

# Photodegradation of High Polymers

## Part V - Photolysis of Poly (Alkylene Polysulfides) in Vacuum

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"Part III -- Photolysis of Poly(Methyl Methacrylate) in Vacuum and in Air," R. B. Fox, L. G. Isaacs, Suzanne Stokes, and L. W. Daasch, NRL Report 5720, Dec. 14, 1961

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## ABSTRACT

The rates of weight loss of several poly(alkylene polysulfides) during exposure to a simulated space environment were measured and compared to the rates of weight loss of several nonsulfur containing polymers. The products of degradation of poly(methylene disulfide and tetrasulfide) and poly(ethylene disulfide and tetrasulfide) were identified and gaseous products were quantitatively measured. The major products of degradation were hydrogen sulfide, carbon monosulfide (which polymerizes on surfaces within the exposure cell), and, for the methylene polymers, carbon disulfide. The tetrasulfide polymers deposited a rubbery film on the walls of the exposure cell which was spectroscopically identical to the exposed poly(alkylene tetrasulfide). A mechanism of degradation compatible with these results is suggested.

## PROBLEM STATUS

This is an interim report; work on the problem is continuing.

## AUTHORIZATION

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# PHOTODEGRADATION OF HIGH POLYMERS

## PART V -- PHOTOLYSIS OF POLY(ALKYLENE POLYSULFIDES) IN VACUUM

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### INTRODUCTION

The passive communication satellites (Echo) which have been placed in orbit are hollow spheres consisting of a thin aluminum film reinforced by a polymer. The satellites were ejected from rockets in space as uninflated balloons. In the vacuum of space, residual gases within the balloon quickly expanded the satellite into the desired spherical shape. Unfortunately, while the satellites have been in orbit, the pressure of solar radiation has caused partial collapse of the spheres, which has resulted in serious losses in reflectivity and unpredictable changes in orbit. Difficulties from solar pressure are expected to be even greater with the larger satellites that are now being planned, and must be overcome before a worldwide system of passive communication satellites can function properly.

An aluminum mesh, which presents a smaller surface area to solar pressure, can be substituted for the aluminum sheet without seriously changing the reflective properties of the balloon. However, the mesh must be incorporated with a plastic film which forms a continuous surface so that a satellite made from the mesh can be inflated. After the balloon is inflated in space, it is desired that this film be removed to minimize distortion of the sphere by solar pressure. Solar radiation is the most convenient source of energy for the removal of this film.

A deductive approach was used with the intention of finding a material with photolytically weak links in the polymer backbone which will undergo reactions yielding gaseous products in a simulated space environment. Several commercially available polymers of widely varying structure and poly(alkylene polysulfides) were evaluated. The poly(alkylene polysulfides) were expected to meet the above requirements since they contain readily photolyzable sulfur-sulfur bonds which are also strong absorbers of the higher wavelengths of ultraviolet radiation.

### MATERIALS

Poly(alkylene polysulfides) were synthesized by the method of Sorenson and Campbell (1) from the appropriate dichloroalkanes and an aqueous sodium disulfide or tetrasulfide solution prepared by heating sodium sulfide and sulfur. Poly(alkylene polysulfides) prepared by this method are linear polymers with hydroxy endgroups which are formed by displacement of chlorine by hydroxyl ions present in the basic solutions. These polymers were swollen by, or slightly soluble in aromatic hydrocarbons, N,N-dimethylformamide, and chlorinated hydrocarbons, and were degraded by strong bases or oxidizing acids. The poly(alkylene polysulfides) which were synthesized are listed in Table 1.

Except for PTMDS, these materials were milled at room temperature into 5 to 20 mil sheets of raw rubber. Some of the polymers were also pressed into disks with a Carver press. A standard curing recipe (2) was used to increase the tensile strengths of PETS and PTMDS in certain experiments; to 100 parts of the poly(alkylene polysulfide)

Table 1  
Synthesized Poly(Alkylene Polysulfides)

Polymer	Repeating Unit	Abbreviation
Poly(methylene disulfide)	$\sim\text{CH}_2\text{SS}\sim$	PMDS
Poly(methylene tetrasulfide)	$\sim\text{CH}_2\text{SSSS}\sim$	PMTS
Poly(ethylene disulfide)	$\sim\text{CH}_2\text{CH}_2\text{SS}\sim$	PEDS
Poly(ethylene tetrasulfide)	$\sim\text{CH}_2\text{CH}_2\text{SSSS}\sim$	PETS
Poly(trimethylene disulfide)	$\sim\text{CH}_2\text{CH}_2\text{CH}_2\text{SS}\sim$	PTMDS

were added 50 parts carbon black, 10 parts zinc oxide, 0.5 parts stearic acid, 0.3 parts benzothiazyl disulfide, and 0.1 parts diphenylguanidine. The mixtures were milled at room temperature into 10 to 20 mil sheets.

