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FUNDAMENTAL INVESTIGATION OF ULTRAVIOLET RADIATION EFFECTS IN POLYMERIC FILM-FORMING MATERIALS

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FOREWORD

This report No. IITRI-C6295-10, was prepared by IIT Research Institute for NASA-Langley Research Center under Contract No. NAS1-12549, IITRI Report No. C6295. This report, entitled "Fundamental Investigation of Ultraviolet Radiation Effects in Polymeric Film-Forming Materials", covers the period July 13, 1973 through April 12, 1974.

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Respectfully submitted,
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ABSTRACT

A literature search from 1958 to present has been conducted on the effect of ultraviolet radiation on polymeric materials, with particular emphasis on vacuum photolysis, mechanisms of degradation and energy transfer phenomena. The literature from 1958 to 1968 was searched manually, while the literature from 1968 to present was searched by using a computerized keyword system. Selected references are reviewed and discussed in this report. The primary objective of this study was to provide the necessary background information for the design of new or modified materials with improved stability to the vacuum-radiation environment of space.

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1. INTRODUCTION

Many applications can be easily identified for a material which can be prepared as a thin film and which is stable in the environment of space. One obvious application would be as a paint binder. Others include solar cell covers, second-surface mirrors, adhesives, and optical windows. Apart from ultraviolet and charged-particle radiation stability, the essential requirements of the ideal material are that it be optically transparent in the spectral region from 3000Å (preferably 2000Å) to at least 25000Å, that it be a film-former, pigmentable, and processable. For a variety of reasons, commercially available materials do not meet these requirements; most are unstable, others have high outgassing potential, and many are simply not adaptable to spacecraft applications.

The purpose of the program described in this report was to develop a comprehensive rationale for "designing" a polymeric material possessing the major characteristics noted. The basic approach is to formulate structure-property relationships: associating stability with polymeric structure or structure-related properties. The program discussed here is the first phase of this effort and essentially consists of gathering, screening and analyzing relevant information. Determining which polymeric structures are most resistant to ultraviolet and charged particle radiations, and indicating means of synthesizing new materials or modifying existing materials are this effort's ultimate objectives.

The primary information we seek is that which correlates UV-induced degradation mechanisms with structural changes which result in increased optical absorption. For this purpose, it is necessary to determine the principal factors affecting the various modes by which a polymer dissipates absorbed UV energy, specifically, to identify those which influence the creation of optically absorbing species. The task is a difficult one because this type of information is highly specific to individual polymer structures.

2. LITERATURE RETRIEVAL

The Information Science (IS) group of IITRI Chemistry Division surveyed the availability of materials at the John Crerar Library and used the information gained there to formulate a computerized keyword search of Chemical Abstracts (CA). The library search identified about 25 summary volumes that are related to some aspects of the program. Citation cards prepared for those items that have been judged by IS to be valuable formed the nucleus of the reference abstract file. In addition, citation cards were prepared for the items that appeared in the bibliographies of those references - thus broadening the base of initial coverage. Additional broadening was achieved via the RAPRA abstracts.

When the initial library survey was completed, the most direct benefit was the accumulation of sufficient keyword frequency of occurrence data to allow formulation of a meaningful profile (search question). The first category (A) consists of terms that express the concept of "Ultraviolet Photochemistry" which is the interaction of interest. The second category (B) consists of terms that characterize the materials and other interactions of interests. Common polymer trade-names and abbreviations were also included in this category. The third category (C) specifies some interactions, other than those that are relevant, that are to be specifically excluded from the retrieval. Thus, the computer retrieval requires that each selected citation possesses at least one occurrence of an index or title term from each of the two categories, A and B, while a single occurrence from the C categories would disqualify it (Table 1).

Each citation card from the computer retrieval contains the title, author, source, index terms for the reference, as well as a special print-out of those terms that were responsible for the selection. A final card summarizes the statistics of the family of keywords, sorted alphabetically. These retrieved citations were manually prescreened by IS prior to their release to the Polymer Group for close technical review and selection of the documents to be ordered. The CA machine search (1969-1974) identified 6,582 references. The period from 1958 to 1969 was searched manually, since it does not currently exist in a machine readable form. The literature coverage was the following:

Abstract Journal			No. of References
Chemical Abstracts (CA)			
	manual	1958 - 1968	12,000*
	machine	1969 - 1974 (April)	6,482
Scientific & Technical Aerospace Reports			
	manual	1968 - Present	50
USGRDR (GRA)		1968 - Present	40

*estimated figure - material was reviewed directly by technical staff - reference abstract cards were prepared for only most pertinent material.

Some 18,500 reference abstracts were identified and technically reviewed for the program. Approximately 500 reference documents were ordered for the program. These included government research reports, published journal articles, reprints, papers from proceedings, excerpts from handbooks, etc. The most significant works are reviewed in this report.

Table 1

Computer Retrieval Keywords

A	B	C
UV	Poly*	Atomic
Ultraviolet	Plastic	Alpha
Ultra-violet	Coating	Beta
Radiat	Paint	Gamma
Photo*	Resin	
	Film	
	Vacuum	
	Absorb*	
	Absorpt*	
	Degrad*	
	Silicone	
	PVC	
	Nylon	
	Teflon	
	Viton	
	Kel-F	
	Lexan	
	Kodel	
	Mylar	
	Kapton	
	Nomex	
	Neoprene	
	Saran	
	Astrel	
	Ekonol	

3. PHOTOLYTIC BEHAVIOR OF POLYMERIC MATERIALS

3.1 Ultraviolet Absorption and Photochemical Effect

The chemical changes resulting from exposure of a polymer to ultraviolet are controlled by the two fundamental laws of photochemistry that apply to any other type of non-polymeric material. The first law (generally known as the Grotthuss-Draper Law) states that only radiations that are absorbed by the material can produce a chemical change. Most polymers contain chemical groups which absorb ultraviolet light. The carbonyl group (C=O) occurs in many polymers and may cause ultraviolet absorption up to 2500-2800Å. Aromatic compounds absorb up to 3500Å; when combined with the carbonyl group they absorb to still higher wavelength. A carbon-carbon double bond (C=C) alone absorbs below 2500Å; but when several double bonds are conjugated they absorb at increasingly higher wavelength eventually reaching the visible range.

The second fundamental law of photochemistry is generally known as the Stark-Einstein law, or law of the photochemical equivalent (ref. 1): each molecule taking part in a photochemical reaction absorbs one quantum of the radiation causing the reaction. Since a quantum of energy is given by the product $h\nu$, according to the Stark-Einstein law the energy absorbed by a reacting molecule is also given by $h\nu$ (the product of Planck's constant and the frequency of the light absorbed).

If moles are substituted for molecules in the Stark-Einstein law, one obtains what is known as the Bohr law. If the energy absorbed by a molecule is $h\nu$, the energy absorbed by a mole is given by $E=Nh\nu = Nhc/\lambda$ (where N is the Avogadro's number and c the velocity of light). Inserting the values for N,c,h, and converting ergs into kilocalories, the Bohr law is obtained (λ is expressed in Angstrom units):

$$E = (2.86 \times 10^5/\lambda) \text{ kcal/mole}$$

The energy E for a given wavelength is usually referred to as the einstein of radiation; this is the energy of an Avogadro's number of photons, that is, the energy absorbed by a mole of absorbing substance. This equation allows a direct comparison between bond energies in polymers and absorbed energy at any given wavelength. For example, for a λ = 4000Å, the einstein is 71 kcal/mole; for a λ = 2537Å (a common wavelength in photochemical work), the einstein is 113 kcal/mole, more than enough to break a carbon-carbon bond. Typical values of bond energies are shown in Table 2.

The relationship between the photochemical effect of a radiation and the energy absorbed is usually expressed as quantum yield or quantum efficiency Φ:

$$\Phi = \frac{\text{number of broken bonds}}{\text{number of quanta absorbed}}$$

3.2 Effects of Impurities and Extraneous Materials

A ultraviolet transparent polymer must be stable to ultraviolet since there can be no damage without absorption. Unfortunately, transparency of a polymer to ultraviolet light is difficult, if not impossible, to achieve. Polyethylene and other saturated polyhydrocarbons, for example, should be inherently transparent at wavelengths higher than 2000Å. However, these polymers degrade under ultraviolet exposure, and the reason is that, to some extent, they do exhibit ultraviolet absorption. This absorption has been ascribed to impurities or structural irregularities in the polymer chains that may act as sensitizers of ultraviolet degradation. The problem of purity is very critical in the study of the photolysis of polymers. Conclusions relating polymer structure to stability can be misleading, if degradation is promoted by an unknown structural irregularity or impurity

Table 2

BOND ENERGY TERMS FOR GENERAL USE[a]

Bond	Bond Energy Term E (K cal./mole, 25°)
C-C	82.6
C=C	145.8
C≡C	199.6
C-N	72.8
C=N	147
C≡N	212.6
C-O	85.5
C=O aldehydes	176
C=O ketones	179
C-S	65
N-N	39
N=N	100
Si-O silicones	106?[b]

[a] All values are deduced from aliphatic compounds and are taken from T.L. Cottrell, "The Strengths of Chemical Bonds," Butterworths Scientific Publications, London, 1958, pp. 270-275.

[b] ? = doubtful value

that is not typical of the polymer structure. These are sites where the degradation reaction is often initiated since the energy required is lower than that required for breaking a regular bond. It is very difficult to determine the nature of the initial absorbing species, because of their very low concentration. The formation of carbonyl groups by oxidation during polymerization or processing of polyolefins may be responsible for the initial absorption and could initiate photolytic degradation (ref. 1a, 2). It has been reported (ref. 3) that aromatic impurities such as phenanthrene, anthracene and naphthalene are present in polyethylene and act as sensitizers of ultraviolet degradation. The use of model compounds in the study of polymer photolysis has the very important advantage that the study is conducted on pure materials.

