A SURVEY OF THE PHOTODEGRADATION OF ORGANIC POLYMERS EXPOSED TO ULTRAVIOLET RADIATION

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ABSTRACT

Some of the variables involved in the photodegradation of organic polymers are examined, with special emphasis given to research on the photochemistry of poly(vinyl chloride). New approaches to the problem of protecting polymers from ultraviolet (UV) radiation in extraterrestrial space are required to replace present hit-and-miss procedures for selecting UV inhibitors. Attention will be focused on those variables that are critical to the successful UV stabilization of polymers. The discussion will center about the nature of the ultraviolet absorbing grouping, the wavelength dependence of the photochemical reaction, and the rate enhancing effect of polychromatic radiation. The absorption spectra of the ultraviolet absorbing groups present in PVC film has been measured by means of single-beam spectrophotometry. These groups are identified as polyenes on the basis of comparison with known polyenes and the wavelength dependence curve of color development. The interaction of the pi-electrons of the polyenes initially present in PVC with antimony trichloride markedly retarded the rate of photodegradation. Useful criteria are presented for the choice of energy-transfer systems for the UV protection of PVC. Monochromatic quantum yields of photolysis for a variety of linear polymers are compared. These quantum yields appear to fall into two classes; those accompanied by chain scission, and those accompanied by crosslinking.

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The quantum yield measured for the photoproduction of hydrogen chloride from PVC at 2537 Å was 9.0×10^{-3}. This yield is in good experimental agreement with the value reported for hydrogen chloride photoproduction from the related polymer poly(vinylidene chloride), i.e., 7.0×10^{-3}. Kinetic evidence is presented for the greater effectiveness of polychromatic light over monochromatic light in photodegradation.

INTRODUCTION

In this paper some of the variables involved in the photodegradation of organic polymers will be examined, with special emphasis given to research on the photochemistry of poly(vinyl chloride). The elucidation of the mechanism by which PVC reacts with ultraviolet radiation provides insight into the photochemical behavior of a variety of polymers. The frequently deleterious property changes in polymers due to their photochemical sensitivity have delayed large-scale utilization of polymers in the space environment. Attempts have been made to protect polymers by classical techniques, such as painting, overcoating, and adding opaque fillers, pigments, and UV-absorbing compounds. These kinds of approaches are a compromise, at best, since the protective schemes often complicate fabrication procedures, as well as adversely affect the physical, chemical, and optical properties for which the polymeric materials were initially chosen. Moreover, traditional techniques of protection from UV have been tailored to familiar terrestrial conditions and are often deficient in the space environment. For example, the commercially employed benzophenone derivatives actually become photosensitizers for the photodegradation of polymers in vacuum below 3000 Å. Although no UV radiation of wavelengths shorter than about 2950 Å penetrates to the surface of the earth, the combined effects of oxygen, water, and climatic temperature

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variations present an exceedingly complex environment. Oxygen will enhance rates of photodegradation, forming carbonyl groups, while rainfall may extend the outdoor life of polymers by washing away autocatalytic products from the site of photodegradation. In extraterrestrial space, although the radiation environment contains photons sufficiently energetic to break most single covalent bonds, the absence of oxygen and water is a simplifying aspect in the analysis of the primary photochemical processes.

AEROSPACE INTEREST IN POLYMERS

A spacecraft structure has the function of carrying instruments or men through space at a minimum weight and cost. Lunar- or planetary-based space structures must be easy to erect and must utilize materials with high strength-to-weight ratios (specific strength). Traditional structures developed with metals which have as their design elements, plates, beams, and struts are adaptable for extraterrestrial service. But when high strength-to-weight ratio, ease in erectability, and low cost persist as governing criteria, then polymers must be given strong consideration. The suitability of polymers for extraterrestrial applications is illustrated in Fig. 1. This is a block diagram comparing the specific strengths of a number of commercially available polymers with three typical lightweight aerospace structural metals.[1-3] The delineated temperature range encompasses the extremes likely to be encountered on the lunar surface and does not imply that the materials must perform over the entire range. In anticipated actual practice, an intermediate temperature exists at which the polymers show optimum flexibility and sufficient specific strength to be unfolded or inflated. For this application, the unplasticized polymers, shown in Fig. 1, are comparable to metals such as aluminum. In addition, the relative ease of fabricating polymers to attain required mechanical and physical properties as well as shapes should lead to their wider spacecraft utilization.