A liquid polymer designated as LP-2 was obtained from Thiokol Chemical Corp. This polymer has the repeating unit  $\sim\text{CH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2\text{SS}\sim$  with thiol endgroups and has a molecular weight of about 4000. A mixture of 85 g of LP-2 and 15 g of Thiokol Chemical Corp. C-5 Accelerator (a mixture of 50% lead dioxide, 5% stearic acid, and 45% dibutyl phthalate) was poured onto a sheet of 1/8-inch-square grid mesh made from 3-mil aluminum wire. This mesh is one of the materials proposed for use in future passive communication satellites. The mesh and the liquid mixture were pressed into a thin layer between glass plates and allowed to cure for 24 hours at room temperature to give a strong flexible sheet.

The FA-3000 Thiokol rubber was obtained from Thiokol Chemical Corp. as a 20-mil cured sheet. It is a disulfide copolymer prepared from bis(2-chloroethoxy)methane and 1,2-dichloroethane.

Poly(n-butyl methacrylate) was prepared by heating the purified monomer with 0.05%  $\alpha,\alpha'$ -azobisisobutyronitrile at 60°C; the polymer was purified by precipitating it several times from tetrahydrofuran solution with methanol. Poly(n-butyl methacrylate) films were prepared by the slow evaporation of methylene chloride solutions of the polymer.

The other polymers which were evaluated were sheets of commercially available materials.

## APPARATUS

Samples were exposed in a quartz irradiation cell connected to a vacuum system by a flange sealed with Apiezon W wax (Fig. 1). Multistage oil diffusion pumps backed by a mechanical forepump provided pressures less than  $10^{-5}$  torr. The cell was located 10 cm from a medium pressure mercury lamp (General Electric UA-3); incident energy at the sample was about  $3 \times 10^{14}$  quanta/sec-cm<sup>2</sup> in the 2000A to 4000A range. Temperatures within the cell were about 35°C, as measured by suspending a thermometer within the cell. A mass spectrometer (Consolidated Engineering Corp., Model 21-620) and a gas chromatograph (Beckman GC-2) were used to identify and measure volatile products. An infrared spectrometer (Beckman IR-5) was employed to identify solid materials and to observe changes in the residual polymers.

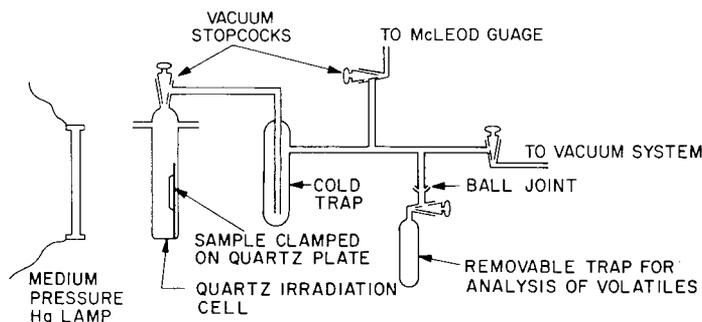


Fig. 1 - Irradiation apparatus

## EXPERIMENTAL PROCEDURE

Polymer sheets of known area and weight were clamped to a supporting quartz plate and placed in the cell. A typical sample had an area of 16 cm<sup>2</sup> and weighed 0.5 g. The clamps were attached so that a minimum area of the sheet was covered by the clamp. The Pyrex top of the irradiation cell was sealed to the quartz portion with Apiezon W wax and the cell evacuated, generally to less than 10<sup>-5</sup> torr. Some exposures were made at pressures up to 10<sup>-3</sup> torr to ascertain the effects of pressure on degradation rates. During the exposures the cell was continuously evacuated to remove volatile products as rapidly as possible.

Volatile degradation products were collected and analyzed only for the uncured sheets of PMDS, PMTS, PEDS, and PETS. These polymers were irradiated about 100 hours. At appropriate intervals volatile products were condensed in a liquid-nitrogen-cooled trap for one-half to three hour periods; between collection periods volatiles were removed through the pump. The exposure was interrupted while the volatile products were transferred to the smaller removable trap (Fig. 1) for analysis. The irradiation was continued and volatile products were again trapped when desired.

In some cases the mixtures of volatile products were separated into individual components in a gas chromatograph prior to identification by mass spectrometric methods. The procedure and the fraction collector have been described by Saunders (3). Once the identity of each volatile product of photolysis of a given poly(alkylene polysulfide) had been established, quantitative measurements of the products were made from the mass spectra.

