AND DISCUSSION

Oxidation of Poly-4-methylpentene

Poly-4-methylpentene is a crystalline, saturated polyhydrocarbon with pendant isobutyl groups on alternate carbon atoms along the polymer chain. It is an interesting polymer structure because there are two potential oxidative sites, the tertiary carbon on the polymer backbone and the tertiary carbon in the isobutyl group. From structural considerations it would be difficult to predict which of the two potential sites would be more susceptible to oxidation because their electron environments are very similar.

Figure 1 shows the IR spectrum of pure isotactic poly-4-methylpentene. It can be seen that the spectrum is free of absorptions in the regions of interest, 1900 to 1600 cm^{-1} . Figure 2 shows the IR spectrum of a sample which has been degraded oxidatively for 2 hr at 190°C.

Four major differences can be observed:

1. The appearance of a band at 3500 cm^{-1} due to hydroxyl terminated linkages.
2. A triplet formation in the carbonyl stretching region, the principal carbonyl absorption being ketonic with underlying absorptions due to peracid, perester, and/or other carbonyl species.
3. A band ingrowth at 888 cm^{-1} due to substituted vinylidene double bonds which form concurrently with the carbonyl groups.
4. A general broadening of the spectrum, especially in the long wavelength regions, which is due to the overall degradation process and oxidative cross-linking.

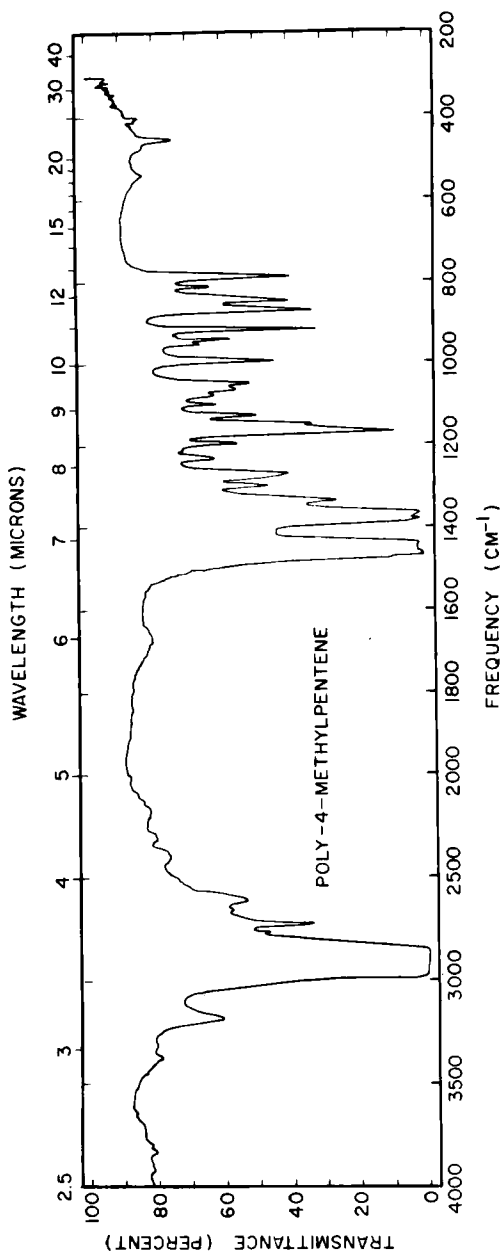


FIG. 1. IR spectrum of poly-4-methylpentene.