Aerospace application of polymers has been approached cautiously because of poorly understood photodegradation and fabrication processes. Polymers are largely batch produced, and quality control between lots, though sufficient for many terrestrial requirements, often does not meet the stringent demands of the space environment. For example, the model polymer used for our studies, PVC, despite an annual production rate of 1.8 billion pounds,[4] still exhibits batch-produced characteristics, such as lack of reproducibility in molecular weight distribution, in stereoregularity, and in the extent of chain perfection (e.g., presence of groups foreign to the basic $(\text{-CH}_2\text{-CHCl-})_n$ structure). Figure 2 shows typical variations in absorption spectra obtained from drawn films of PVC prepared from the same batch of resin. The significance of these spectra to the photodegradation of PVC and the technique used to measure the absorption will be discussed later. It is sufficient here to state that since the rate of photodegradation is proportional to absorbed flux, the variations in absorbance at any given wavelength noted in Fig. 2 will reflect variations in the rates of photodegradation. As a consequence of this variable absorbance, the concentration of UV stabilizer must be adjusted since either too low or too high concentrations of the UV-stabilizer will not inhibit the photodegradation.[5]

SOME ASPECTS OF PVC PHOTODEGRADATION

The vacuum photolysis of PVC can be explained by a reaction scheme in which the effect of absorption of ultraviolet radiation is the elimination of hydrogen chloride, resulting in the formation of a conjugated polyene structure, possible accompanied by crosslinking. The essential problem has been to determine what variables govern the ultraviolet photodegradation of

PVC. In this paper, attention will be focused on those variables that are critical to the successful UV stabilization of polymers. The discussion will center about the nature of the ultraviolet absorbing groupings, the wavelength dependence of the photoelimination reaction, and the rate-enhancing effect of polychromatic radiation.

Since alkyl chlorides show no ultraviolet absorption maxima (in the gas or liquid phase) at wavelengths greater than 2000 Å, the observed photodegradation of PVC at wavelengths up to about 3300 Å has been puzzling. Following the lead of earlier suggestions[6,7] that the presence of a conjugated unsaturated system (i.e., polyene) is responsible for the photochemical sensitivity of PVC, we have looked carefully for spectroscopic evidence of the anticipated ultraviolet absorption maxima characteristic of a mixture of dienes, trienes, tetraenes, pentaenes, and longer polyenes. Initial efforts employing a conventional double-beam, ratio-recording spectrophotometer afforded only poor quality spectra which consisted of a broad absorption envelope, lacked any unambiguous maxima or minimas, and was characterized by steadily increasing absorption with decreasing wavelength. Lately, it has proved possible to measure directly the absorption spectra of the ultraviolet absorbing species by means of single-beam spectrophotometric techniques. The essential optical elements for the instrument (light source, monochromator of 190 Å band pass, and photodetector) are part of the apparatus employed in our UV degradation studies. This apparatus (Fig. 3), consisting of a windowed vacuum chamber, the spectrophotometer elements, and a time-of-flight mass spectrometer, provides a dynamic analytical technique for the simultaneous measurement of rates of photon absorption and of photolytic product formation. The optical arrangement, used for measuring the absorption spectra of the test polymer in vacuum before and after irradiation, is a necessary in situ measurement to prevent possible reaction of the irradiated film with atmospheric oxygen. The sensitivity of the single-beam spectrophotometer is attributed, primarily, to its high-intensity, well-collimated monochromatic source which permits the measurement of smaller absorption cross sections than can be measured by a double-beam, ratio-recording spectrophotometer. In the usual time interval (15 seconds) used to scan from 2000 to 3400 Å, no measurable change in the optical density of the PVC film was noted, guaranteeing that no significant photodegradation occurred during the scan interval. Absorption spectra of PVC film obtained by single-beam and ratio-recording techniques are shown in Fig. 2. The single-beam spectra are of good quality, containing maxima and minima, that were used to identify the ultraviolet absorbing species in PVC film by comparison with the spectra of known polyenes.

These spectra of PVC film and the attendant wavelength dependence curve of color development as shown in Fig. 4 (to be discussed later) have a common explanation: The unirradiated PVC film contains a mixture of polyenes, consisting predominantly of dienes, trienes, tetraenes, and pentaenes which originate from disproportionation reactions during synthesis and from thermal dehydrochlorination reactions during processing. These conjugated unsaturated groupings present in the polymer as chain imperfections provide the absorbing sites for ultraviolet radiation. The absorption of this radiant energy leads to electronic excitation which, although initially localized in the double bonds, is transmitted along the chain and ultimately induces the cleavage of a carbon-chlorine bond. This bond is the most readily broken since dissociation requires only 73 kcal/mole, compared to 87 and 83 kcal/mole for cleavage of the carbon-hydrogen and carbon-carbon bonds, respectively.

METHODS OF INHIBITING UV DEGRADATION OF POLYMERS

The present goal of our research is an understanding of the photochemical reactions of polymers that occur in the unique environment of extraterrestrial space and, concurrently, an application of this knowledge to the general development of efficient methods of inhibiting UV degradation of polymers without deleterious concomitant changes in the engineering properties of these materials. Methods based on sound theories must be developed to replace present hit-and-miss procedures for selecting UV inhibitors or synthesizing new UV resistant polymers.