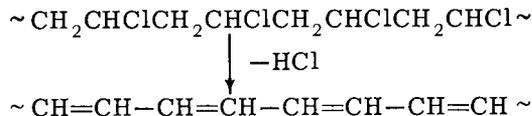
After a suitable length of exposure, the cell was opened and the polymer was reweighed to determine weight losses. Further exposures of the same sample were made as desired.

Carbon disulfide was photolyzed in order to prepare an authentic sample of polymerized carbon monosulfide (4,5). About 20 ml of carbon disulfide was placed in the irradiation cell, the cell was evacuated to remove air, sealed, and exposed to the ultraviolet source for two days. The dark brown deposit of poly(carbon monosulfide) was washed with more carbon disulfide to remove sulfur which was also a photolytic product.

## WEIGHT LOSSES

In order to photodegrade to gaseous compounds, a polymer molecule must be converted by ultraviolet energy into molecules small enough to be volatile at the conditions of exposure. The backbone of the polymer must cleave during the process or this part of

the polymer will remain intact and constitute a nonablative residue. A high initial rate of weight loss for a given polymer does not necessarily mean that the polymer will eventually degrade completely to gaseous compounds. For example, the chlorine atoms in poly(vinyl chloride) constitute over half the weight of this polymer. Elimination of hydrogen chloride



could theoretically lead to more than a 50% weight loss, but this process would not remove a film of this material since the backbone of the polymer is still intact. In fact, in the example above, crosslinking of polymer chains via the double bonds that are formed would probably yield an intractable residue that would be even less likely to degrade to gaseous compounds.

Since the density and thickness of the polymer sheets varied with the sample, the rates of degradation of different polymers were compared on the basis of rate of weight loss per unit area of exposed surface rather than as percentage weight loss based on the original weight of the sample. Weight loss is the result of various reactions occurring in the sheet and is independent of the thickness of the sheet if all the light incidence to the surface is absorbed.

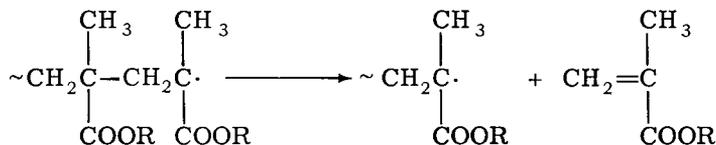
The rates of degradation of the polymers which were evaluated in this study are listed in Table 2. It should be noted that the rates of degradation of these polymers are probably not linear with time, but tend to decrease with increasing radiation dose. Since the initial rates of weight loss of the nonsulfur containing polymers were considerably lower than the rates of the poly(alkylene polysulfides), these polymers were not extensively investigated. However, poly(n-butyl methacrylate) was exposed a sufficient length of time to establish that the rate of degradation decreased with increasing radiation dose. After about 75 to 100 hours of exposure, the rate of weight loss of poly(n-butyl methacrylate) was reduced to about one-tenth of its initial value and the residual polymer had undergone sufficient crosslinking to render it completely insoluble. There have been

Table 2  
Polymer Degradation Rates

Polymer	Hours Exposed	(Gms. Wt. Loss/cm <sup>2</sup> -hr.) × 10 <sup>4</sup>
PMDS	150	1.27*
PMTS	150	4.07*
PEDS	150	0.80*
PETS	150	2.27*
Cured PETS	150	0.44*
Cured PTMDS	150	0.60*
Thiokol FA-3000	150	0.44*
Cured LP-2	150	1.50*
Chlorinated poly(isobutylene)	25	0.11
Poly(methyl methacrylate)	72	0.059
Poly(n-butyl methacrylate)	115	0.094
Poly(tetrafluoroethylene)	20	0.042
Poly(oxymethylene)	24	No weight loss detected
Poly(propylene)	24	No weight loss detected

\*Calculated from Data of Fig. 2.

several reports that the photodegradation of poly(methyl methacrylate) (6) and poly(n-butyl methacrylate) (7) yields exclusively monomer. These exposures were carried out at temperatures in excess of 130°C. Work at this Laboratory has shown that at about 25°C the degradation mechanism of these polymers is considerably more complex than merely an unzipping reaction:



In addition to monomer, the volatile products of the photolysis of poly(methyl methacrylate) comprised methyl formate, methanol, hydrogen, methane, carbon monoxide, and carbon dioxide (8). Our semiquantitative measurements of the volatile photolytic products of poly(n-butyl methacrylate) showed that more n-butyl alcohol than monomer was formed.