3.3 Relationship Between Absorption and Stability

Although ultraviolet instability is undoubtedly related to ultraviolet absorption, the relationship between transparency and stability is not simple to predict For example, traces of keto groups in polyethylene make the polymer very sensitive to ultraviolet light, whereas poly(methylmethacrylate) with one keto group for each repeating unit is among the polymers with the highest ultraviolet stability. It appears that some polymer structures, unlike others, have a mechanism for dissipating absorbed energy that otherwise would cause breakdown of the chain. Absorbed energy can be dissipated as heat or re-radiated at longer wavelength. A better understanding of these phenomena would probably explain why the same absorbing group may have a negative effect on ultraviolet stability in a certain polymer structure and be relatively harmless in another structure.

An interesting question is whether the effect of ultraviolet on polymers can be predicted on the basis of a knowledge of the effect of gamma or other ionizing radiation. A few studies have been concerned with comparing the effect of ultraviolet and gamma radiation on polymers. Charlesby has demonstrated for poly(methylmethacrylate) (ref. 4) that the degradation process due to ionizing and ultraviolet irradiation is the same; only the efficiency of the two processes differ, since the energy absorbed per main chain cleavage is about 550 eV with ultraviolet radiation and about 65 eV with gamma radiation. A part from this difference in efficiency, Charlesby concludes that the two reactions are very similar and result in the formation of similar free radicals, as seen by EPR. (It must be noted that "ionizing" radiations do not normally produce ionization in organic polymers, and the observed effects are generally explained in terms of free radical reactions with no participation of ionic species). In a following paper, however, Charlesby (ref. 5) points out an important difference between gamma and ultraviolet irradiation of poly-(methylmethacrylate): the susceptibility of an ester group in polymethylmethacrylate to undergo homolysis by ultraviolet radiation is about 40 times that with gamma radiation, when compared to the susceptibility of the main chain. This pronounced difference is ascribed to the fact that while gamma radiation is absorbed at random by the polymer chain, absorption of ultraviolet is selective at the keto group of the ester link. It may be concluded that the selective absorption of ultraviolet light is responsible for the different effect of ultraviolet and gamma radiation. This consideration is certainly applicable to polymer structures other than poly(methylmethacrylate).

It is interesting to note that some high-temperature aromatic polymers that are highly stable to gamma-radiation, such as the polyarylsulfones, are very unstable to ultraviolet radiation (ref. 6,7,8). This behavior is often observed with aromatic structures exhibiting high absorption in the ultraviolet region.

A few studies have appeared on the wavelength dependence of photodegradation in organic polymers. As a general rule, the lower the wavelength of the radiation absorbed the greater is the damage (ref. 9). However, it has been found that, in the case of aromatic polyamides, the most damaging radiation lies in the near ultraviolet region (ref. 10). The reason for this unusual behavior is not explained. It is difficult to see how a less energetic ultraviolet radiation could cause more damage than a shorter, more energetic radiation that is equally absorbed by the polymer.

3.4 Physicochemical Aspects of Polymer Photolysis

It is important to consider the various events that may follow absorption of a photon by a certain group in a polymer molecule. Most organic molecules lie in a singlet ground state. Absorption of a photon raises the molecule to an excited singlet or triplet state. If the molecule has sufficient energy in the excited state, whether it be singlet or triplet, bond dissociation may take place. This bond-breaking process is relatively slow and is statistically more probable in the long-lived triplet state. If a C-H bond is broken, the process of excitation and decomposition can be represented as follows:

$$RH \xrightarrow{h\nu} RH^*$$

$$RH^* \longrightarrow R\cdot + H\cdot$$

This decomposition process must compete with other deexcitation processes. The excited molecule may revert to the ground state by radiationless transitions and the emission of heat. Reversion to the ground state may also be accomplished by photon emission: the excited molecule re-radiates part of the energy at a longer wavelength as the electron returns to the ground state. This phenomenon is known as fluorescence or phosphorescence, depending on whether the excited state is a singlet or a triplet, and whether or not there is a time lag in the re-radiation process. These harmless deexcitation processes allow the excited molecule to return to the ground state without producing a chemical change:

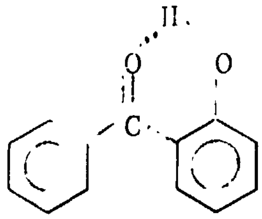
$$RH^* \longrightarrow RH + \text{heat}$$

$$RH^* \longrightarrow RH + h\nu$$

Reversion to the ground state may also be accomplished by transfer of electronic energy to another group in the vicinity of the excited molecule:

$$M_1^* + M_2 \longrightarrow M_1 + M_2^*$$

Such electronic energy transfer is believed to play an important role in polymer photodegradation, particularly where long-lived triplet states are involved (ref. 11). The importance of energy transfer processes becomes apparent if one considers that photolytic degradation is not entirely a consequence of absorption of a photon by the particular group undergoing degradation. Very often energy is transfered to this "weak" group from a different absorbing group in the polymer or from an absorbing impurity. Some workers have devoted considerable attention to the study of polymer photolysis in the presence of "sensitizing" impurities, such as the photolysis of silicones in the presence of naphthalene (ref. 12) or the photolysis of polypropylene in the presence of phenanthrene (ref. 13). Electronic energy transfer is involved in the sensitized degradation process. An interesting case of intramolecular energy transfer is the photolysis of polymethylphenylsiloxane (ref. 14), in which photodegradation occurs predominantly at the methyl group, although the phenyl group is responsible for absorption It is interesting at this point to observe the similarity between a "stabilizer" and a "sensitizer" of ultraviolet degradation. Both molecules are strong ultraviolet absorbers and will reach an excited state as a result of photon absorption. The "sensitizer" will return to the ground state by transfer of energy to the polymer, therefore initiating degradation. The stabilizer will return to the ground state by re-radiating the absorbed energy as heat or as a photon of longer wavelength. For a stabilizer to be effective it is essential that the energy of excitation be dissipated quickly. Since transfer of energy to the polymer is a competitive process, the rate of deexcitation is very critical. It is interesting to observe that while benzophenone is a sensitizer of photochemical reactions and is quite reactive in its excited state, o-hydroxy benzophenone is very stable to ultraviolet, and is in fact used as ultraviolet stabilizer. There is substantial evidence that the reason for the stability of o-hydroxybenzophenone is the ability of the photoexcited molecule to return to the ground state through a radiationless transition so that the energy is given up in the form of harmless heat (ref. 19,20). This behavior is undoubtedly associated with the capability of the o-hydroxybenzophenone to form an intramolecular six-membered hydrogen-bonded ring:



The excited state induced by absorption of a quantum of light is deactivated through a reversible mechanism that leaves the stabilizer molecule unchanged and does not cause any chemical effect in the polymer.

Recently it has been demonstrated that compounds that do not absorb the incident radiation can also stabilize the polymer by abstraction of the excited state energy from the polymer molecule. Guillet refers to these types of compounds as "quenchers" (ref. 15). Heskins and Guillet (ref. 16) have shown that 1,3-cyclooctadiene can quench the excited triplet state in polyvinylketones and ethylene-carbon monoxide copolymers and stabilize these polymers against photodegradation. There is strong evidence that the mechanism of action of nickel chelates of thiobisphenols (ref. 17), that are known to be good stabilizers for polyolefins, involves primarily an energy transfer mechansim. The stabilizing effect of pyrene and p-terphenyl in poly(methylmethacrylate) was also interpreted in terms of an energy transfer mechanism (ref. 18).

4. PHOTODEGRADATION OF VARIOUS POLYMER CLASSES

In this section, some important classes of polymeric materials are reviewed with a brief discussion of their photolytic behavior. It should be noted that because of proprietary interests, much of the literature pertaining to polymer photochemistry does not appear in scientific journals. Much of the data on photostabilization, for instance, is to be found in the patent literature. The publications reviewed here are the ones which have the greatest scientific merit and the ones that deal more specifically with the mechanisms of photolysis. Particular consideration has been given to studies dealing with photolysis in vacuum, although some studies performed in air have been included, depending upon their technical relevance, and whether or not any study performed in vacuum was available on that particular polymer.

4.1 Polyethylene

A pure polyethylene chain should not absorb radiations of wavelength higher than 2000Å. In reality, polyethylene does absorb in the ultraviolet due to impurities or irregularities in the polymer chain. Since impurities and irregularities may vary with the sample and the source of the polymer, the interpretation of the results and the comparison of data of different authors is particularly difficult. The formation of carbonyl groups as a result of oxidation during polymerization or processing is often blamed for ultraviolet absorption and consequent instability of polyethylene. Charlesby and Partridge (ref. 1a,2) have shown that carbonyl groups are indeed present in polyethylene and that the ultraviolet and gamma induced thermoluminescence and phosphorescence of polyethylene are associated with the presence of carbonyl impurities.