The results of our studies on the photodegradation of PVC and an improved understanding of the chemistry of excited electronic states of molecules have revealed the possibility of diverting photons to electronic excitation processes other than photodegradation. For example, interaction of the mobile pi-electrons of the polyenes in PVC with an appropriate electron acceptor would be expected to reduce the efficiency of energy transfer from the unsaturated carbon-carbon bonds to a carbon-chlorine bond in the allylic position of the polyene system. A test of this concept is shown in Fig. 5 in the markedly retarded rate of PVC photodegradation effected by the addition to a PVC film of 0.1 percent (by weight) antimony trichloride ($SbCl_3$), a good electron acceptor and UV absorber. The spectrophotometric scans in this figure show the change in optical density (Δ O.D.) for the two PVC films in vacuum exposed to the radiant flux from a 250-watt medium-pressure, mercury-arc lamp for one hour in vacuum. (This corresponds to a flux of $\simeq 10^{16}$ photons cm^{-2} sec^{-1} from 2380 to 4000 Å, or approximately one UV solar flux equivalent.) The rate of yellow color development achieved in the film containing 0.1 percent $SbCl_3$ as measured by (Δ O.D.) at 4000 Å was 90 percent more retarded than the rate of color development for the untreated film. Although the $SbCl_3$-treated PVC film eventually discolored, its rate of photodegradation constantly lagged that of the untreated PVC film. Related schemes for energy transfer are being studied in our laboratories.

WAVELENGTH DEPENDENCE OF PHOTODEGRADATION OF PVC

The wavelength dependence, as described by the "photochemical action" curve of Fig. 4, displays a pronounced maximum at 2540 Å, corresponding to the region of maximum photochemical sensitivity. This plot shows the change in optical density (Δ O.D.) per incident photon as a function of the incident monochromatic flux. The vacuum photodegradation threshold of 3320 Å (86 kcal/mole) is based on evidence given in a previous publication.[6] The wavelength dependence measurement defines the choice of energy-transfer systems for the UV protection of PVC. For example, $SbCl_3$ was selected because it is an electron acceptor with respect to the electron-donating pi-electron system of the polyene and its ultraviolet absorption spectrum exhibits maxima at 2400 and 2580 Å. Similarly, an energy-transfer system which can absorb photons capable of photodissociation processes and subsequently divert them by emission at wavelengths above the threshold could protect PVC from photodegradation. Generally, an additional requirement is that these photoexcitation processes occur at rates that are very rapid compared with rates of photodegradation.

QUANTUM YIELD COMPARISONS

Before methods of UV stabilization of polymers can be systematically achieved, the photodegradation process must be identified and its efficiency measured. One measure of this efficiency is the quantum yield, the number of molecules produced per photon absorbed. Some progress toward this measurement is presented in Fig. 6 where quantum yields for volatile photoproduct formation are compiled for a group of linear polymers whose backbones undergo chain scission or crosslinking reactions.[7-16] Examples of these types of backbone reactions are shown in this figure. The quantum yields cited and those which we have determined have values less than unity. In fact, the values of the quantum yield are about 2 to 3 orders of magnitude less than unity. This appears to be the rule, rather than the exception, for photochemical reactions of polymers. In other words, the number of moles of photolytic product tends to be much less than the number of quanta absorbed by the polymer. Processes evidently occur which diminish the number of molecules formed by photodissociation. A possible explanation is that in a large molecule the energy is absorbed at one site, but then the electronic excitation is partitioned over many bonds so that the probability of a single bond breaking is small, or the absorbed energy is dissipated by quenching reactions. The small value of the quantum yield is desirable from an application standpoint, although it places stringent demands on the sensitivity of the experimental method for measuring the rates of formation of volatile products.

A conclusion that can be made from this array of quantum yields is that although different chemical bonds are broken and different products are formed, the value of the quantum yields of product formation for polymers undergoing chain scission are surprisingly close in agreement. In contrast, a range of quantum yields is obtained for those polymers which crosslink during photodegradation. For the crosslinking polymers larger quantum yields are displayed by those polymers which are internally photosensitized by a phenyl group bound to each repeat unit (mer) like poly(styrene) or externally photosensitized by an ultraviolet absorber like the residual toluene in the case of poly(t-butyl acrylate). On the other hand, the smaller quantum yields are typical of those polymers in which the initial ultraviolet absorption occurs at groups foreign to the basic molecule. In PVC, these sites are conjugated unsaturated groupings. The quantum yield for the photoproduction of hydrogen chloride from PVC at 2537 Å was measured and its value is 9.0×10^{-3}. This quantum yield is in good experimental agreement with the value reported for hydrogen chloride photoproduction from the related polymer, poly(vinylidene chloride), i.e., 7.0×10^{-3}.[11] These low quantum yields indicate that a polymer free of foreign groups would exhibit high photochemical stability. Alternatively, UV protective schemes that can compete with these inefficient photodissociative processes are feasible.[17] Furthermore, the quantum yields of analogous polymers for which measurements are not available may be predicted.