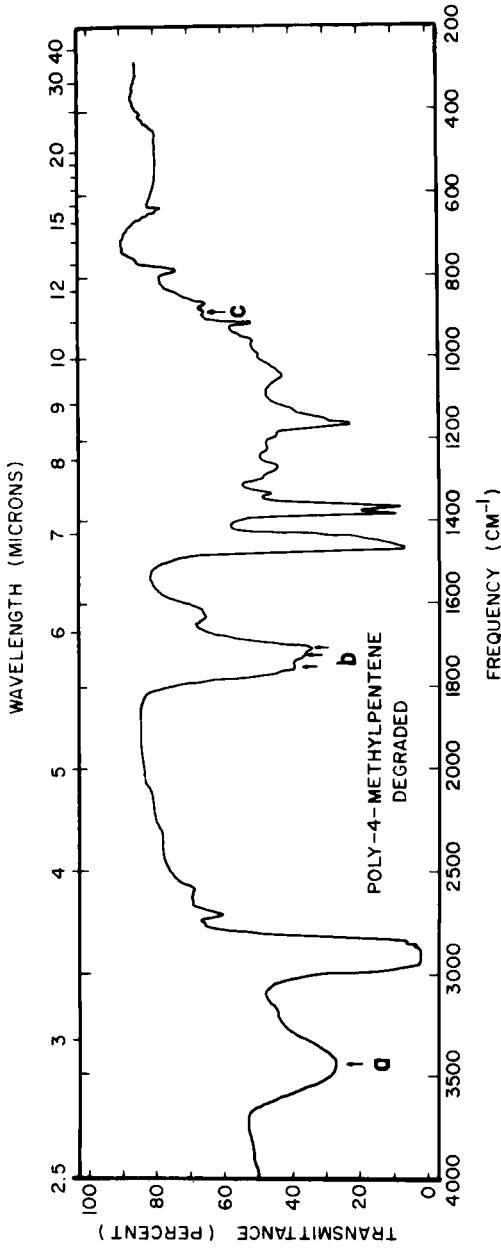


FIG. 2. IR spectrum of poly-4-methylpentene oxidized.

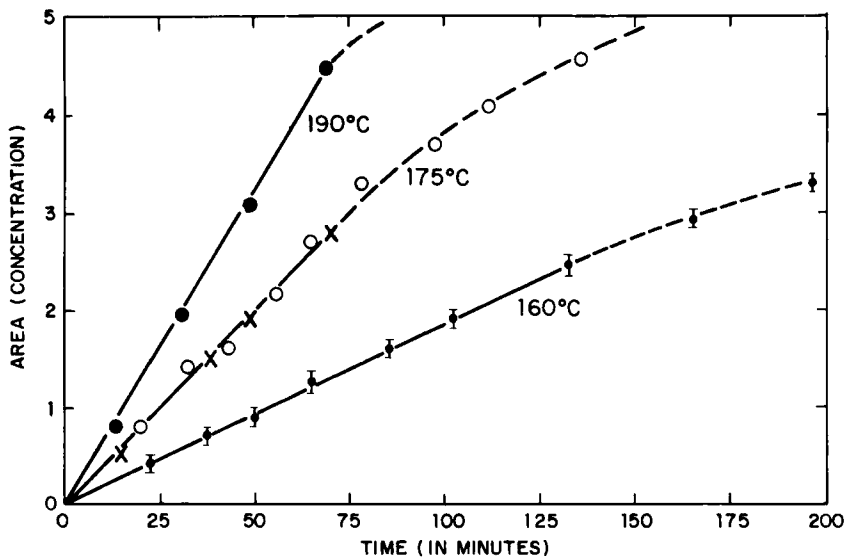


FIG. 3. Rate of total carbonyl ingrowth for poly-4-methylpentene (160-190°C).

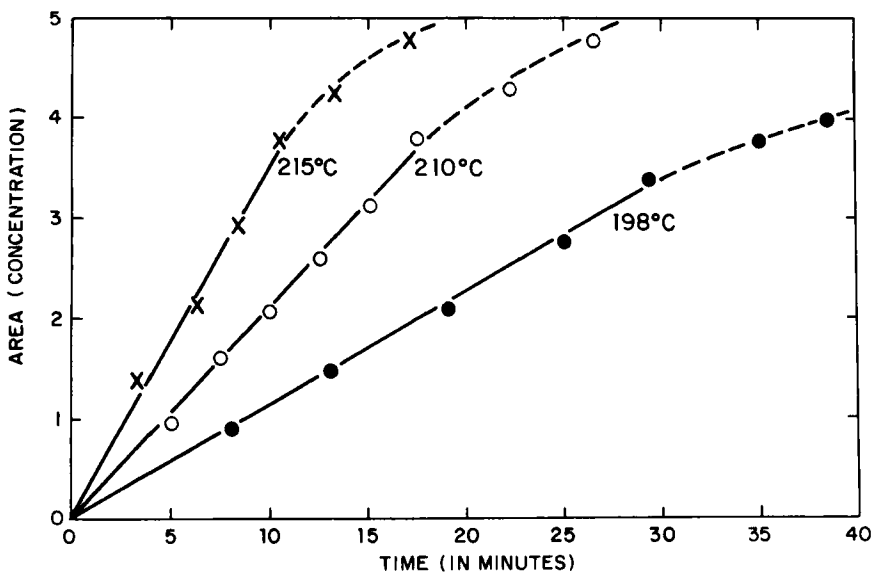


FIG. 4. Rate of total carbonyl ingrowth for poly-4-methylpentene (198-215°C).