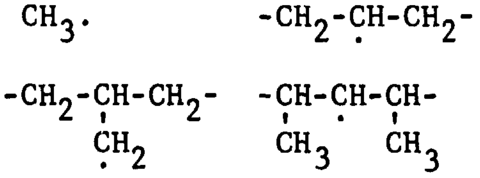
Polyethylene undergoes much faster physical change upon irradiation in air than in nitrogen (ref. 21). Charlesby (ref.22) exposed polyethylene to 2537Å radiation both in oxygen and in nitrogen; he found that ultraviolet exposure results in an increased absorbance in the 2000-2800Å region, and ascribed the absorbtion to conjugated unsaturation. Cotten (ref. 23) showed that both chain-scission and cross-linking take place on irradiation of polyethylene in air, and that scission is favored in the highly crystalline region. Since the diffusion rate of oxygen into amorphous regions is greater than in crystalline regions, cross-linking occurs preferentially in the amorphous regions (ref. 24). Ohnishi (ref. 25) irradiated polyethylene in vacuum with electrons at -78°C and by EPR, found allyl radicals, these allyl radicals are converted to alkyl radicals under 2537Å irradiation. The total radical concentration does not change, indicating the existence of an alkyl-allyl equilibrium:

$$\mathrm{-CH_2-\dot{C}H-CH{=}CH-} \rightleftarrows \mathrm{-\dot{C}H-CH_2-CH{=}CH-}$$

Pivovarov (ref. 3) reported that polyethylene always contains phenanthrene, anthracene and naphthalene as impurities, and that these aromatic compounds act as sensitizers of ultraviolet degradation.

4.2 Polypropylene

Several free radical species have been detected by Yoshida (ref. 26) and Browning (ref. 27) in the EPR spectrum of irradiated polypropylene:



$$\mathrm{CH_3\cdot} \qquad \mathrm{-CH_2-\underset{\cdot}{C}H-CH_2-}$$

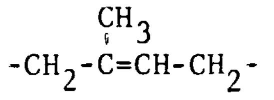
$$\mathrm{-CH_2-\underset{\underset{\underset{\cdot}{CH_2}}{|}}{C}H-CH_2-} \qquad \mathrm{-\underset{\underset{CH_3}{|}}{C}H-\underset{\cdot}{C}H-\underset{\underset{CH_3}{|}}{C}H-}$$

Milinchuk (ref. 28) has observed the same type of allyl-alkyl free radical equilibrium described for polyethylene in the ultraviolet irradiation of polypropylene in the absence of air. In the presence of air, peroxy radicals derived from both the allyl and alkyl radical are formed. Klinshport (ref. 29) finds that the transformation is reversible and in the dark the alkyl radical is transformed into allyl radical. Malinskaya (ref. 13) has studied the photolysis of polypropylene containing phenanthrene as sensitizer. He found by EPR the same radicals described by Yoshida and Browning; he suggests that the samples studied by these workers contained undetected amounts of aromatic impurities. McTigue (ref. 30) reported that pigments are beneficial for ultraviolet stability of polypropylene and that carbon black is the most effective.

4.3 Unsaturated Polyhydrocarbons

A paper by Golub (ref. 31) reviews the photolysis in vacuum of the following unsaturated polymers

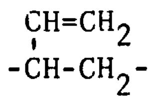
1,4 polyisoprene:



$$-CH_2-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-$$

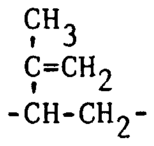
1,4 polybutadiene: $-CH_2-CH=CH-CH_2-$

1,2 polybutadiene:



$$-\overset{\overset{CH=CH_2}{|}}{CH}-CH_2-$$

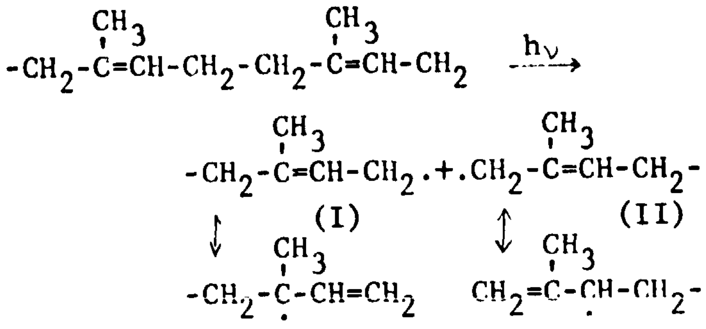
3,4 polyisoprene:



$$-\overset{\overset{\overset{CH_3}{|}}{C=CH_2}}{\overset{|}{CH}}-CH_2-$$

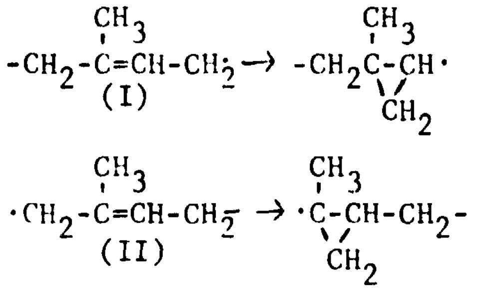
These polymers were found to undergo a radiation induced cis-trans isomerization.

In the irradiation of 1,4 polyisoprene and 1,4 polybutadiene, the energy absorbed by the double bond is diverted into breaking C-C bonds connecting the repeating units:

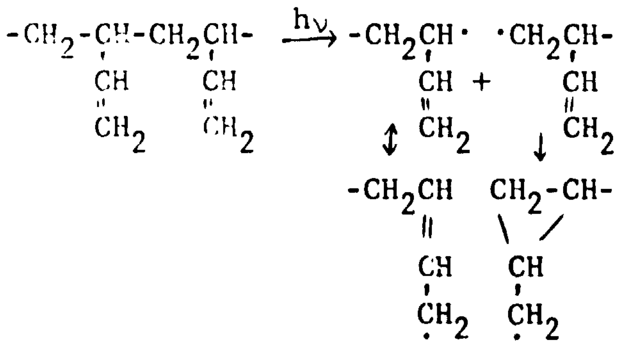


The C-C bond connecting the repeating units is the weakest bond in the chain, with a strength (55 kcal/mole) which is lowered from the normal C-C bond strength by the resonance energy of the two allyl radicals formed on chain scission.

The formation of cyclopropyl groups during photolysis is explained as follows:



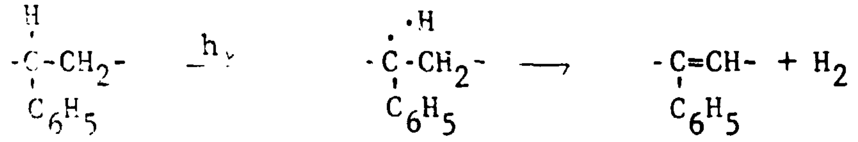
With 1,2-polybutadiene and 3,4-polyisoprene a similar process of chain cleavage takes place:



Cyclopropyl group formation takes place by a process similar to the one shown for 1,4-polyisoprene.

4.4 Polystyrene

In spite of the large amount of literature on the photolysis of polystyrene, only two studies, one by Fox (ref. 32) the other by Grassie (ref. 33), deal with the mechanisms of photolysis in vacuum. These workers exposed films of polystyrene to 2537Å radiation in vacuum. They found that ultraviolet radiation causes almost exclusively cross-linking. Chain scission was negligible, unless oxygen was present. Yellowing was very pronounced, even in the absence of oxygen. Grassie suggests that color is due to conjugated unsaturation, and he points out that on melting a degraded film that was yellow the color of the melt turns immediately black. He indicates that the photolytic process that is energetically more favorable involves removal of the hydrogen atom from the tertiary carbon:

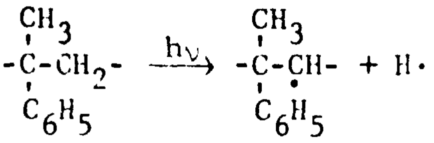


$$-\underset{C_6H_5}{\overset{H}{C}}-CH_2- \xrightarrow{h\nu} -\underset{C_6H_5}{\overset{\cdot H}{\dot{C}}}-CH_2- \longrightarrow -\underset{C_6H_5}{C}=CH- + H_2$$

Cross-linking results from recombination of the tertiary radicals formed by hydrogen abstraction. As a general rule, the more reactive the removed hydrogen, the less reactive the resulting free radical; therefore, cross-linking occurs. Alternately, the less reactive the hydrogen, the more reactive the new free radical, and chain scission becomes the predominant reaction.

4.5 Poly(α-methylstyrene)

Substitution of a methyl group for the α-hydrogen in polystyrene results in a structure that degrades in a totally different way. In polystyrene, the photolysis involves exclusively cross-linking, whereas in poly(α-methylstyrene) photolysis involves exclusively chain scission:



$$-\overset{CH_3}{\underset{C_6H_5}{C}}-CH_2- \xrightarrow{h\nu} -\overset{CH_3}{\underset{C_6H_5}{C}}-\dot{C}H- + H\cdot$$

The reason for the different behavior is due to the fact that a relatively stable tertiary radical is formed with polystyrene while an unstable secondary radical is the precursor to the more rapid chain scission occurring in poly(α-methylstyrene). The less stable the radicals, the more likely are they to decompose rather than to combine to give cross-links (ref. 34).

Stokes and Fox (ref. 35) have studied the photolysis of poly(α-methylstyrene) films in vacuum. Monomer is formed by depolymerization and the monomer yield increases with increasing temperature. At 27°C, the quantum yield for random scission was 10^{-3} and for monomer formation 7×10^{-3} (approximately 7 monomer units for each scission). At 155°C, the quantum yield for scission was 2×10^{-2} and for monomer formation 0.5 (approximately 25 monomer units for each scission).