The accelerating effect of oxygen on the rate of a photochemical process is seen by comparing the value of the quantum yield (obtained by the authors) of HCl production from PVC irradiated at 3000 Å in vacuum with the value[10] from irradiation in air. Moreover, in the presence of oxygen, photodegradation was observed at 4350 Å (65.7 kcal/mole), which is 1030 Å above the threshold for photodegradation measured in vacuum.[6] Since the dissociation of a secondary carbon-chlorine bond required 73 kcal/mole, the energy deficit must be supplied by the exothermic reaction with oxygen whose concentration becomes important in determining terrestrial rates of PVC photodegradation. The oxygen sensitivity of many photochemical reactions illustrates the importance of performing vacuum studies at a continuous pressure of below 10^{-6} torr.

SYNERGISTIC EFFECT OF POLYCHROMATIC RADIATION

We reported[7] previously that to attain equal Δ O.D.'s (i.e., equal extents of reaction) the absorbed flux required for monochromatic irradiation is about 10 times greater than the absorbed flux required for polychromatic irradiation. As shown in Fig. 6, this result is confirmed by the quantum yield for HCl photoelimination at 2537 Å when compared with that yield obtained by polychromatic irradiation supplied by the medium-pressure mercury arc. Although the incident fluxes are approximately equal, the value of the quantum yield with polychromatic radiation is about 10 times greater than that at 2537 Å. This is a striking confirmation that the rate of dehydrochlorination reaction and the rate of formation of a conjugated polyene structure are directly proportional. The greater effectiveness of polychromatic light over monochromatic light in photodegradation is not completely understood, but the effect should be considered in photodegradation studies. Synergistic effects also may be important in the polychromatic photolysis of other polymers. This may be an explanation for the large polychromatic quantum yield displayed by poly(methyl methacrylate),[16] but a monochromatic quantum yield for methyl formate formation is unavailable at present for comparison.

CONCLUDING REMARKS

The large-scale utilization of polymers in extraterrestrial space depends on the development of efficient methods for inhibiting ultraviolet degradation. A knowledge of the variables affecting the photodegradation of PVC permits the construction of a framework on which an understanding of the photochemistry of a large variety of polymers can be built. Ultimately, the recognition of similar variables in analogous polymers can lead to the designing of feasible energy-transfer systems that can compete effectively with photodissociation processes. Moreover, this knowledge can be applied to an understanding of photooxidation processes of polymers in the terrestrial environment. Finally, measurement of the quantum yield permits a quantitative ranking of the photosensitivities of a large variety of linear polymers. Although the application of photochemical research to development problems has been stressed in this paper, much is still to be understood about the interaction of ultraviolet radiation with macromolecules.

