

Photolytic Degradation of Some Poly(alkylene Polysulfides)*

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Synopsis

Poly(methylene disulfide), poly(methylene tetrasulfide), poly(ethylene disulfide), and poly(ethylene tetrasulfide) have been subjected to ultraviolet radiation in vacuum at 50°C. Weight losses during photolysis include both low molecular weight compounds and readily condensable polymeric materials; the latter account for the greater proportion of the weight losses. Carbon monosulfide, isolated as its polymer, and hydrogen sulfide are major photolytic products. Carbon disulfide is a major product from the methylene but not from the ethylene polymers. The tetrasulfide polymers during irradiation form volatile products which on condensation give the original polymer. A mechanism of degradation compatible with these findings is suggested.

INTRODUCTION

Polymers which undergo rapid degradation under ultraviolet irradiation in vacuum are of interest in certain aspects of the space program. In view of the known photoinstability of the sulfur-sulfur bond¹ and the absorption maxima² of disulfide and tetrasulfide linkages at 258 and 286 m μ , respectively, poly(alkylene polysulfides) might be expected to qualify even though such polymers are quite stable under terrestrial conditions.³ A preliminary study indicated that, in terms of weight loss per unit area of exposed surface, polysulfides degraded an order of magnitude faster than polymers such as poly(methyl methacrylate), poly(*n*-butyl methacrylate), or chlorinated polyisobutylene. A detailed investigation of the photodegradation of four poly(alkylene polysulfides) in vacuum at 50°C. was therefore undertaken; the results are reported herein.

EXPERIMENTAL

Materials

Poly(methylene disulfide) (PMDS), poly(methylene tetrasulfide) (PMTS), poly(ethylene disulfide) (PEDS), and poly(ethylene tetrasulfide)

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(PETS) were synthesized by the method of Sorenson and Campbell⁴ from the appropriate dichloroalkanes and an aqueous sodium di- or tetrasulfide solution. The polymers, after being washed with hot water and dried under vacuum, were milled at room temperature into sheets 5–20 mils thick.

Apparatus

The samples were exposed in a quartz cell connected to a vacuum system by a flange sealed with Apiezon-W wax. A multistage oil-diffusion pump backed by a mechanical fore-pump provided pressures of less than 10^{-4} torr. The cell was located 10 cm. from a medium-pressure mercury lamp (General Electric UA-3); incident energy at the sample was about 3×10^{14} quanta/sec.-cm.² in the 2000–4000 Å. range. Temperatures within the cell during the irradiation were $50 \pm 2^\circ\text{C}$. as determined with an iron-constantan thermocouple. A Consolidated Engineering Corp. Model 21-620 mass spectrometer was used in the identification and measurement of volatile products.

Procedure

Polymer sheets of known area and weight were clamped to a supporting quartz plate and placed within the cell; the cell was connected to the system and evacuated continuously during exposures. At appropriate intervals volatile products were condensed in a cold trap with liquid nitrogen; between these collection periods the volatile products were exhausted through the pump. Removal of the gases through the pump had no observable effect on the vacuum which was obtained. The exposures were interrupted to allow the transfer of volatile compounds to a small removable trap for analysis. The irradiation was then continued and volatile products were again condensed. After a suitable length of exposure, the cell was opened and the polymer reweighed. Further exposures of the same sample were made as desired.