4.6 Fluorocarbon Polymers

Many papers have been published on the effects of gamma irradiation on fluorocarbon polymers, but very little has been published on ultraviolet irradiation. Bowers (ref. 36) studied the cross-linking of fluoropolymers by irradiation at elevated temperatures. The source used was a Pen-Ray quartz mercury lamp, emitting radiation principally at 1849 and 2536Å. Under nitrogen, ultraviolet irradiation of poly(chlorotrifluoroethylene) at 250°C resulted in degradation while only minor degradation was observed with poly(tetrafluoroethylene) at 325°C; no cross-linking was noted. With Teflon 100 FEP (a copolymer of tetrafluoroethylene and hexafluoropropene) both scission and cross-linking occur and the latter increases with increasing temperature.

Stephenson (ref. 37) studied the photolysis of polytetrafluoroethylene both in nitrogen and vacuum. Unlike other polymers, the drop in tensile strength and elongation by irradiation with 2537Å ultraviolet light is more rapid in vacuum than in nitrogen. A study of the wavelength dependence of photodegradation of poly(tetrafluoroethylene) showed that the efficiency in producing degradation increases with decreasing wavelength (ref. 37). A study of the absorption spectrum of polytetrafluoroethylene (as well as of other unfluorinated polyhydrocarbons with no natural absorption in the ultraviolet) showed that polymer absorption and luminescence in the UV range are due to aromatic impurities (ref. 3).

4.7 Poly(methylmethacrylate)

The photolysis of poly(methylmethacrylate) has been studied in great depth by several workers. The photolytic process is very similar to poly(α-methylstyrene), in that the polymer undergoes random chain cleavage with no cross-linking. Photodegradation at room temperature produces small amounts of volatile materials, but the formation of monomer by "unzipping" increases with increasing temperature.

Fox (ref. 9) points out that because of the low absorption coefficient of poly(methylmethacrylate) at 2537Å, this radiation can penetrate a thin film with only slight attenuation, whereas with more highly absorbing polymers a "skin" effect is produced. The photolysis of poly(methylmethacrylate) was studied in vacuum at 25°C with a medium pressure mercury lamp. The quantum yield for random scission is 4×10^{-2}. Methyl formate, methanol and methylacrylate are formed in quantum yields of 0.14, 0.48 and 0.20, respectively, indicating a depolymerization of about five monomer units for chain break (ref. 38).

Charlesby and Thomas (ref. 4) studied the photolysis in vacuum, air and nitrogen. Surprisingly, the quantum yields in air or nitrogen are lower than in vacuum. Fox (ref. 9) points out that oxygen might act as an inhibitor by scavenging secondary polymer radicals which are precursors to chain scission. While nitrogen might suppress the diffusion of gases from the film, it is difficult to see how this could affect the rate of scission.

Many workers have noted the appearance of a new band at 2850Å in ultraviolet irradiated poly(methylmethacrylate). This new band appears by irradiation either in air or vacuum, and remains with the polymer even after reprecipitation, indicating that the absorbing group is part of the chain (ref. 38). Fox (ref. 38) ascribes the 2850Å absorption to a carbonyl chromophore formed by secondary reactions after homolysis of the ester. Frolova (ref. 39) ascribes it to conjugated unsaturation in the chain, because the absorption shifts to higher wavelengths during irradiation. He supports this conclusion with a study of the IR spectrum of the irradiated polymer that shows new bands at 1615 and 1640cm^{-1} indicative of the presence of olefinic unsaturation.

Electron spin resonance spectra of ultraviolet and gamma irradiated poly(methylmethacrylate) are identical, indicating that the same free radicals are present in the irradiated polymers (ref. 40,4).

4.8 Poly(methylacrylate)

A study by Fox (ref. 41) indicates the formation of a weak band at 2800Å on irradiation in vacuum at 2537Å. The main volatile products are formaldelyde, methanol and methylformate (from ester group decomposition), along with CO_2 and hydrogen. The rate of CO_2 formation increases with dose; since the end-group concentration increases with dose, it is suggested that CO_2 comes from the terminal end groups.

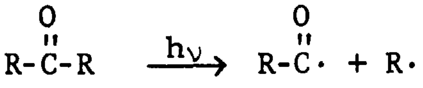
4.9 Poly(ethylacrylate)

A study by Jacobs (ref. 42,43) shows that both cross-linking and chain scission take place during irradiation. The time necessary to produce insoluble gels increases with decreasing temperature. Below the glass transition temperature (-17°C) there is no formation of insoluble products. It appears that when the mobility of the chain is reduced, the recombination of radicals to give cross-links is less likely to occur.

4.10 Polyketones

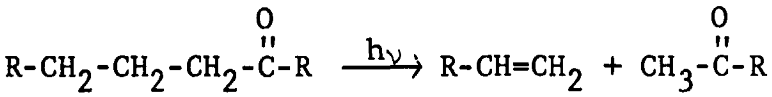
The study of the photolysis of polyketones is particularly interesting because the photolysis of simple aliphatic ketones is a well understood process. Two primary reactions are known to occur in the photolysis of aliphatic ketones:

Norrish Type I:



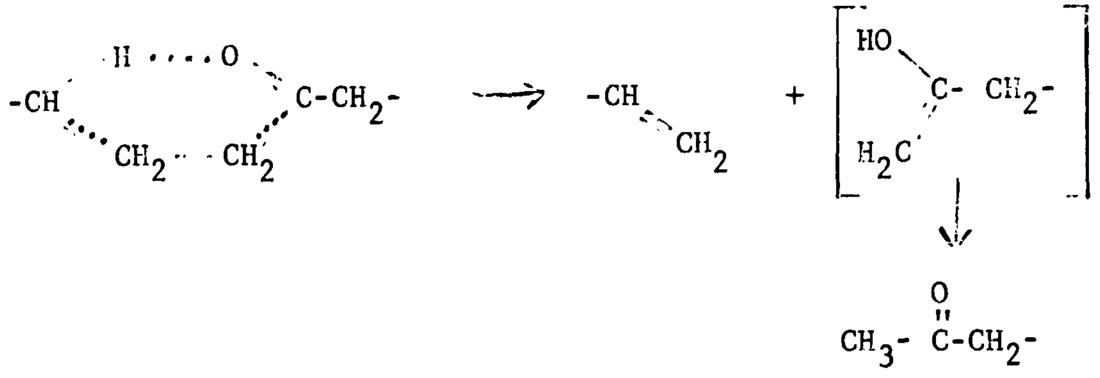
$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{h\nu} R-\overset{O}{\overset{\|}{C}}\cdot + R\cdot$$

Norrish Type II:



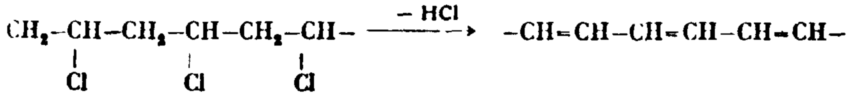
$$R-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-R \xrightarrow{h\nu} R-CH=CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-R$$

Wissbrun (ref. 44) studied the photolysis of poly(methylvinylketone) at 3130Å. An increased absorption below 2500Å was observed, and acetaldehyde, carbon monoxide and methane were formed in quantum yields of 0.06, 0.003, and 0.0006 at 80°C. Guillet (ref. 45) studied the photolysis of poly(methylvinylketone) and polyethylene-carbon monoxide copolymer. He finds that the photolysis of polyketones is described very well by the Norrish type I and II. It is interesting to note that the Norrish type II follows a molecular mechanism that does not involve formation of free radicals:



4.11 Polyvinylchloride

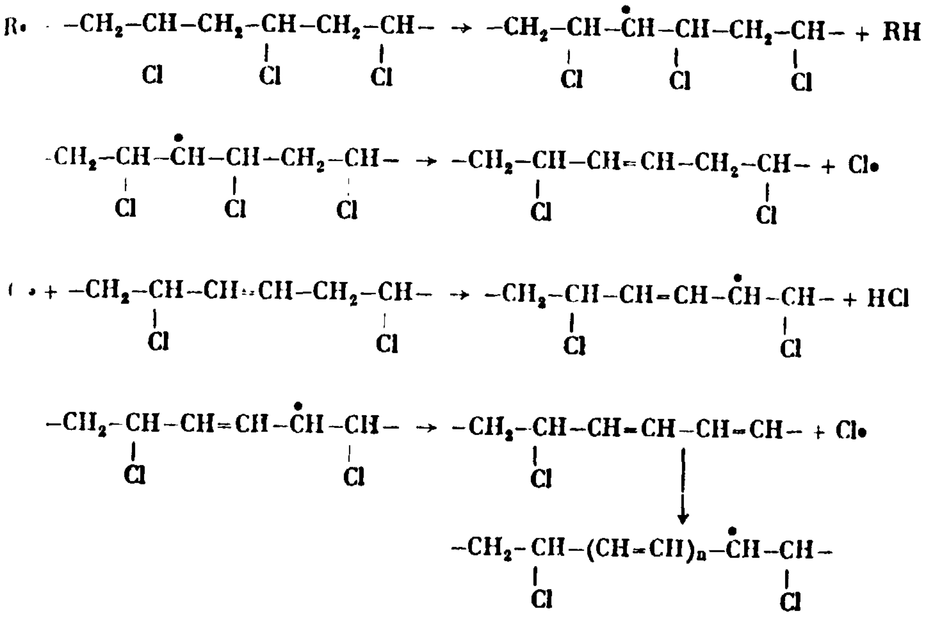
The spectroscopic changes produced by ultraviolet irradiation in vacuum of PVC films have been studied by Golub (ref. 96). The main photolytic effect is the formation of a conjugated polyene system through progressive loss of HCl:



$$\mathrm{CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-} \xrightarrow{-\mathrm{HCl}} \mathrm{-CH=CH-CH=CH-CH=CH-}$$

As the sequence of conjugated double bonds increases, absorption increases progressively from the ultraviolet to the visible portion of the spectrum. Consequently, PVC films become increasingly colored on irradiation. The quantum yield for HCl formation is independent of wavelength below 3400Å, which is the effective photochemical cut-off wavelength.