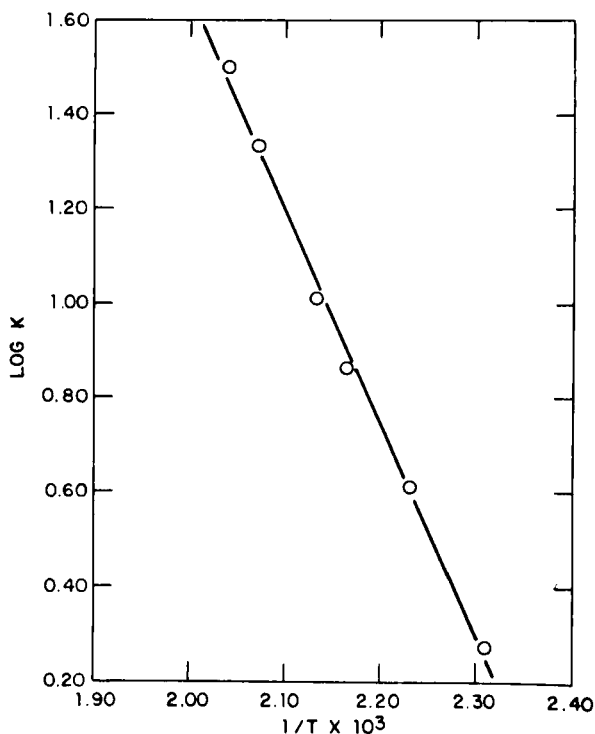


FIG. 5. Arrhenius plot from carbonyl ingrowth of poly-4-methylpentene. $E_A = 20.1$ kcal/mole.

From IR data it is possible to derive the kinetics of the degradation by measuring the rate of carbonyl ingrowth as a function of temperature because the sample thickness and molar absorptivity remain constant throughout the experiment. Consequently, the absorption band area is a direct measure of the concentration of carbonyl species. These data are shown in Figs. 3 and 4. An Arrhenius plot from which the activation energy for carbonyl formation was found to be 20.1 kcal/mole is shown in Fig. 5.

The mechanism of the degradation cannot be derived from this IR data because both oxidative sites would be expected to yield carbonyl and double bond structures subsequent to oxygen attack. Utilizing TGA-MS and TGA-GC-MS data, it is possible to determine both the kinetics and mechanisms of degradation. Fig. 6 shows the thermograms for isothermal degradations of this polymer in air between 160 and

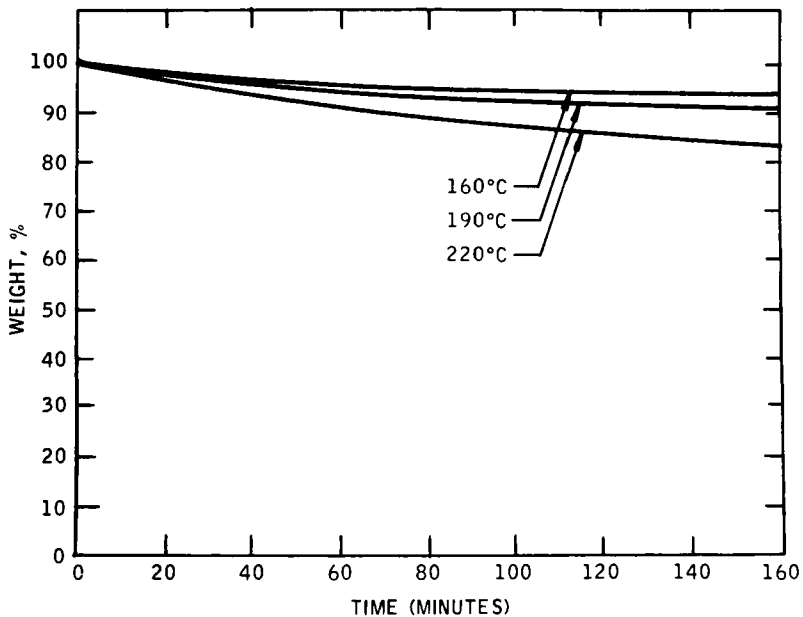


FIG. 6. Isothermal oxidative thermograms of poly-4-methylpentene.