Volatile products were separated in a gas chromatograph with a 12-ft. Ucon 50HB-2000 column operated at 100°C . The individual components were identified and determined quantitatively in the mass spectrometer. The procedure and fraction collector have been described by Saunders.⁵

RESULTS AND DISCUSSION

Weight Loss

The rates of weight loss of the four poly(alkylene polysulfides) are shown in Figure 1. Since the thicknesses of the exposed sheets varied from one sample to another and the incident radiation was entirely absorbed in the surface layers of the sample, the results are given in terms of weight loss per unit area of exposed surface, rather than as per cent weight

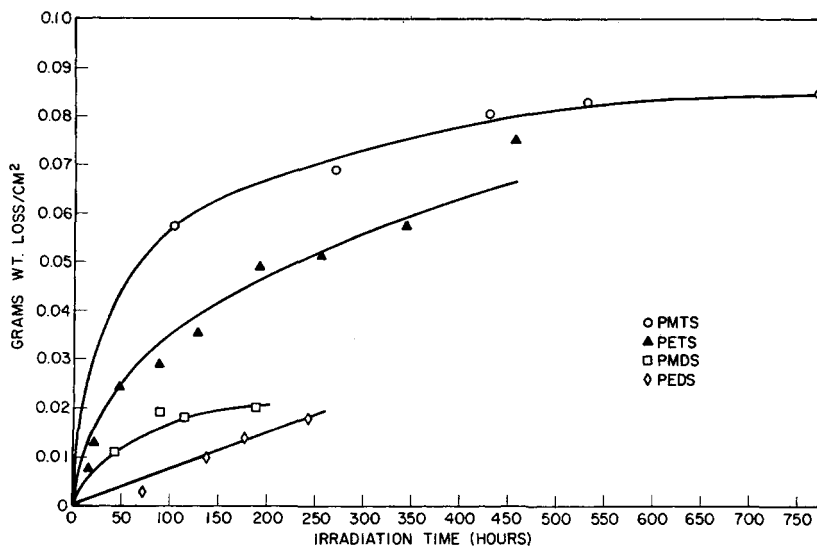


Fig. 1. Weight loss per square centimeter of exposed surface against hours of irradiation.

loss. However, the highest points on the curves for PMTS and PETS represent weight losses of 80 and 51%, respectively, for the particular polymer samples from which the data were obtained. Tetrasulfide polymers had higher rates of degradation than the disulfide polymers, and each methylene polysulfide had a higher rate of degradation than the corresponding ethylene polysulfide.

It is evident that a decrease in rates of weight loss with time has occurred. As the irradiation proceeds, considerable embrittlement with cracking and curling of the sample takes place. Therefore, the average absorbed intensity of radiation will tend to decrease in exposures greater than about 100 hr. It is also possible that consumption of more photolabile structures in the early stages of irradiation may result in changes in the rates of evolution of volatile materials as well as in the composition of the exposed sample surfaces. The infrared spectra of degraded and undegraded material were indistinguishable, however. A degraded sample of PETS which had been remilled and exposed gave a weight loss curve similar to that of the original material.

Degradation Products

Two types of degradation products were encountered during the photolysis of the polysulfides: (a) low molecular weight volatile compounds and (b) solid polymeric materials.

Volatile Compounds. The volatile products found in the photolysis of the polysulfide samples are listed in Table I. The products were classified as major or minor on the basis of the mass spectra. Pure samples of methanethiol, thioformaldehyde, and thioacetaldehyde were not available

TABLE I
Volatile Photolysis Products

Polymer	Major products	Minor products
PMDS and PMTS	H ₂ S, CS ₂	CH ₃ SH, HCHS
PEDS and PETS	H ₂ S	CS ₂ , CH ₃ CHS

to determine the sensitivity of the mass spectrometer to these compounds. However, in each mass spectrum, the total peak heights of the base peaks of each of the minor constituents were less than 10% of the peak heights of the base peaks of the major constituents. Traces of water and carbon dioxide were found with the volatile products. Extremely long evacuation periods before irradiation reduced the total quantities of water and carbon dioxide, indicating that they were not formed by photolytic reactions.

The major products, carbon disulfide and hydrogen sulfide, were formed by second-order reactions as shown in Figures 2 and 3. With carbon disulfide, particularly, there was an initial increase in the rate of formation. This initial increase may occur during the attainment of thermal equilibrium or may possibly be due to unidentified absorbing surface impurities consumed during the early stages of irradiation. The effect of an absorbing impurity would be to reduce the intensity of radiation giving rise to the measured products.