The following free-radical mechanism has been proposed for the dehydrochlorination reaction:



$$\mathrm{R\cdot\ -CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-} \rightarrow \mathrm{-CH_2-\underset{Cl}{CH}-\dot{C}H-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}- + RH}$$

$$\mathrm{-CH_2-\underset{Cl}{CH}-\dot{C}H-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-} \rightarrow \mathrm{-CH_2-\underset{Cl}{CH}-CH=CH-CH_2-\underset{Cl}{CH}- + Cl\cdot}$$

$$\mathrm{Cl\cdot + -CH_2-\underset{Cl}{CH}-CH=CH-CH_2-\underset{Cl}{CH}-} \rightarrow \mathrm{-CH_2-\underset{Cl}{CH}-CH=CH-\dot{C}H-\underset{Cl}{CH}- + HCl}$$

$$\mathrm{-CH_2-\underset{Cl}{CH}-CH=CH-\dot{C}H-\underset{Cl}{CH}-} \rightarrow \mathrm{-CH_2-\underset{Cl}{CH}-CH=CH-CH=CH- + Cl\cdot}$$

$$\downarrow$$

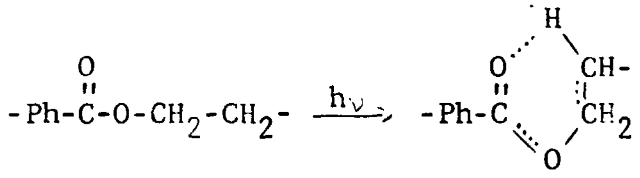
$$\mathrm{-CH_2-\underset{Cl}{CH}-(CH=CH)_n-\dot{C}H-\underset{Cl}{CH}-}$$

4.12 Polyacrylonitrile

Jellinek (ref. 46) reported that exposure of polyacrylonitrile to 2537Å irradiation in vacuum results in cross-linking and formation of HCN. Fox (ref. 9) points out that the longest wavelength absorption maximum of the nitrile group is about 1600Å. Polyacrylonitrile should therefore, be very transparent to ultraviolet. However, absorption occurs with a maximum at 2650Å that is somehow associated with the polymer structure itself. The chromophore causing the absorption has not been identified.

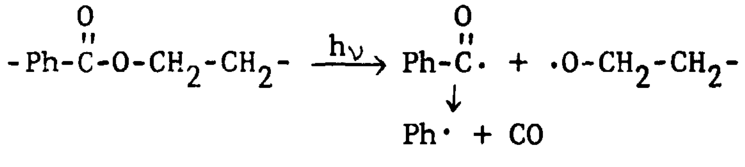
4.13 Polyesters

Three recent papers have been published by Day and Wiles on the photolysis of poly(ethyleneterephthalate) in nitrogen and air (ref. 47, 48, 49). As a result of irradiation, an increase in carboxyl groups was observed, that was ascribed to the decomposition of the ester group by a Norrish Type II process:



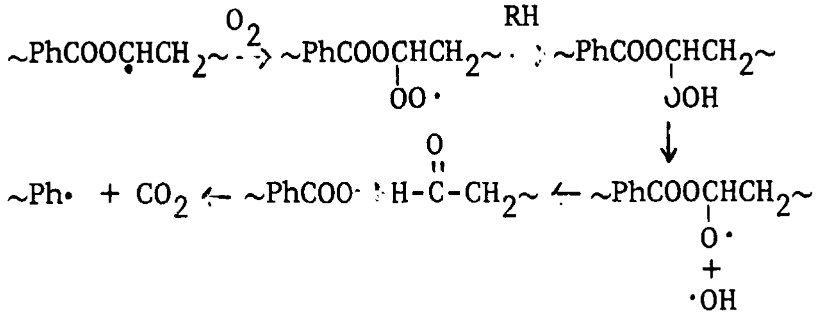
$$\text{-Ph-COOH} + \text{CH}_2\text{=CH-}$$

They found that CO and CO_2 were the major volatile products and that CO_2 was formed primarily in the presence of air. The formation of CO was explained on the basis of a Norrish Type I cleavage reaction:



$$\text{-Ph-}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-O-CH}_2\text{-CH}_2\text{-} \xrightarrow{h\nu} \text{Ph-}\overset{\text{O}}{\overset{\|}{\text{C}}}\cdot + \cdot\text{O-CH}_2\text{-CH}_2\text{-}$$
$$\downarrow$$
$$\text{Ph}\cdot + \text{CO}$$

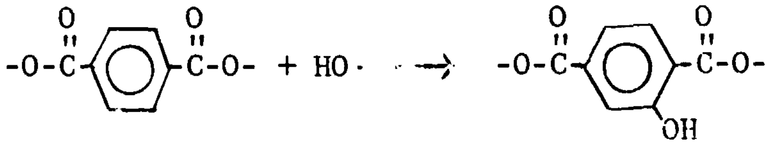
The fact that CO_2 formation takes place primarily in the presence of oxygen suggests that hydroperoxidation is involved:



$$\sim PhCOO\underset{\bullet}{C}HCH_2\sim \xrightarrow{O_2} \sim PhCOO\underset{OO\cdot}{C}HCH_2\sim \xrightarrow{RH} \sim PhCOO\underset{OOH}{C}HCH_2\sim$$

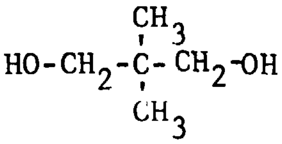
$$\sim Ph\cdot + CO_2 \leftarrow \sim PhCOO\cdot + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\sim \leftarrow \sim PhCOO\underset{O\cdot}{C}HCH_2\sim + \cdot OH$$

Another phenomenon observed in poly(ethyleneterephthalate) irradiated in the presence of air is the appearance of a fluorescent band at 4600Å. This band was ascribed to the formation of an hydroxylated derivative resulting from the attack of the OH radical (formed from the reaction above) on the phenyl ring:



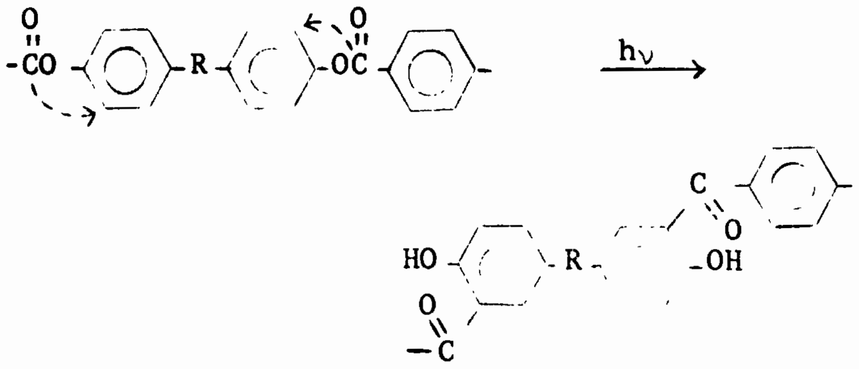
The nature of the fluorescent product was confirmed by Pacifici (ref. 50) who compared the fluorescence spectrum of irradiated poly(ethyleneterephthalate) with that of synthetic hydroxylated polyesters.

It has been reported (ref. 51) that polyester compositions based on neopentylglycol exhibit superior ultraviolet resistance. This is probably due to the fact that the cleavage of the ester via Norrish Type II cannot occur because of the absence of hydrogen on the carbon atom β to the hydroxyl groups in neopentylglycol:



$$HO\text{-}CH_2\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2\text{-}OH$$

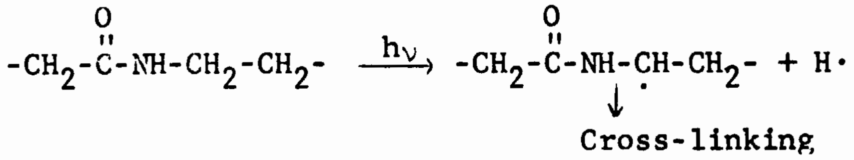
A paper by Cohen (ref. 42) describes a number of aromatic polyesters that under ultraviolet irradiation rearrange to an o-hydroxybenzophenone structure according to the photo-Fries reaction:



These polyesters are reported to be useful as coatings for protecting substrates ordinarily sensitive to ultraviolet light. We did not find any work dealing with the ultraviolet irradiation of polycarbonates.