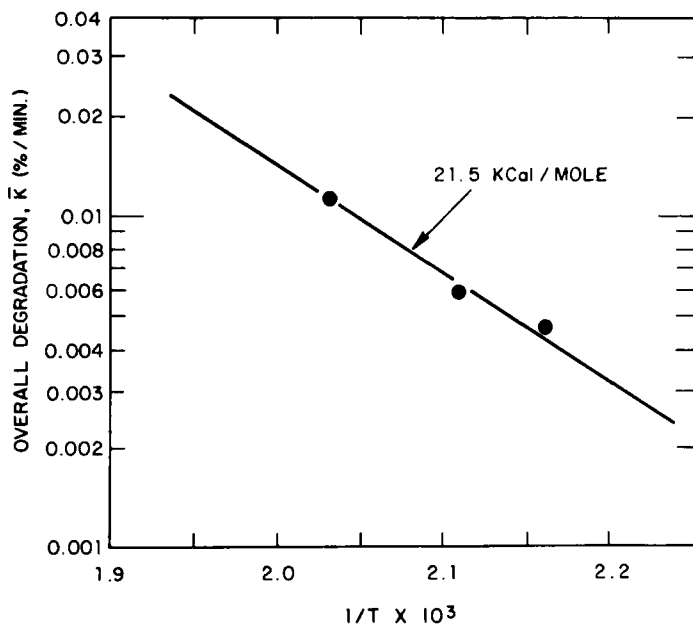


FIG. 7. Arrhenius plot from isothermal oxidative thermograms for poly-4-methylpentene.