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FIGURE TITLES

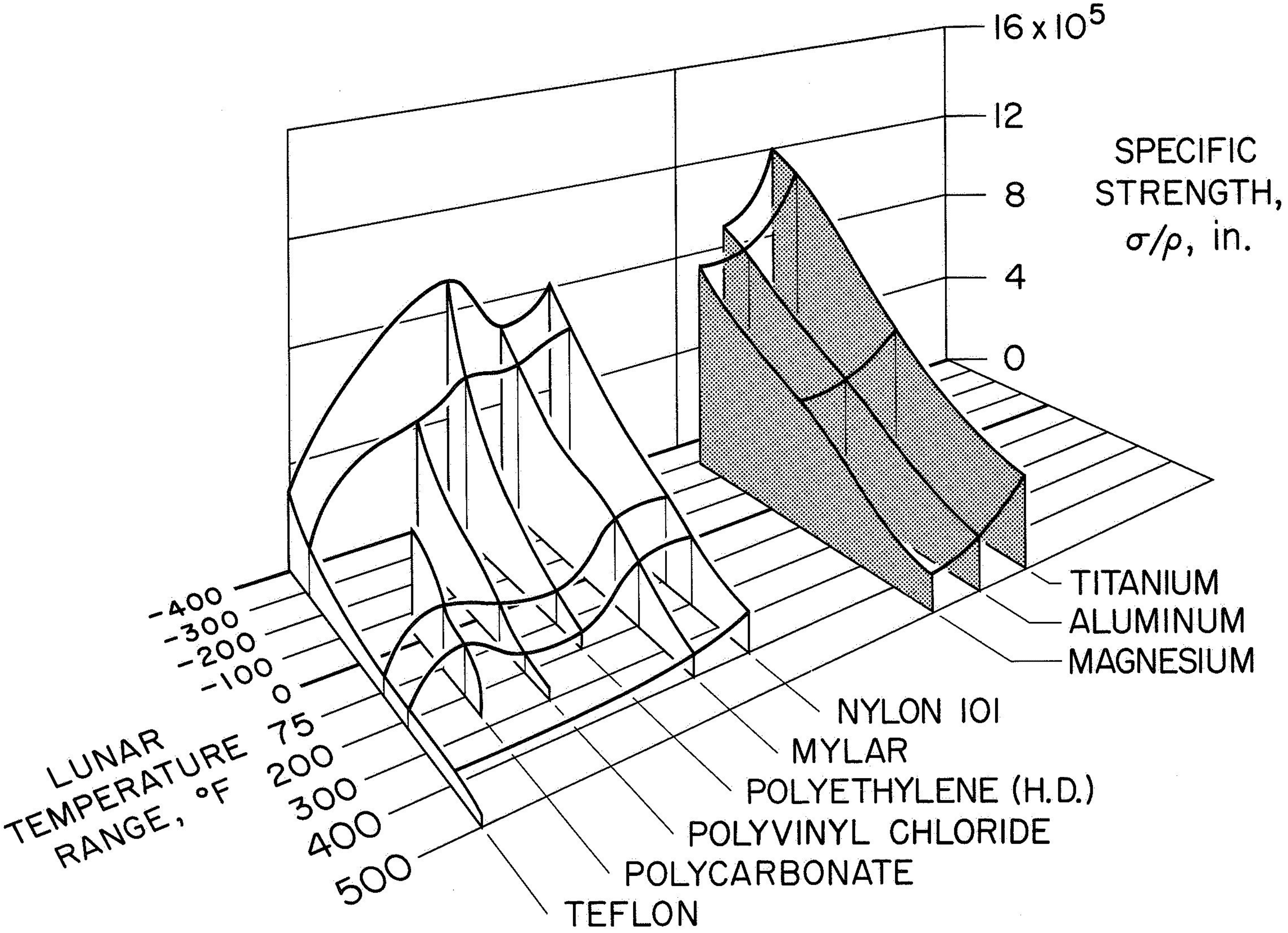


Figure 1.- Comparison of specific strengths of useful engineering materials.

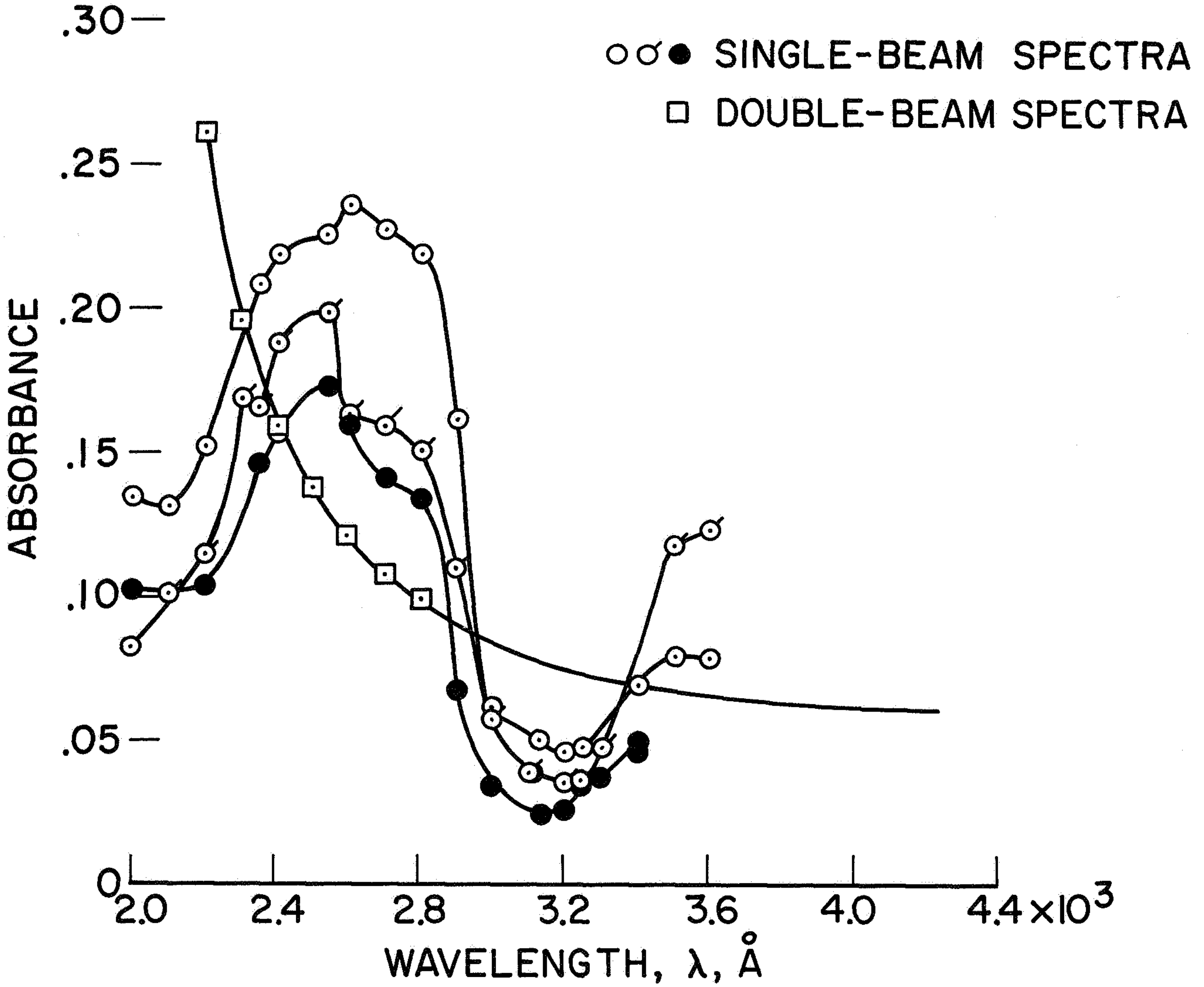


Figure 2.- Absorption spectra of PVC films.