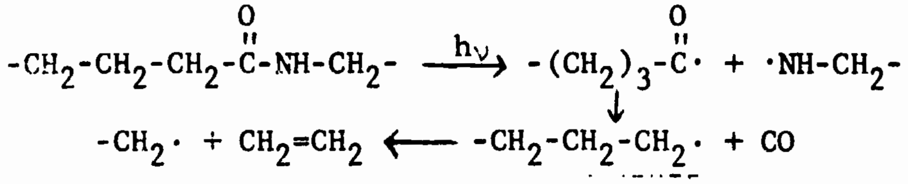
4.14 Polyamides

A paper by Moore (ref. 53) deals with the photolysis of Nylon 66 and of model N-alkyl amides both in nitrogen and air. Both crosslinking and chain scission were found to occur. The mechanisms proposed are basically in agreement with the mechanisms proposed previously by Rafikov (ref. 54). The mechanism for cross-linking involves elimination of an hydrogen atom from the carbon adjacent to the nitrogen atom followed by combination of two radicals:



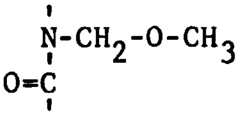
$$-CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2- \xrightarrow{h\nu} -CH_2-\overset{O}{\overset{\|}{C}}-NH-\underset{\substack{\cdot\\ \downarrow \\ \text{Cross-linking}}}{CH}-CH_2- + H\cdot$$

The mechanism for chain scission involves cleavage of C-N bonds with subsequent formation of CO and ethylene:

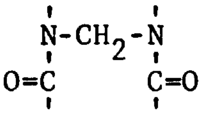


$$\begin{tikzcd} -CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2- \arrow[r, "h\nu"] & -(CH_2)_3-\overset{O}{\overset{\|}{C}}\cdot + \cdot NH-CH_2- \arrow[d] \\ -CH_2\cdot + CH_2{=}CH_2 & -CH_2-CH_2-CH_2\cdot + CO \arrow[l] \end{tikzcd}$$

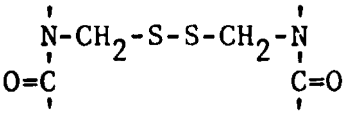
Brick (ref. 55,56) reported some structural modifications of Nylon 6 that produce a fiber crimping effect. The following Nylon 6 modifications were considered:



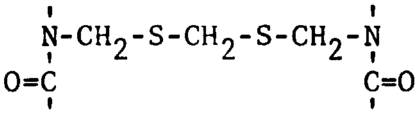
$$\begin{array}{rl} & | \\ & N-CH_2-O-CH_3 \\ & | \\ O= & C \\ & | \end{array}$$



$$\begin{array}{rlcl} & | & & | \\ & N-CH_2- & & N \\ & | & & | \\ O= & C & & C=O \\ & | & & | \end{array}$$



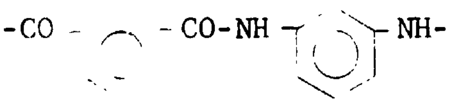
$$\begin{array}{rlcl} & | & & | \\ & N-CH_2-S-S-CH_2- & & N \\ & | & & | \\ O= & C & & C=O \\ & | & & | \end{array}$$



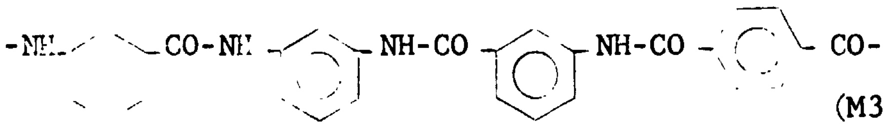
$$\begin{array}{rlcl} & | & & | \\ & N-CH_2-S-CH_2-S-CH_2- & & N \\ & | & & | \\ O= & C & & C=O \\ & | & & | \end{array}$$

These structures were reported to possess good ultraviolet stability (with the exception of the disulfide). Comparative data with the ultraviolet stability of unmodified Nylon 6 were not given.

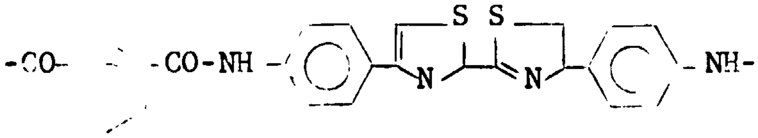
A paper by Johnson (ref. 10) discusses the photodegradation of three aromatic polyamides:



(NOMEX) (1)



(M3P) (2)



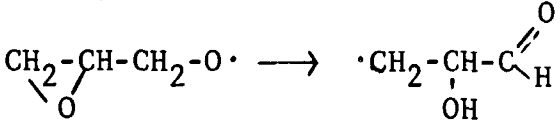
(BTA) (3)

A study of the wavelength dependence of photodegradation shows that all three polymers are degraded by light of much longer wavelength than that which is harmful to other polymers. Polymer (1) and (2) show degradation maxima at 3600 and 3700Å; polymer(3)is degraded significantly even by visible light (particularly 4140Å). The mechanism of degradation is not known.

A study by Krasny (ref. 57) on the photostabilization of Nomex fibers confirms that Nomex is particularly sensitive to photodegradation in the wavelength region of 3600-3900Å. Ultraviolet stabilizers exhibiting strong absorption in this critical wavelength region were found to be unsatisfactory because of polymer incompatibility or other undesirable effects.

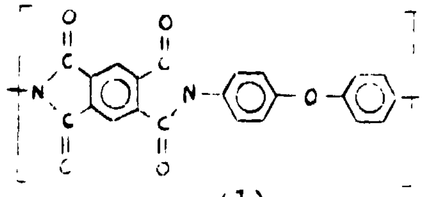
4.15 Polyethers

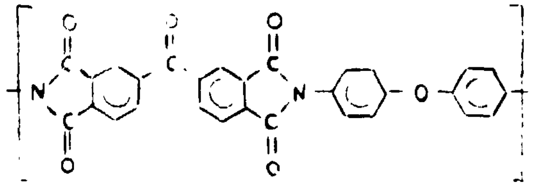
Kelleher (ref. 58) studied the photoxidation of poly(oximethylene) and found that random chain scission occurs followed by extensive depolymerization to formaldehyde. A similar process occurred in a oxyethylene-oxymethylene copolymer, except that depolymerization appeared to stop at the ethylene unit. Grassie (ref. 59) studied the photoxidation of poly(oxymethylene) at 2537 and 3650Å. Hydrogen and carbon monoxide were the main decomposition products. Irradiation in air produced well defined changes in the hydroxyl and carbonyl regions of the infrared spectrum. Irradiation at 2537Å was approximately 100 times more effective than 3650Å irradiation. Sukhareva (ref. 60) studied the spectra of ultraviolet irradiated epoxy coatings and observed the appearance of a band with a frequency of $1685 cm^{-1}$ that was ascribed to the carbonyl group. Carbonyl group formation takes place by a radical mechanism of epoxy decomposition at the terminal groups, leading to the formation of free radicals that can subsequently isomerize:

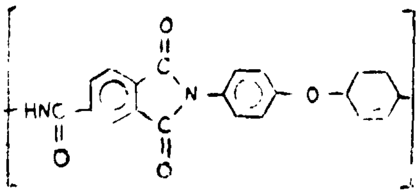


4.16 Polyimides and Polyamide-imides

Alvino (ref. 61) studied the ultraviolet stability of the following polyimides and polyamide-imide:


(1)

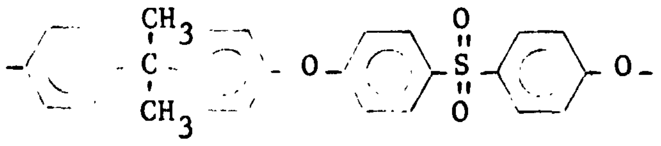

(2)


(3)

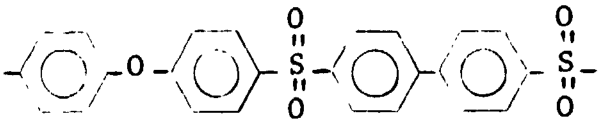
He found that these polymers were sensitive to ultraviolet light, especially in the presence of moisture. the mechanical and electrical properties of (3) deteriorated more rapidly than those of (1) and (2) under both wet and dry conditions. The increase in deterioration rate on going from dry to wet environment was much greater for (1) and (2) than for (3), indicating that (3) had greater hydrolytic resistance. The electrical properties of (1) and (2) were unaffected by ≤ 6000hr irradiation in a dry environment.

4.17 Polysulfones

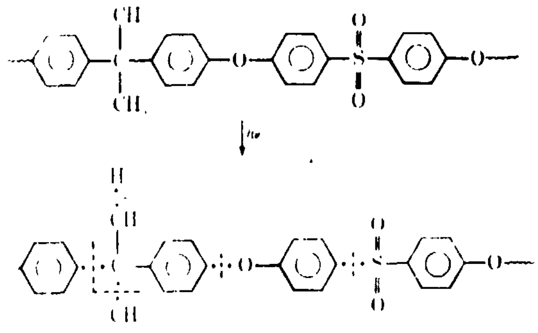
Aromatic polysulfones have been reported to possess outstanding resistance to high energy radiation (ref. 6). Their ultraviolet stability, however, is very poor. Poor ultraviolet stability has been reported for the Union Carbide polysulfone (ref. 7):



and for the 3M polysulfone ("Astrel" 360) (ref. 8):



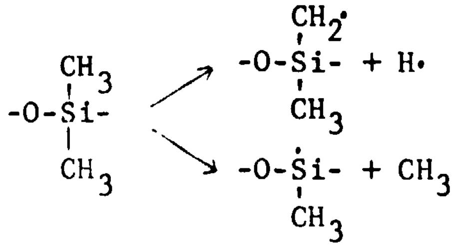
The work of Gesner and Kelleher (ref. 7) provides a good description of the photo-oxidative behavior of the Union Carbide polysulfone, which is consistent with a random chain scission mechanism. In the initation process, scission apparently takes place at every bond except the aromatic C-C and C-H bonds:



The work of Alvino (ref. 8) on 3M polysulfone shows some interesting analogies with the results obtained by Gesner and Kelleher on the Union Carbide polysulfone. Both works indicate the formation of short chain molecules with acid functionalities (sulfonic acid groups) resulting from chain scission reactions.