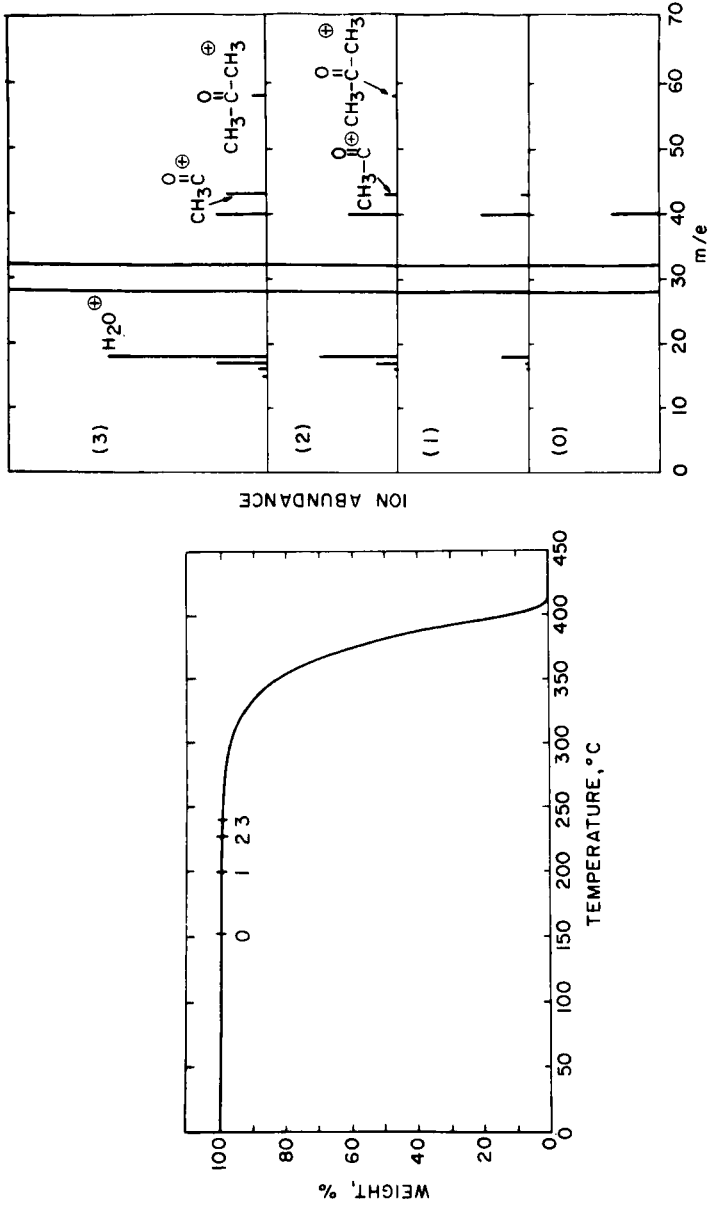


FIG. 8. TGA-MS analysis of poly-4-methylpentene in air.

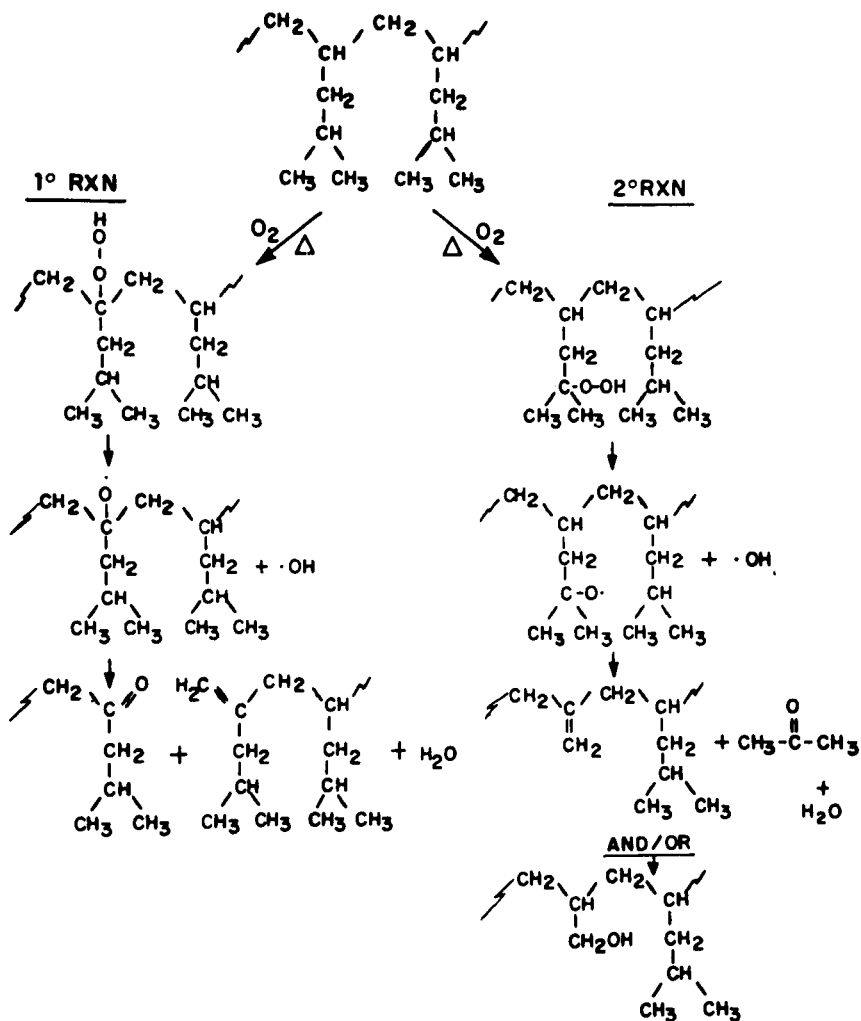


FIG. 9. Proposed mechanism for oxidative degradation of poly-4-methylpentene.

220°C. An Arrhenius plot constructed from this thermal data is shown in Fig. 7 where the activation energy for overall degradation is found to be 21.5 kcal/mole.