The rates of degradation of the poly(alkylene polysulfides) listed in Table 2 were obtained from the plots shown in Fig. 2. The amounts of weight loss per sq cm decreased with exposure time; the values given in Table 2 were arbitrarily calculated from the weight loss at 150 hours in order to compare the polysulfides with the other polymers that were evaluated.

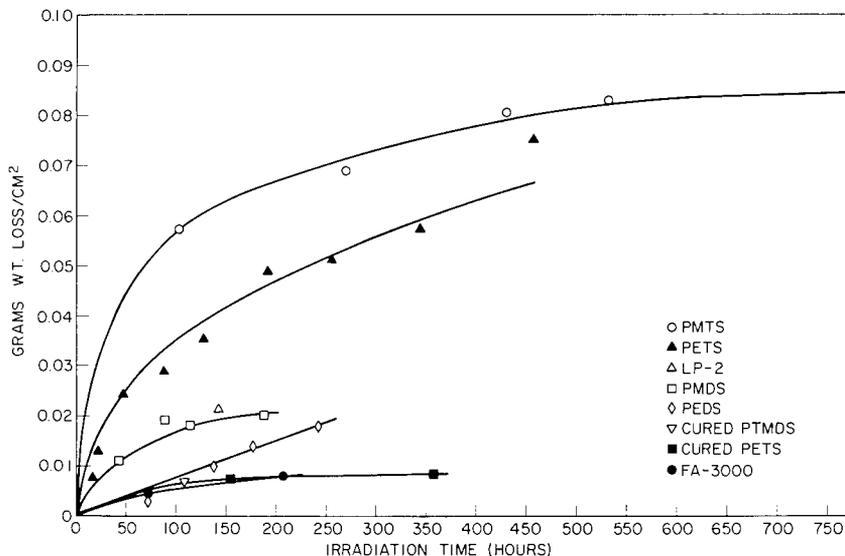


Fig. 2 - Grams of weight loss per square centimeter of exposed surface against hours of irradiation for the poly(alkylene polysulfides)

No differences in degradation rates or products were observed in samples prepared by milling or by pressing or in different synthetic preparations of the same poly(alkylene polysulfide). Variations in pressure from 10<sup>-3</sup> to < 10<sup>-5</sup> torr had no effect on the rates of weight loss.

## DEGRADATION PRODUCTS

Obviously, the total weight loss of a polymer sample should be accounted for by an equal weight of volatile products. Table 3 lists the products condensed by liquid nitrogen found in the photolysis of uncured sheets of PMDS, PMTS, PEDS, and PETS. On the basis of peak heights in the mass spectra, the minor constituents constituted less than 10% of the products condensed by liquid nitrogen.

Water was also found with the volatile products. Extremely long evacuation periods before irradiation removed most of the water, indicating that it had been absorbed on the polar polymer surfaces, rather than formed by photolytic reactions. The loss of water represented negligible weight loss, as was demonstrated by determining weight losses over prolonged periods of evacuation at pressures below  $10^{-5}$  torr. Also, carbon dioxide, found in very small amounts in the samples of volatile products of PEDS and PETS, was probably not a product of photolysis.

In Table 4, the weights of each gas are compared to the total weight loss occurring during the exposure. Weights of the gases were calculated from the areas under plots of gas pressure (in microns of mercury) against irradiation time (Figs. 3 and 4). Pressures were determined in the usual way by empirical calibration of the mass spectrometer with known compounds. It is apparent from these data that hydrogen sulfide and carbon disulfide, constituting about 90% of the liquid-nitrogen-condensed products, account for less than half the total weight losses found in these exposures. This discrepancy is the result of the deposition of two different materials which condense on the walls of the cell rather than in the liquid-nitrogen-cooled trap.

Table 3  
Liquid-Nitrogen-Condensed Products

Polymer	Major Volatile Products	Minor Volatile Products
PMDS and PMTS	H <sub>2</sub> S, CS <sub>2</sub>	CH <sub>3</sub> SH, HCHS
PEDS and PETS	H <sub>2</sub> S	CS <sub>2</sub> , CH <sub>3</sub> CHS

Table 4  
Weights of Volatile Products Compared with  
Total Weight Loss of Polysulfides

Polysulfide	Total Weight Loss (g)	Weight Volatile Products (g)	$\frac{\text{Weight Volatile Products} \times 100}{\text{Total Weight Loss}}$ (%)
PMDS	0.0592	H <sub>2</sub> S 0.0049	40.9
		CS <sub>2</sub> 0.0193	
PMTS	0.9157	H <sub>2</sub> S 0.1110	38.8
		CS <sub>2</sub> 0.2439	
PEDS	0.0345	H <sub>2</sub> S 0.0075	21.8
PETS	0.2994	H <sub>2</sub> S 0.0195	6.5