While hydrogen sulfide was evolved during the photolysis of all four polymers, the largest amounts were obtained from the methylene polymers. Correspondingly, carbon disulfide was a major product of the methylene polymers only; the ethylene polymers yielded only traces of carbon disulfide. The source of these compounds is related to that of the polymeric products and will therefore be discussed below.

Polymeric Products. In Table II, the weight of each major volatile compound, calculated from the total pressure of each gas developed during the entire exposure, is compared to the total weight lost by the sample during that exposure. It is apparent from the data in the last column that the products collected in the liquid-nitrogen trap account for less than half the observed weight losses. The remainder of the weight loss is primarily

TABLE II
Comparison of Volatile Product Weights with Total Weight Losses

Polysulfide	Total weight loss, g.	Product	Major volatile products	
			Weight, g.	% of total weight loss
PMDS	0.0592	H ₂ S	0.0049	40.9
		CS ₂	0.0193	
PMTS	0.9157	H ₂ S	0.1110	38.8
		CS ₂	0.2439	
PEDS	0.0345	H ₂ S	0.0075	21.8
PETS	0.2994	H ₂ S	0.0195	6.5

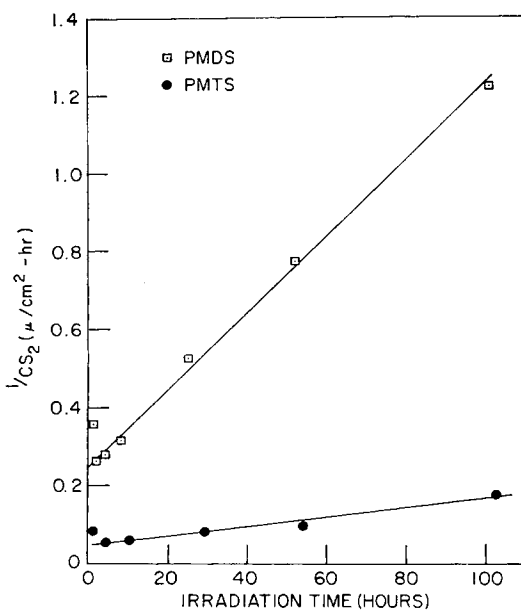


Fig. 2. Second-order plot of carbon disulfide formation.

due to materials formed from substances which volatilized from the polysulfide samples and condensed on the cell walls.

One of these materials was a polymer of carbon monosulfide which appeared only on surfaces within the cell which were exposed to ultraviolet radiation. The other materials were light-yellow, rubbery films which were deposited on the cell walls outside the irradiation zone only during photolysis of the poly(alkylene tetrasulfides). The higher rates of weight loss of the tetrasulfide polymers, compared to the disulfides (Fig. 1), are attributed to formation of these films. Comparison of infrared spectra of the light-yellow films showed them to be identical to the poly(alkylene tetrasulfide) from which each was produced. The most plausible explanation for the formation of these films is that the tetrasulfide polymers upon irradiation in vacuum form reactive species which are sufficiently volatile to travel the short distance to the cell wall, where they react to reform the original tetrasulfide. It is possible that the films are formed from short polymer chains which are volatilized by the heat of the lamp; such volatilization may be enhanced by the photodegradation of the polymer surface. However, it is unlikely that chains short enough to be volatile would constitute such large percentages of the tetrasulfide polymers and not of the disulfides, which were prepared by the same synthetic method and should have comparable molecular weights.