TGA-MS data are shown in Fig. 8. Mass spectra were recorded at Points 0 to 3 of the thermogram. Point 0 is the spectrum recorded

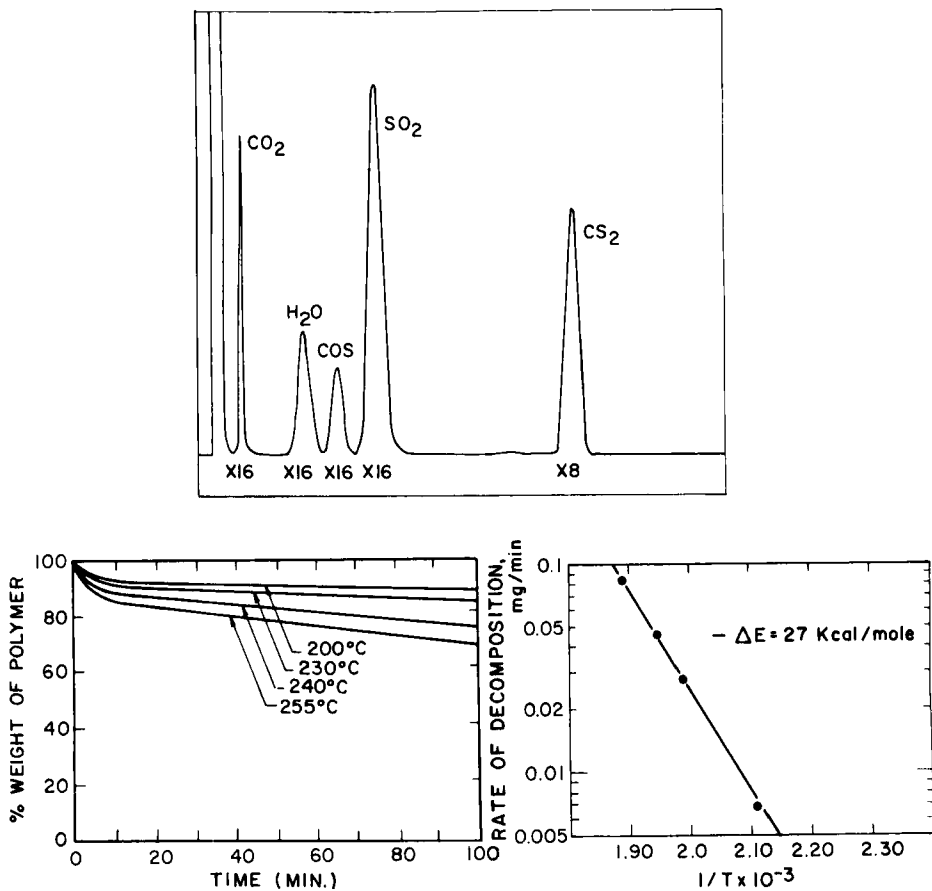


FIG. 10. Thermogram, Arrhenius plot, and chromatogram from thermal oxidation of polymethylene sulfide.

TABLE 1. Quantitative Analysis of Off-Gases

Component	Relative mole %
SO ₂	20
CS ₂	8
COS	13
H ₂ O	42
CO ₂	17

prior to degradation at 140°C and shows mass peaks associated primarily with the air background. The mass spectrum recorded at Point 1 corresponds to 200°C and shows, in addition to the background spectrum, peaks at m/e 18 and 43 due to the molecular ion of water and the acetyl ion from the fragmentation of acetone. Previous calibration established that the sensitivities of the two peaks are nearly identical. Hence, from the relative peak heights, a 3:1 mole ratio of water to acetone can be approximated. It is interesting to note that Spectrum 1 was obtained before a detectable weight loss was observed

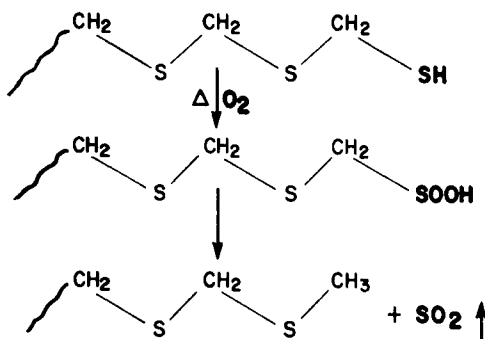


FIG. 11. Proposed mechanism for formation of sulfur dioxide through oxidation of ---SH end group in polymethylenesulfide.