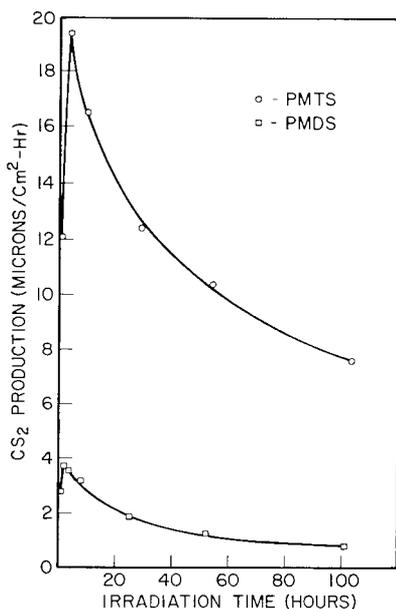


Fig. 3 - Microns of CS<sub>2</sub> formed per square centimeter of exposed surface per hour of irradiation against hours of irradiation

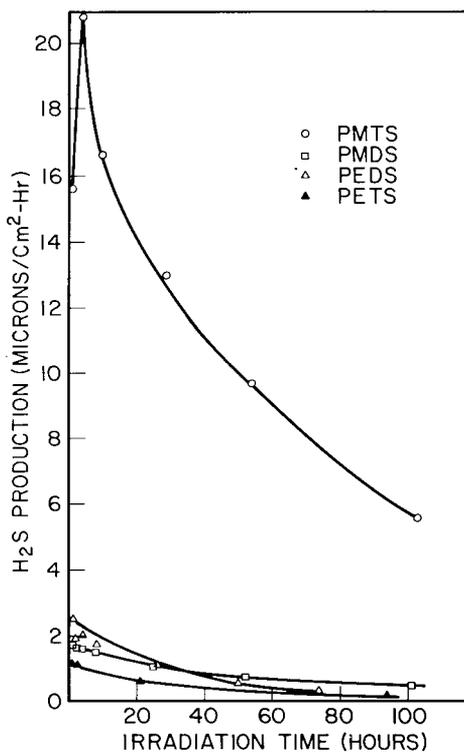


Fig. 4 - Microns of H<sub>2</sub>S formed per square centimeter of exposed surface per hour of irradiation against hours of irradiation

One of these materials was a white to yellow rubbery substance which was produced only during the photolysis of the tetrasulfide polymers. The infrared spectrum of this rubber was identical to that of the poly(alkylene tetrasulfide) from which it was formed. Evidently, upon irradiation the tetrasulfide polymers form reactive species which are volatile enough to travel a few inches to the cell wall where they reform the original tetrasulfide. Since this phenomena was not observed in the photolysis of the disulfide polymers, the sulfur atoms in the tetrasulfide linkages are probably involved.

The second condensed material was an insoluble brown film which formed during the irradiation of both cured and uncured polysulfides. The infrared spectrum of this material (Fig. 5) was identical with that of polymerized carbon monosulfide, prepared by the photolysis of carbon disulfide (4,5). Carbon monosulfide is a reactive gas but has been shown not to be a free radical in the usual sense (9). It polymerizes to an insoluble brown material when irradiated with ultraviolet light. Condensing the gas to a liquid or solid causes it to polymerize, a reaction which also proceeds slowly in the gaseous state, evidently by collision with the walls of the container (10).

Under our usual exposure conditions, carbon monosulfide was not condensed in the liquid-nitrogen-cooled traps, showing that ultraviolet-induced polymerization of this compound was complete within the cell. Some exposures were made with the irradiation cell covered with aluminum foil except for a small opening directly in front of a poly(ethylene disulfide) sheet. This arrangement allowed a considerable amount of light to strike the polysulfide sheet, but reduced the surface area within the cell which was exposed to ultraviolet light by about 90%. Carbon monosulfide did not polymerize on the surfaces of the cell which were shielded from ultraviolet light. Instead, most of the carbon monosulfide