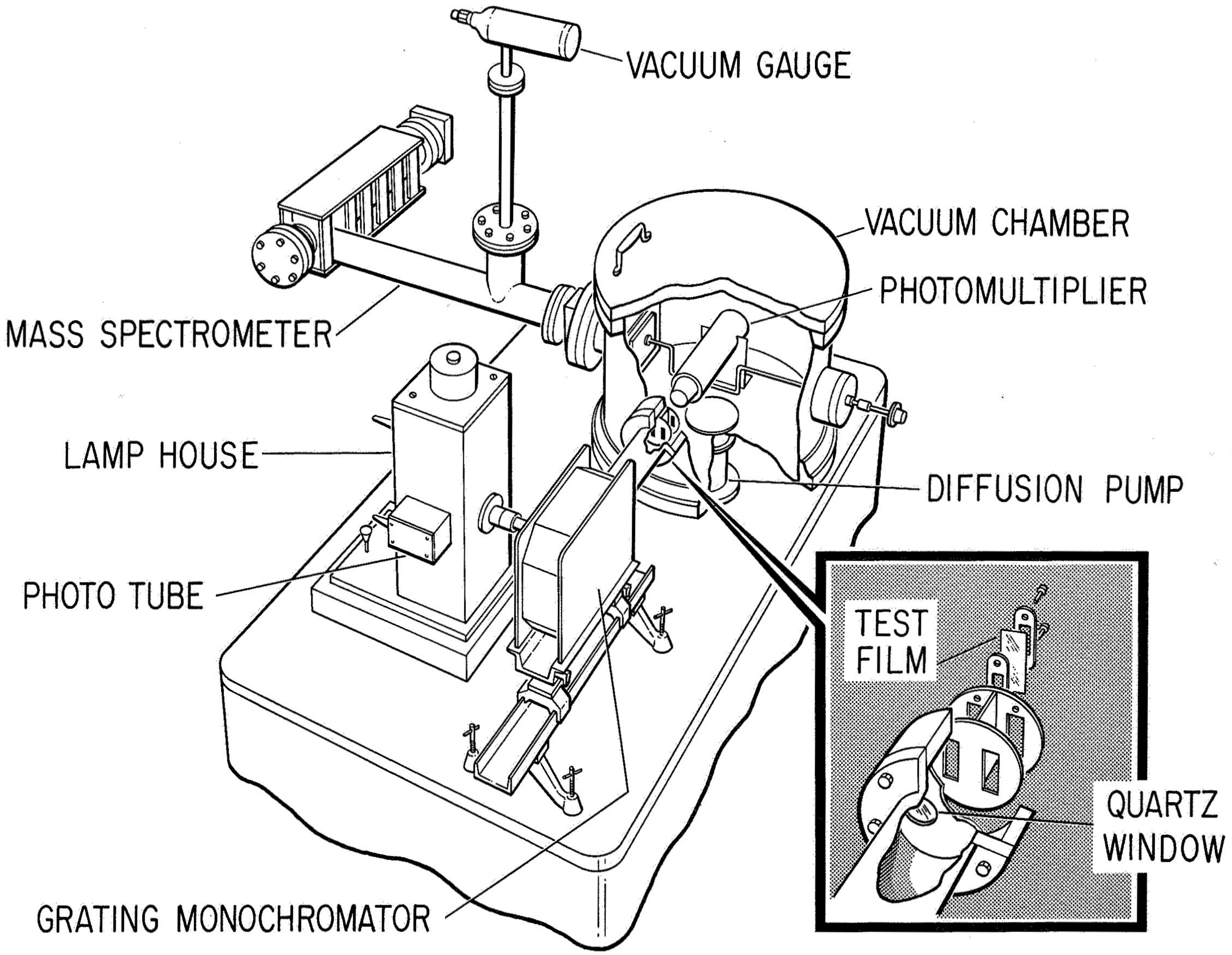


Figure 3.- Experimental apparatus.