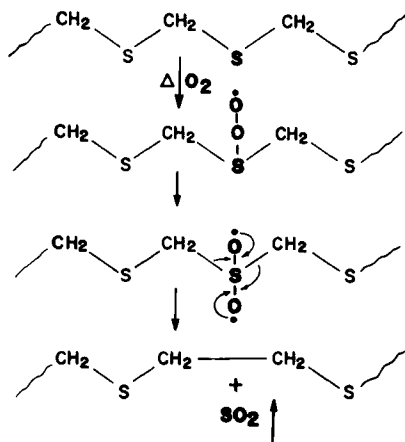


FIG. 12. Proposed mechanism for formation of sulfur dioxide through oxidation of sulfur atoms in polymethylenesulfide.

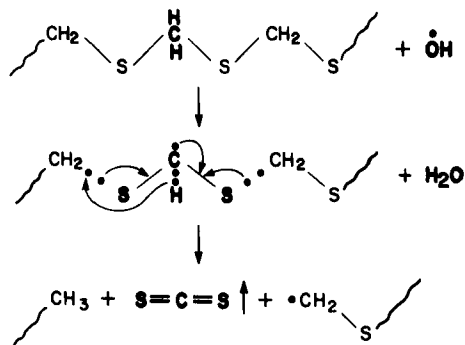


FIG. 13. Proposed mechanism for formation of carbon disulfide and water from degradation of polymethylene sulfide.

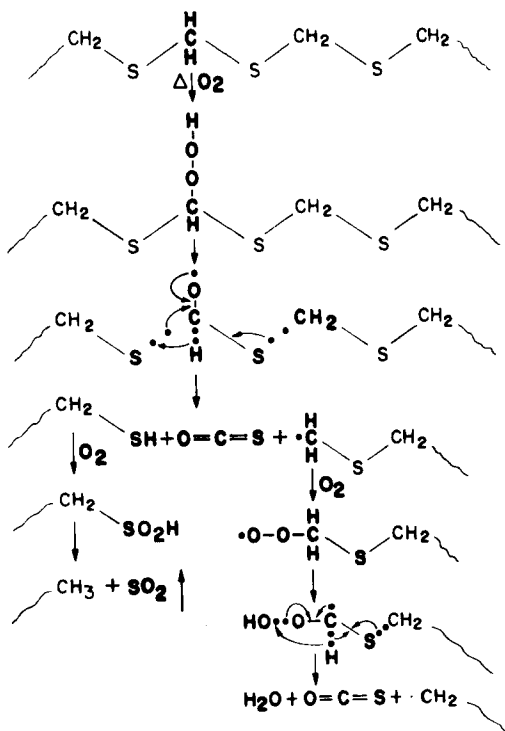


FIG. 14. Proposed mechanism for formation of carbonyl sulfide from degradation of polymethylene sulfide.