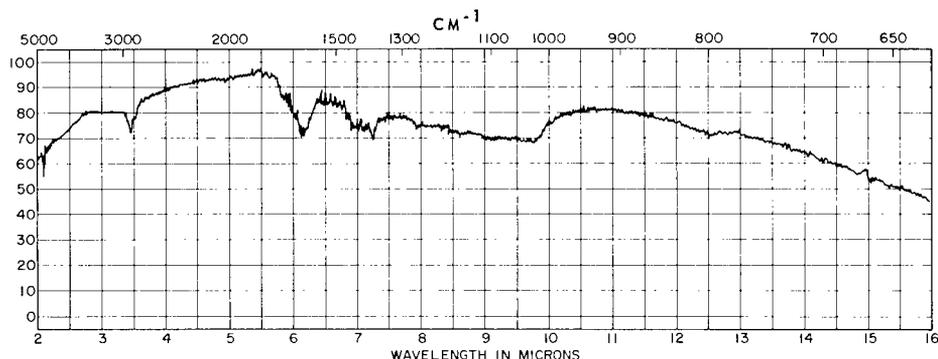


Fig. 5 - Infrared spectrum of poly(carbon monosulfide)

passed out of the cell and was condensed by liquid nitrogen in the cold trap where it subsequently polymerized. Examination by infrared spectroscopy showed this material to be identical to the polymerized carbon monosulfide formed as a film within the irradiation cell.

In this experiment the ratio of hydrogen sulfide to carbon disulfide was unchanged from exposures in which the cell was not shielded with aluminum foil. This evidence indicates that most of the carbon monosulfide is a direct product of photolysis of poly(alkylene polysulfides), rather than a product of photolysis of carbon disulfide. Further evidence of this fact is found in the photolysis of poly(methylene polysulfides), which yielded much more carbon disulfide than did the poly(ethylene polysulfides), but formed polymerized carbon monosulfide at a qualitatively slower rate.

#### RESIDUAL POLY(ALKYLENE POLYSULFIDES)

Infrared spectroscopy showed the residual sheets of exposed samples of poly(alkylene polysulfides) to be chemically unchanged even after 80% of the original material had been removed by degradation (Figs. 6 and 7). The increase in the absorption band at  $6.2\mu$  is accounted for by the deposition of poly(carbon monosulfide) (Fig. 5), which forms on all surfaces which are exposed to ultraviolet radiation. Results similar to those shown in Figs. 6 and 7 were found for all the poly(alkylene polysulfides) which were studied, although none of the others were degraded to such an extent as were PMTS and PETS.

Further evidence that the residual polysulfides were chemically unchanged after undergoing extensive weight losses was found in another experiment. A sample of PETS which had lost about one-third of its original weight was remilled and again exposed under the same conditions. A plot of weight loss per sq cm of surface against irradiation time for this remilled sample was identical to the results from the original sheet.

Poly(alkylene polysulfides) are considerably superior as photoablative materials to any of the other polymers which were evaluated. Furthermore, the unchanged infrared spectra of the residual samples indicates that this process could continue to complete photodegradation of these materials. Although inspection of Fig. 2 shows that the rates of weight loss of the polysulfides decrease with time, this is attributed in part to the physical effect of the deposition of a layer of polymerized carbon monosulfide on the surface of the samples. This layer may absorb much of the effective radiant energy and may also hinder the migration of volatile materials out of the sample. In the infinitely larger volume of space, the frequency of collisions of molecules of carbon monosulfide should be lowered so much that polymerization of carbon monosulfide should not occur to any appreciable extent.