4.18 Silicones

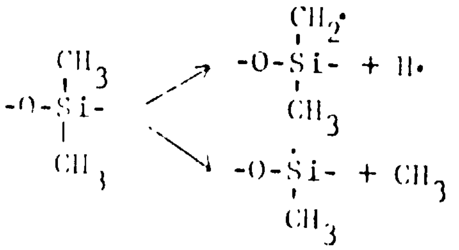
Siegel and Judeikis (ref. 12) studied the photolysis of poly(dimethylsiloxane) samples containing naphthalene as sensitizer. The samples were irradiated in the cavity of an ESR spectrometer. A mercury arc lamp having essentially zero output below 2400Å was employed. The process by which the polymer molecules become excited involves a transfer of electronic energy from naphthalene in an excited triplet level. Decomposition occurs via Si-C and C-H bond rupture. In the initial stage of photolysis, the following reactions take place with essentially equal probability:

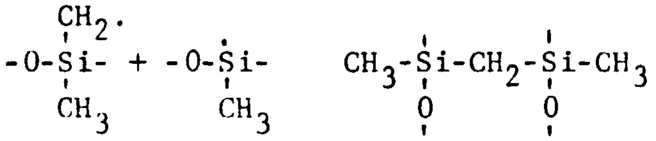


All the resulting radicals were identified by means of their ESR spectra, with the exception of the hydrogen atoms that presumably react immediately to form H_2 and $-CH_2\cdot$ radicals.

Zhuzhgov (ref. 14) studied the photolysis of poly(methylphenylsiloxane) in the cavity of an ESR spectrometer. No sensitizer was added, but absorption was promoted by the presence of the phenyl group in the polymer. The ESR spectrum indicated the formation of $CH_3\cdot$ and $-CH_2\cdot$ radicals. Formation of $CH_3\cdot$ radicals appears to involve a two-step process requiring the absorption of two quanta of light (biphotonic mechanism). No evidence was found in the ESR spectrum for the formation of silicon radicals, which must have formed at the same time as the methyl radicals. Volatile products were hydrogen, methane and ethane in the ratio 25:70:5. The same volatile products were also reported by Siegel for poly(dimethylsiloxane) (ref. 10).

Delman (ref. 62) studied the effect of ultraviolet irradiation in air on a methylsiloxane resin. Infrared spectrocopy was employed in this study. Formation of Si-CH_2-Si linkages was observed as a result of irradiation at wavelengths above 2810Å from a Zenon arc lamp:





$$\underset{CH_3}{-O-\overset{CH_2\cdot}{Si}-} + \underset{CH_3}{-O-\dot{S}i-} \qquad CH_3-\underset{O}{Si}-CH_2-\underset{O}{Si}-CH_3$$

On the other hand, Si-OH and Si-CH_2-CH_2-Si linkages were formed when the resin was exposed to the shorter wavelength of a mercury vapor lamp. The different effects on the resin induced by the two ultraviolet sources are attributed to the fact that the mercury vapor lamp radiation is sufficiently energetic to cause the excitation of oxygen molecules. The excited oxygen molecules prevented the formation of Si-CH_2-Si linkages by interacting with the Si. radicals (formed by cleavage of Si-C bonds) to produce Si-OH.

Siegel and Stewart (ref. 63) studied the photolysis of poly (dimethylsiloxane) in the vacuum-ultraviolet region (this region starts at 2000Å and extends to shorter wavelengths where it merges with the X-ray region). The wavelengths employed were 1470 and 1236Å. Analysis of the data indicated that the breaking of the Si-CH_3 bond is the most probable reaction occurring at both wavelengths. A comparison with the photolysis of a mixed methylphenyl silicone polymer demonstrated the strong protective effect produced by aromatic substituents in this region of the ultraviolet spectrum. This was determined from quantum yield measurements for the formation of volatile products.

A similar stabilizing effect of aromatic substituents is known to occur when silicones are exposed to high energy, ionizing radiation, presumably because of the ability of the aromatic ring to dissipate some of the absorbed energy before bond rupture occurs (ref. 64).

5. CONCLUSIONS AND RECOMMENDATIONS

The design of a polymer structure that is stable to the ultraviolet environment of space must take into consideration the fundamental fact that most polymers absorb the short wavelength, unfiltered ultraviolet radiation below 3000Å, that exists above the upper atmosphere of earth. Furthermore, the quantum yield for photochemical reactions is higher for the short wavelength ultraviolet, that is, the damage per quantum absorbed increases with decreasing wavelength.

The design of a polymer structure that would be highly transparent down to 2000Å appears to be an interesting approach. In this respect, it should be interesting to investigate the photolysis of pure polymethylene, the simplest of all polyhydrocarbon structures. Nothing has been published on its photodegradation. Also, high purity aliphatic and fluoroaliphatic polyethers should meet the requirement of transparency to the short wavelength ultraviolet. However, these polymers may be expected to be sensitive to the presence of adventitious impurities or residual catalysts that would cause absorption and initiate photodegradation. This is known to be the case, for example, of the fundamentally transparent methylsilicones, in which traces of absorbing impurities have been found to sensitize photodegradation (ref. 12).

Previous work has considered the use of various metallocene absorbers as a means of stabilizing organic coatings to the short wavelength ultraviolet of space (ref. 65, 66). Unfortunately, several problems are associated with the use of ultraviolet stabilizers, such as compatibility with the polymer, possible migration of the stabilizer additive, volatility and extractability. These problems can be overcome by having a polymer structure in which the ultraviolet stabilizer is part of the polymer chain. An example of this approach is the synthesis of polymers or copolymers based on acrylate and methacrylate monomers containing pendant ultraviolet stabilizing groups, such as phenylsalicilate (ref. 67) or 2-hydroxy-4-alkoxybenzophenone (ref. 68). Therefore, an interesting approach that should be investigated is the development of a polymer structure capable of completely dissipating the absorbed ultraviolet energy by luminescence (fluorescence or phosphorescence) or by the emission of heat. These effects would allow de-excitation of the absorbed radiation without chemical change in the polymer structure. Since these are the mechanisms of action of ultraviolet stabilizers, the theory of ultraviolet stabilization would be directly applicable to the design of such a polymer structure.

Another interesting approach is to study how certain mechanisms of degradation that are energetically favored can be prevented by appropriate structural modifications of the polymer. An example of this approach would be a polyester structure with no hydrogen on the carbon atom in β to the oxygen link in the ester group; the lack of β-hydrogen would prevent chain cleavage by a Norrish Type II. For example, it has been reported that polyesters based on neopentylglycol exhibit superior ultraviolet resistance (ref. 51). Although the reason for this behavior was not explained, the improved stability is probably due to the lack of β-hydrogen in the ester structure based on neopentyl glycol.

Another interesting approach is the study of polymeric structures in which the photochemical reaction does not involve chain cleavage or other degradative effect, but it produces a chemical rearrangement that has no appreciable effect on the physical and optical properties of the polymer. This is the case, for example, of the Fries rearrangement of aromatic polyesters that rearrange under ultraviolet irradiation to a stable o-hydroxybenzophenone structure (ref. 52). This approach could be extended to the study of fully aromatic polycarbonates (phenyl carbonates, like phenyl esters, are known to undergo the photo-Fries rearrangement). A study of the photolysis of a model compound such as diphenylcarbonate would provide directly applicable information.

Since photolytic reactions normally involve free radical processes, EPR spectroscopy of polymers irradiated under vacuum can be very useful for the study of radical species occurring during photodegradation. In this type of work, the use of model compounds has the advantage that the results are generally easier to interpret and yet are directly applicable to the polymer itself.

Aromatic polyamides exhibit unusual ultraviolet behavior, in that near ultraviolet radiation (3600-3700Å) is more damaging than ultraviolet of shorter wavelength (ref. 10). Since nothing is known about their mechanism of photodegradation, a study of the irradiation of model aromatic amides by EPR spectroscopy would be very useful in order to understand, and possibly prevent, this effect. Ultraviolet stabilizers that absorb in the critical 3600-3900Å region have been considered for Nomex stabilization, but have the inherent disadvantage that they also absorb visible light (ref. 57). It should be interesting to evaluate ultraviolet "quenchers" that would stabilize the polyamide by extraction of the excited state energy rather than by absorbtion in the near ultraviolet.

Perhaps the least understood aspect of polymer photodegradation is the progressive increase in ultraviolet absorption at longer wavelengths that gives rise to the well known "polymer yellowing". Many workers have studied the mechanisms of photolysis in terms of its effect on chain scission, cross-linking or other chemical or physical changes, but little has been done to explain the reason for the "polymer yellowing" that always accompanies other degradative phenomena. Production of color is usually associated with the delocalization of electrons that accompanies multiple conjugated unsaturation. For example, formation of polyene (a chain of conjugated double bonds) has been indicated as the cause of yellowing in irradiated PVC (ref. 69). However, the mechanism of color formation during irradiation of most polymer structures is not known. Since optical stability is of primary importance in space coatings, consideration should be given to the study of the nature of colored by-products and to the mechanism of their formation Since carbonyl groups occur in many polymers (such as acrylics, polyesters, polyamides, polyurethanes and even in polyolefins as structural irregularities), and since free radical decomposition reactions (Norrish Type I or equivalent) lead to the formation of R-CO·radicals, it seems to us that recombination of R-CO radicals to form α-diketo groups may be a possible cause of color formation during polymer photolysis.