Since the disulfide polymers did not form light-yellow films, the two central sulfur atoms of the tetrasulfide linkages must be involved. The reactive intermediates may be diradical species such as $\text{SSCH}_2\text{CH}_2\text{SS}$ and

SSCH_2SS or their heterocyclic intramolecular combination products. To produce such species, two scissions of the polymer chain are required. The product of the first scission must be sufficiently stable to exist until the next scission occurs; such stability may be imparted through a three-electron bond as proposed by Owen, MacKnight, and Tobolsky.⁶

Interrupting the exposures and cleaning the cell at frequent intervals showed that most of the light-yellow film formation took place in the first 200 hr. of exposure. The eventual retardation of this phenomenon may be the result of exhaustion of most of the tetrasulfide linkages on the sample

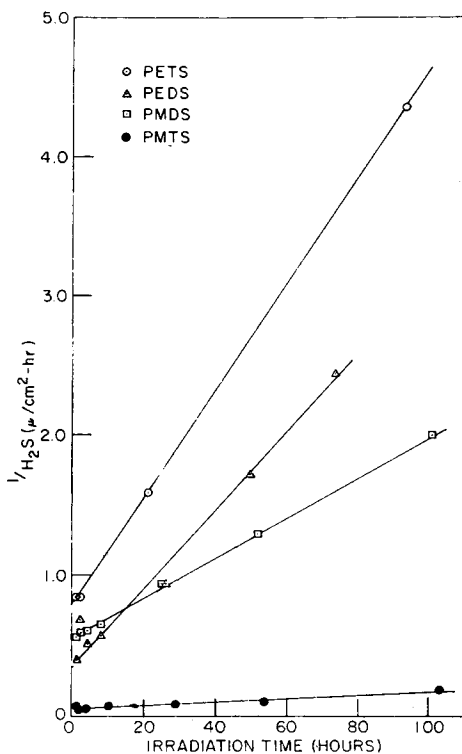


Fig. 3. Second-order plot of hydrogen sulfide formation.

surface. Polysulfides have some distribution in the number of sulfur atoms in the sulfide linkages,⁷ and thus a polysulfide which by synthesis should be a tetrasulfide will actually contain some trisulfide and pentasulfide linkages. If these assumptions are correct, the surface eventually contains mostly linkages of fewer than four sulfur atoms, and other reactions which expose fresh tetrasulfide linkages on the sample surface become the rate-controlling reactions in production of the light-yellow film. The reduction in rate of light-yellow film formation is probably responsible for a large part of the decreasing rate of weight loss (Fig. 1) for the tetrasulfide polymers.

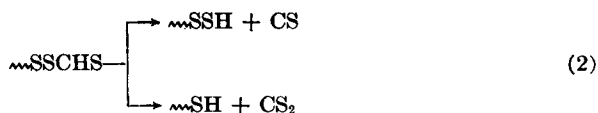
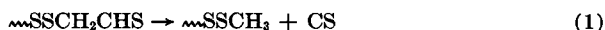
A brown film of polymerized carbon monosulfide was deposited on the walls of the cell during photolysis of each of the poly(alkylene polysulfides). Visual observation indicated that polymerized carbon monosulfide was deposited at a slower rate by the methylene polysulfides than by equal-sized samples of the ethylene polysulfides. The identity of the film was established by comparison of its infrared spectrum with that of a sample of polymerized carbon monosulfide prepared by photolyzing carbon disulfide in the absence of air.^{8,9} The carbon monosulfide initially formed polymerizes to an insoluble brown material upon condensation¹⁰ or by a wall reaction.¹¹

Under the usual exposure conditions, carbon monosulfide or its polymer did not condense on unexposed cell walls or in the liquid-nitrogen-cooled traps, showing that photoinitiated polymerization of this compound was complete within the irradiation zone. Some exposures were made with the cell covered with aluminum foil except for a small opening in front of the polysulfide sheet. This arrangement permitted ultraviolet radiation to strike the polymer sample, but reduced the area of the cell walls exposed to ultraviolet light by about 90%. Carbon monosulfide did not polymerize on the surfaces which were shielded from ultraviolet light. Instead, most of the carbon monosulfide passed out of the cell and was condensed by liquid nitrogen in the cold trap where it subsequently polymerized. Spectroscopic examination showed this material to be identical to polymerized carbon monosulfide obtained from the cell walls.