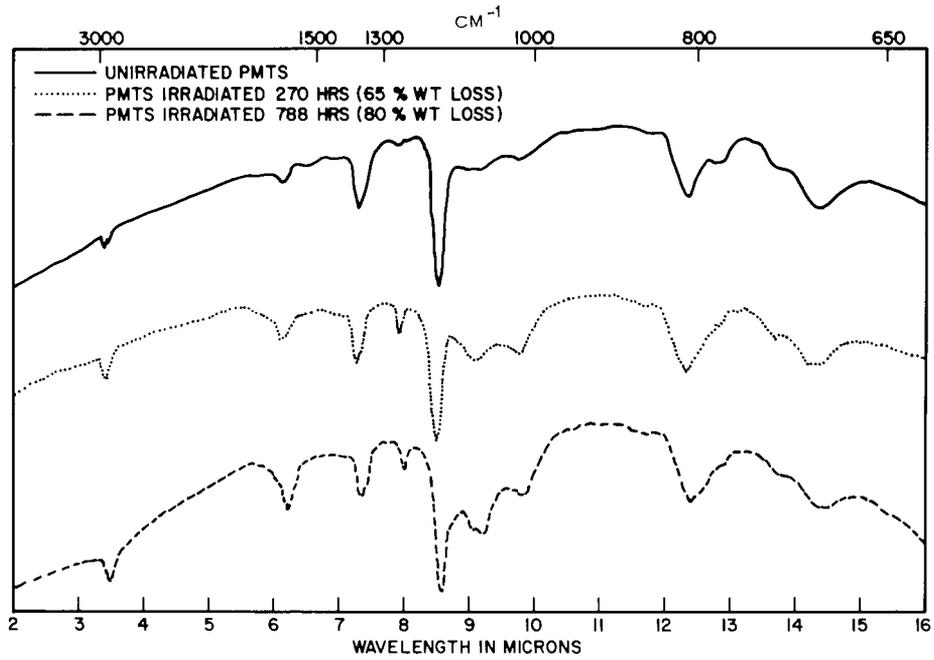


Fig. 6 - Infrared spectra of PMTS before and after degradation

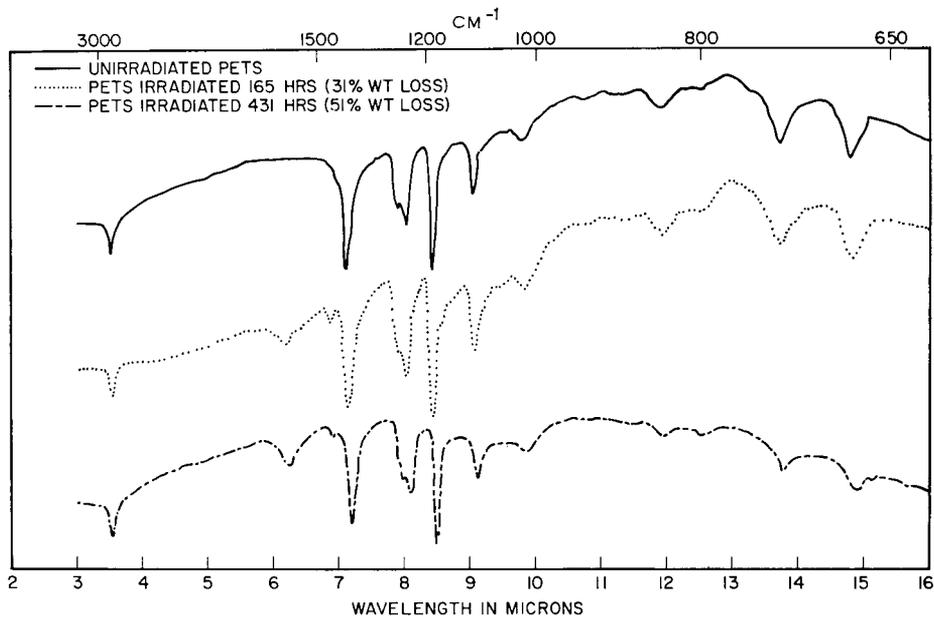


Fig. 7 - Infrared spectrum of PETS before and after degradation

Except for PMTS, the residual polymer sheets were cracked and curled after exposures sufficient to cause 25% to 50% weight loss. The concomitant reduction of the surface incident to the ultraviolet radiation probably also lowered the rates of weight loss. The PMTS samples, however, partially melted during exposures and adhered to the quartz plate which was used to support the samples.

#### MECHANISM OF POLY(ALKYLENE POLYSULFIDE) PHOTOLYSIS

At least two major reactions occur in the photolysis of poly(alkylene polysulfides). The phenomena observed in the photolysis of the tetrasulfide polymers, the deposition of the same tetrasulfide on the walls of the irradiation cell, evidently involves the interior sulfur atoms of the tetrasulfide groups. Species such as  $\text{SSCH}_2\text{CH}_2\text{SS}$  and  $\text{SSCH}_2\text{SS}$ , formed by scission of adjacent tetrasulfide groups, may be reactive intermediates which are volatile enough to travel from the polymer sample to the cell wall where they subsequently polymerize to reform the original tetrasulfide polymer. Owen, MacKnight, and Tobolsky (11) have proposed that the odd electrons which result from scission of a tetrasulfide linkage between the 2 and 3 sulfur atoms form a three-electron bond between the remaining sulfur atoms:



This three-electron bond is expected to be more stable than a free radical, and thus an intermediate such as  $\text{SSCH}_2\text{SS}$  might exist long enough to be removed from an exposed poly(alkylene tetrasulfide) sheet.

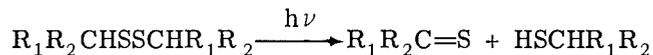
Poly(alkylene polysulfides) have a distribution of the number of sulfur atoms in a polysulfide linkage. Thus, a polymer prepared to be a tetrasulfide will actually have some trisulfide and lower sulfide linkages, and some pentasulfide linkages (12). During the degradation of the tetrasulfide polymers, visual observation showed that most of the white film was deposited during the first 50 to 100 hours of degradation; the highest rates of weight loss of the tetrasulfide polymers also occurred during this period (Fig. 2). A plausible explanation is that adjacent tetrasulfide linkages on the surface of the sample were undergoing scission to form the proposed intermediates. After such sites were exhausted or nearly exhausted, the surface was composed of polymers with polysulfide linkages of less than four sulfur atoms and therefore the rates of degradation decreased. This slight difference in chemical makeup is unlikely to be detected by infrared spectroscopy, since the surface constitutes a small percentage of the total polytetrasulfide sheet.