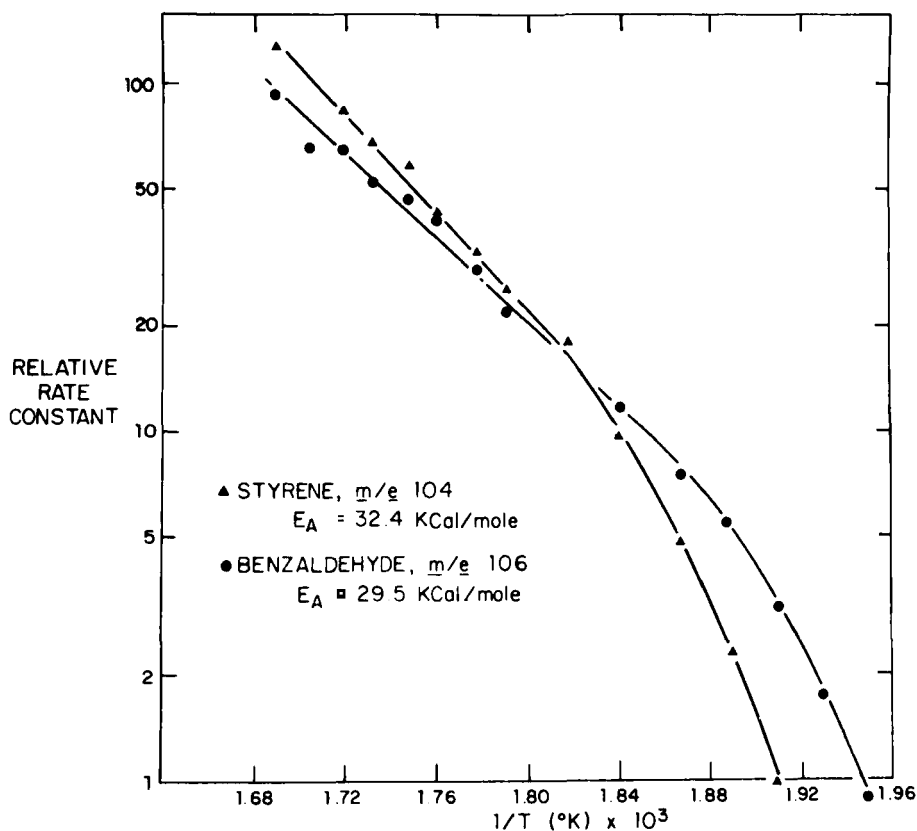


FIG. 15. Rate of formation of styrene and benzaldehyde from degradation of polystyrene.

on the thermogram. This is a good example of the rapid response and high sensitivity of the TGA-MS technique. Spectra 2 and 3, taken at 230 and 240°C, respectively, show the same 3:1 mole ratio of water to acetone. These two spectra also show the molecular ion of acetone at m/e 58 which is much less intense than the acetyl ion. During the later stages of oxidation, water, acetone, and some low molecular weight hydrocarbon fragments were evolved.

A TGA-GC-MS experiment to determine the quantitative ratio of water to acetone showed the ratio to be 3.2:1. This indicates that the relative susceptibility to oxidation of the tertiary carbon on the polymer backbone is 2.2 times greater than that of the tertiary carbon on the pendant isobutyl group. Based on these data, the proposed mechanisms for the degradation are shown in Fig. 9.

Polymethylene Sulfide

Polymethylene sulfide (PMS) is an interesting example of how these techniques can be utilized to supplement limited thermo-oxidative data obtained from other spectroscopic methods. IR spectra of PMS films oxidized for varying periods of time showed no significant changes in polymer structure during the initial stages of degradation. TGA-MS and TGA-GC-MS analysis of the degradation products yielded sufficient information to describe the thermo-oxidative behavior. Figure 10 shows an Arrhenius plot for the oxidation degradation kinetics derived from isothermal thermograms. TGA-MS analysis of the off-gases identified the major volatile components as water and sulfur dioxide. Lesser amounts of carbon disulfide, carbonyl sulfide, and carbon dioxide were also evolved. Quantitative analysis of the off-gases by TGA-GC-MS gave the results shown in Table 1. From these data a material balance of 0.9:2.0:1.2 for C:H:S in the polymer can be calculated. This ratio is in good agreement with the theoretical value of 1:2:1 anticipated for PMS, and indicates that the accountability is sufficient to propose the mechanisms in Figs. 11-14.

Under thermal conditions the only volatile components evolved were thioformaldehyde and trithiane (presumably from trimerization of thioformaldehyde), thus indicating that PMS degrades via depolymerization or unzipping following homolytic cleavage of a C-S bond.

Kinetic Expressions for Individual Reactions Occurring in Polymer Degradation

It is frequently of interest to determine the kinetics of individual reactions occurring during the degradation of polymer systems. TGA-MS can be used to accumulate this type of data, and polystyrene provides an interesting example. In the early stages of degradation, styrene monomer and benzaldehyde are evolved simultaneously. The individual rates of evolution can be obtained by plotting the molecular ion peak intensities (m/e) 104 and 106 as a function of temperature as shown in Fig. 15. From these data the activation energies for the formation of styrene and benzaldehyde under oxidative conditions can be calculated from the Arrhenius equation as 32.4 and 29.5 kcal/mole, respectively. It is interesting to note the dependence of the degradation rate constant with temperature as illustrated in the curves shown in Fig. 15.

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