In these exposures the ratios of carbon disulfide to hydrogen sulfide were unchanged from exposures in which the cell was not shielded. This shows that carbon monosulfide is a direct photolytic product of the poly(alkylene polysulfides) and does not result from secondary photolysis of carbon disulfide. Further evidence for this conclusion is found in the photolysis of the poly(methylene polysulfides), which yielded about 100 times more carbon disulfide than did the poly(ethylene polysulfides), but deposited poly(carbon monosulfide) at a slower rate.

Mechanism

Wherever alkylthio radicals can form, as is surely the case with the irradiated disulfides and is likely to be the case for the tetrasulfides, the termination of the radicals would be expected¹² to result in the formation of fragments having thiol and thione endgroups. Photolysis of the thione should yield carbon monosulfide by analogy to the photolysis of aldehydes, although this reaction must compete with carbon disulfide formation from the methylene polymers [eqs. (1) and (2)].



The fact that carbon disulfide was observed as a major product only during photolysis of the methylene polymers and that the yields of carbon monosulfide from these polymers were relatively small indicates that the above reactions are reasonable.

Hydrogen sulfide may form, along with olefin, as the result of the photolysis of the polymer-thiol fragment.¹³ Any reaction which could lead to a mercapto radical could also be responsible for the hydrogen sulfide formation.

Although direct measurements were not made of the rates of formation of either of the solid polymeric products, it is clear that both carbon disulfide and hydrogen sulfide are the products of second-order reactions. Generally, it has been found that the volatile photodegradation products from polymers are dependent on the total radiation absorbed or on the intensity of that radiation. Intensity effects were not determined, but the second-order rates for carbon disulfide and hydrogen sulfide can be explained on the basis of such effects or on the basis of the above reactions, which are probably dependent on both intensity and scission-product concentrations.

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Résumé

Le disulfure de polyméthylène, le tétrasulfure de polyméthylène, le sulfure de polyéthylène et le tétrasulfure de polyéthylène ont été soumis à une irradiation ultraviolette à 50°C sous vide. Les pertes en poids subies pendant la photolyse comprennent des composés de bas poids moléculaire et de matériaux polymériques facilement condensables; ceux-ci sont responsables de la plus grande perte en poids. Le monosulfure de carbone, isolé sous forme de polymère et l'acide sulfhydrique sont les principaux pro-

duits photolytiques. Le disulfure de carbone est un produit prépondérant dans le cas des polyméthylènes mais pas dans celui des polyéthylènes. Les polymères tétrasulfurés forment lors de l'irradiation, des produits volatils qui, par condensation, régénèrent le polymère initial. Un mécanisme de dégradation, en accord avec ces résultats, est proposés.

Zusammenfassung

Poly(methylenedisulfid), Poly(methylenetetrasulfid), Poly(äthylendisulfid) und Poly(äthylentetrasulfid) wurden einer Ultraviolettbestrahlung in Vakuum bei 50°C unterworfen. Die Gewichtsverluste während der Photolyse betreffen sowohl niedermolekulare Verbindungen als auch leicht kondensierbare polymere Stoffe; letztere liefern den grösseren Beitrag zum Gewichtsverlust. Kohlenstoffmonosulfid, als Polymeres isoliert, und Schwefelwasserstoff sind die Hauptprodukte der Photolyse. Schwefelkohlenstoff ist ein Hauptprodukt aus den Methylen-, aber nicht aus den Äthylgruppenpolymeren. Die Tetrasulfidpolymeren bilden während der Bestrahlung flüchtige Produkte, welche bei der Kondensation wieder das ursprüngliche Polymere bilden. Ein mit diesen Befunden vereinbarer Abbaumechanismus wird angegeben.

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