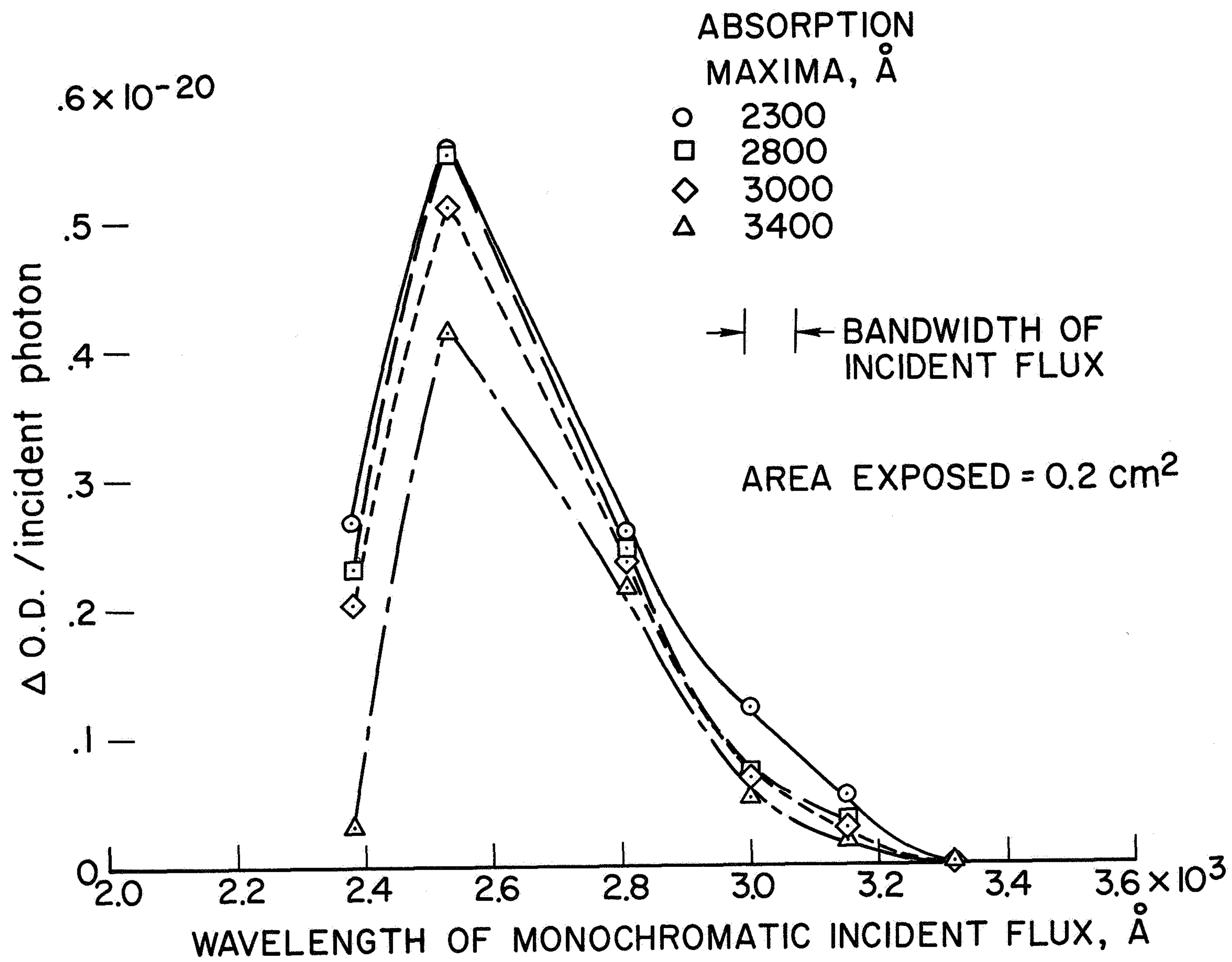


Figure 4.- Wavelength dependence of photodegradation of PVC films.