Another possible explanation of the deposit of white film is that low-molecular-weight chains are volatilized from the polymer sheet by the heat of the lamp. It is also possible that photolytic reactions occurring in the polymer enhance migration of volatile materials from within the polymer sample. However, no volatile materials were produced or white film deposited on the cell walls when evacuated polymer samples were heated. Also, the appearance of the white film only on the cell walls and nowhere else in the system indicates it is caused by a reactive species rather than merely a volatile one.

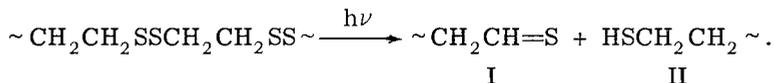
The higher rates of weight loss of the tetrasulfides compared to the corresponding disulfides is attributed to the formation of the white film. More research is required to ascertain if this postulated reaction does indeed occur and to synthesize polymers with no polysulfide linkages having less than four sulfur atoms. Such a structure, based on the present state of knowledge in this field, should photodegrade very readily.

At least one other route of photodegradation must be advanced to account for the other major products of photolysis; carbon monosulfide, hydrogen sulfide, and, for the

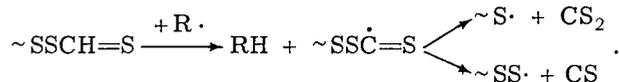
methylene polymers, carbon disulfide. Rosengren (13) has postulated that the following reaction occurs in the photolysis of disulfides:



where  $R_1$  is an alkyl group and  $R_2$  is hydrogen or an alkyl group. Extension of this reaction scheme to poly(alkylene polysulfides), PEDS for example, gives:



However, no mercaptans were found in the residual sheet material or the volatile products, except methyl mercaptan, a minor product of PMDS and PMTS. If such a reaction does occur in the photolysis of poly(alkylene polysulfides) the products evidently continue to react. Structures such as II may yield hydrogen sulfide upon further degradation. Abstraction or elimination of hydrogen from moieties such as I, followed by carbon-carbon bond cleavage, would yield carbon monosulfide. The intermediate analogous to I for the methylene polymers is  $\sim SSCH=S$ . Abstraction or elimination of hydrogen from this structure should yield both carbon monosulfide and carbon disulfide, depending on whether a carbon-sulfur or a sulfur-sulfur bond is subsequently broken



This degradation route is supported by the experimental evidence; carbon disulfide was a major photolytic product of the methylene polymers, but not of the ethylene polysulfides.

If these postulated reactions are an important degradation route, the relative ease with which hydrogen is abstracted should have an effect on the rates of degradation of the poly(alkylene polysulfides). Pryor and Guard (14) found that hydrogen atoms which are alpha to a disulfide linkage are comparable to benzylic hydrogens in ease of abstraction or elimination in free radical reactions. Since the hydrogen atoms in the poly(methylene polysulfides) are in an alpha position to two polysulfide linkages, it is likely that these hydrogens are even more labile than those of the other polysulfides. In support of this postulate, Fig. 2 shows that PMTS has a higher rate of weight loss than any of the other polymers, and the rate of weight loss of PMDS is higher than that of any of the other disulfide polymers.

## SUMMARY

Weight losses of chlorinated poly(isobutylene), poly(methyl methacrylate), poly(n-butyl methacrylate), poly(tetrafluoroethylene), poly(oxymethylene), poly(propylene), and several poly(alkylene polysulfides) were determined after exposure in a simulated space environment. The poly(alkylene polysulfides) were found to have considerably higher rates of weight loss than the other polymers. The degradation products of poly(methylene disulfide and tetrasulfide) and poly(ethylene disulfide and tetrasulfide) were identified and, for gaseous products, quantitatively measured. From this information a degradation mechanism was postulated with these main features; the production of intermediates such as  $SS(CH_2)_nSS$  in the photodegradation of tetrasulfide polymers and extraction of hydrogen atoms from carbon atoms to yield hydrogen sulfide, carbon monosulfide, and, for methylene polysulfides, carbon disulfide.

## ACKNOWLEDGMENTS

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Photolysis Echo (passive communication satellite) Polymer degradation Poly(alkylene polysulfides) Photodegradation Polysulfides Carbon monosulfide Irradiation cell Ultraviolet radiation						

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