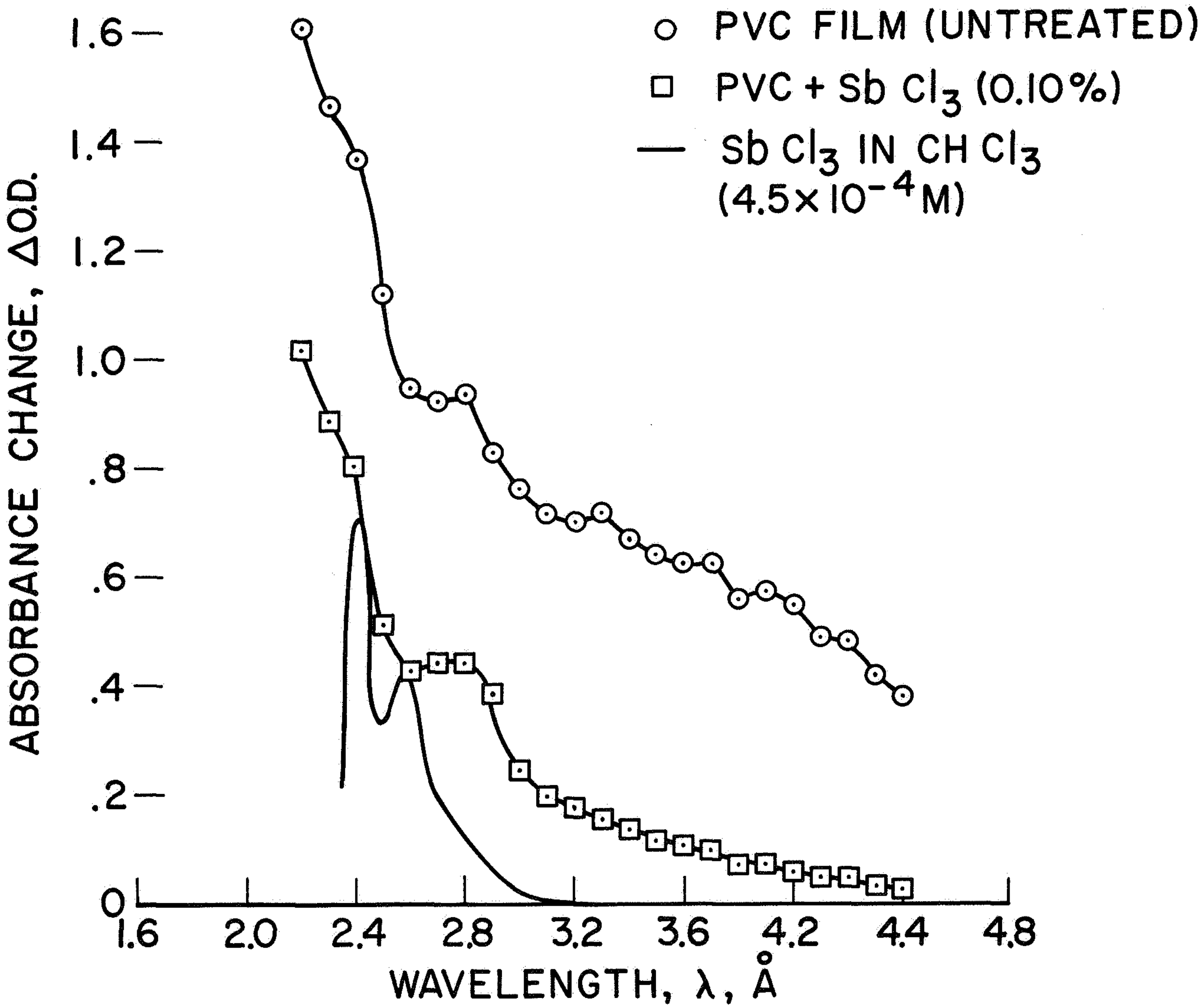
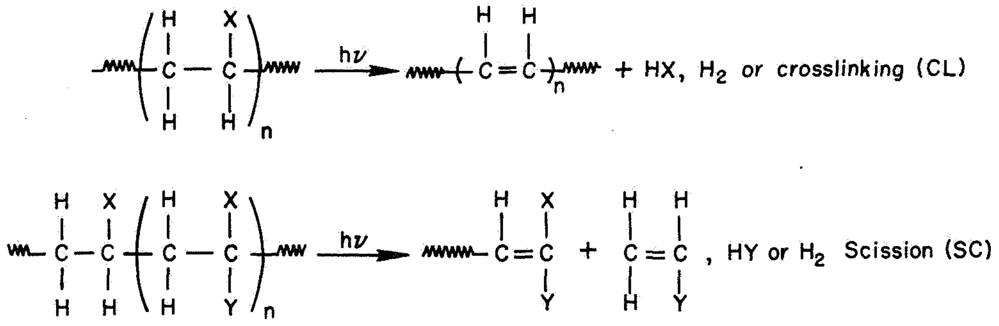


Figure 5.- Effect of antimony trichloride on the rate of photodegradation of PVC films.



Polymer	Irradiation Wavelength	Primary Volatile Product	Bond Broken	Quantum Yield of Prod. (Vac)x10^2	Backbone Reaction	Reference
* Poly(t-Butyl Acrylate)	2537 Å	Isobutene	C-O	8.30	CL	8
Poly(Styrene)	"	H_2	C-H	4.30	"	9
Poly(Vinyl Chloride)	"	HCl	C-Cl	0.90	"	
"	3000	HCl	C-Cl	0.30 (13)**	"	10 **
Poly(Vinylidene Chloride)	2537	HCl	C-Cl	0.70	"	11
Poly(Isoprene)	"	H_2	C-H	0.04	"	12
Cellulose	2537	H_2	C-H	0.80	SC	13
Poly(Methyl Acrylate)	"	Methyl Formate	C-C	0.80	"	14
Poly(α-Methyl Styrene)	"	α-Methyl Styrene	C-C	0.70	"	15
Poly(Vinyl Chloride)	Med. Press. Hg Arc	HCl	C-Cl	8.0	CL	7
Poly(Methyl Methacrylate)	"	Methyl Formate	C-C	14.0	SC	16

* Contained residual toluene (0.1%)

** Value in air

Figure 6.- Some typical photochemical reactions of linear polymers.