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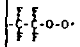
APPENDIX

Polyethylene 1

Material	Environ Cond	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref
					Phys. and Optical Effects	Photolysis Products		
HDPE (Sholex 6000)	Vac. 10^{-3}mm, Hg r.t.	Co-60 then with Toshiba HP400, HP Hg lamp 10^7 rad. λ 390mm with UV-39 filter		Japan Electron Optics Lab Corp. Type 3BX-RSR Hitachi EDS-2, UV Spectrometer fractionation	Lower viscosity, more than 50% gel, Decrease in solubility and mw.	Alkyl free radical 258nm, alkyl radical dienes 236nm, dienyl free rads 285mμ, triene 275mμ, gelation	1) Photoirradiation w/o filter gives alkyl radicals which when heated at r.t 10hr gives the allyl rads. due to hydrogen migrations. 2). Photoirradiation with UV-39 filter main chain scission occurs CH_3-CH-CH_2-CH_2~ type free rad is observed which revert to alkyl free rad on heating and further to the allyl free rads. Photoirradiation after γ radiation showed lower mw than mere γ-radiation, also the viscosity average m.w. was lower.	70
PE Model Cpds. N-Decane Vaseline	Vac.	Atomic pile BEPO, at Harwell		PE IR Spect. Iodometry		Trans viny' vinylene vinylidene	Total unsaturation obtained from IR and iodometry is not in good agreement. The difference may be due to interaction of reagent with residual reactive center. Double bond production is not directly proportional to radiation dose, due to reverse hydrogenation reaction. Approximate energy associated with each event is 5 eV which is the magnitude of bond energies involved.	71
Poly A,B,C,D (Linear PE) Poly E (Random copolymer of ethylene and butene-1) Poly F (Block copolymer of ethylene-butene-1)	Vac	Electron radiation 100 Mrad Dose		Material balance viscometry, density determination.	Discoloration, change in density, embrittlement, mw decrease	H_2O and CO_2 99% (Oxdn Prod)	Linear PE: O_2 uptake 35 ml/g, 100°C. Reaction rate and O_2 uptake declined with thickness. Density 0.995/23°- 20ml/g at 100°C. Elongation 600% after 5 ml/g O_2. Decrease of viscosity on uptake of O_2. Branched PE: O_2 uptake 180 ml/g, 100°C, density 0.933 to 0.96 O_2 uptake has a sharp rise approximately 30 ml/g. Decrease in viscosity slower than linear PE on uptake of O_2. Autoxidation of PE is largely diffusion dependent and is confined to disordered regions. Crosslinks primarily interfere with chemicrystallization while branches affect the post-crystallization reaction.	72
PE (Marlex 5003) DYNK-1 · ow density PE)	Air	^{60}Co γ-ray, 0.67 Mrad/hr GE 1-Mev resonant transformer electron beam generator, 108 Mrad/hr Hanovia 65-4-A-10 325 W HP Hg Lamp 184.9nm to visible	2,6-di-t-BU-4-methylphenyl 0.02%	Beckman DK-2 ESR, IR		λ max. Diene 236mμ Triene 275mμ Tetraene 308mμ Pentaene 340mμ Free Radicals Alkyl 258mμ Dienyl 285mμ Trienyl 353mμ Tetraenyl 359mμ Pentaenyl 396mμ	Resolution of the 236mμ absorption to diene is reaffirmed. Also of the higher polyenes·triene, tetraene and pentaene are reaffirmed. The resolutions of the higher polyenyl has been made, however, the Δλ max has not been elucidated.	73
a) Marlex 5003 b) PE (low density) c) PE (isotactic)	Air -196 r t.	See above 0.66 Mrad/hr dose rate.		Beckman DK-2		Sample °C G(diene) a) 35 0.28 -196 0.20 b) 35 0.16 -196 0.17 c) 35 0.071 -196 0.072	It was observed that unlike conjugated dienes, the trienes are not one of primary products, but require prior presence of diene group. Higher polyenes stability at r.t. suggests free radical migration for its occurence. Conversion of allyl to alkyl free radical is an endothermic process. Reactions involving carbonium ion and free radicals satisfy both UV and ESR spectra requirements for allyl-alkyl free radical interconversion; a distinct possibility. Hydrogen atom migration is a plausible mechanism for higher polyenyl.	74

Polyethylene 2

(Teflon Included)

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref.
					Phys. and Optical Effects	Photolysis Products		
WNC18 Alkathene Bakelite DFD 4400 Alkathene 2 (all low density PE)	Air -175 r.t	Co-60 γ ray, 3.0 Mrad/hr	Biphenyl benzene, 1-hexene	Unicam SP800			Dienes are formed as a single primary reaction. The radicals were differentiated by optical (trapped electron) and thermal (dienes) bleaching Thermal H atom (H_t) was studied by adding benzene which gives cyclohexadienyl radical. G (H_t) = 1.8 and G(·ϕH) = 1.55. By this method ion formation was ruled out and long chain radical ruled in. Trapped electron optical density was distinguished by "deep" (or amorphous) and "shallow" (or crystalline) electron traps with degree of bleachability. Shallow trap readily destroyed by high dose radiation.	75
PE PP PF PTFE PVC		DRSh-1000	Naphthalene Phenanthrene Anthracene	UV Spectrometer, Viscometry, ESR Luminescence spectra	Intrinsic, viscosity decrease		1.)The 200nm absorption in purified PE, PF, PTFE, PP are due to presence of some derivatives of naphthalene,phenanthrene and authracene.2.) Addition of these impurities accelerated photodecomposition. 3.) The transition of naphthalene to the photoreactive state is a two-quantum process, which takes place via the triplet state of the sensitizer. 4.) Phenol, p-phenylenediamine, 1-and 2-naphthylamine and naphthol derivatives have sensitizing effects.	3
PTFE (forms of rod, blocks or sheet) a) Teflon T.F.E. (fluorocarbon Co.) b) Teflon 7 (DuPont Co.)	Vac. and Air	Co-60 γ source (UCLA Labs, Atomic Intn'l., AF Cambridge Res. Labs. and Physics Intn'l) $FeSO_4$ dosimetry		Varian V-4502, X-band ESR		 Chain peroxide  Propagating peroxide	At 10^6 to 10^8 rads, the chain to propagating radical ratio is 10 1. In air peroxide radicals are formed in the same ratio. In air-saturated rod the same two radicals form with chain peroxide predominating at 10^7 rads. The rate and extent of decay were inversely proportional to dosage. The radical concentration in air-saturated PTFE as a function of total dose is linear thus, PTFE is useful as dosimeter. Dose-depth curve obtained from radical concentration vs thickness gave linear curve.	76

Abbreviations as follows

HDPE·	High density polyethylene
PE	Polyethylene
PP:	Polypropylene
PF	Polyformaldehyde
PTFE·	Polytetrafluoroethylene
PVC:	Polyvinylchloride

Polypropylene 1

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results: Phys. and Optical Effects	Results: Photolysis Products	Conclusions	Ref.
PP (Isotatic) PET (Mylar) Ethyl benzoate (Model cpd)	Vac.	Hg lamp, >320nm (Corning filter) Weather-ometer Zenon and Carbon Arc		IR	Weight loss Viscosity decrease Brittle Discoloration.	PP PP-hydroperoxide ($3400cm^{-1}$) CO CH_3COCH_3 H_2O PP ketone. (ϕ=0.1) $\phi x10^4$ PET COOH CO CO_2 Vac 17.2 6 1 1.1 Air 18.3 8.7 8.7	Photoxidative changes are confined to the surface. Photosensitizing impurities are carbonyl and peroxide products from thermal oxidation or from ozone. Photoxidation of PET produces COOH, CO and CO_2 in air. In the absence of air, crosslinking occur. Ethvlbenzoate forms COOH by Norrish Type II in air and vac.	77
PP (Ziegler-Natta Type) (Asahi Chem.)	Vac. 30°C	LP 10W Hg lamp 210nm (Toshiba UV25 filter)		Luongo's IR Shimadzu RI-27 IR	Degree of swelling decrease	Ash residue (TiO_2) gel fraction.	Degree of swelling decrease with irradiation time in decalin. Gel fraction increase with irradiation time in TCE. These factors indicate crosslinking occurred in vacuo. PP is transparent to light longer than 200nm. The acceleration of photochemical acceleration is attributed to TiO_2 found in the polymer ash. IR indicates very little change before and after exposure.	78
PP (Isotactic) A 50% crystalli B 80% crystalline	Vac. 200°K to 300°K	DKSH-1000 Zenon lamp.		RE-1301 Radio-spectrometer (EPR)		Allyl radical Alkyl radical	(1) The kinetics of transformation from allyl-alkyl in UV and alkyl to allyl in the dark at 77-300°K has a step-wise character. (2) The alkyl—allyl transformation is connected with hyper equilibrium excitation of the polymer's crystalline lattice. (3) A theoretical discussion of the kinetics of phototransformation of radicals of amorphous and crystalline phases has been confirmed experimentally.	29
PP (Isotactic)	Vac 110°C O_2 atm. 10^{-2} torr	DRSH-500 lamp $\lambda \geq$ 253nm	Phenanthrene	EPR IR UV Spect.		$R\text{-}C\dot{O}$ ($3600\text{-}3400cm^{-1}$) $R\text{-}\dot{O}$ ($1920\text{-}1720cm^{-1}$)	Heating PP films at 110°C in O_2 atm. indicated formation of ROO- and R-O. Heating oxidized PP in vacuo at 120-130°C for 14 days led to decomposition of R-OO without change of RO. Photolysis of PP with 10^{-2} wt.% of phenanthrene at 77°K caused methyl radicals to form after 12 hrs. Rate of formation of radicals is proportional to the square of the intensity.	15

Polypropylene 2

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref.
					Phys. and Optical Effects	Photolysis Products		
PP (Isotactic)	Vac. -196°C N_2 atm. 10^{-5} torr	(given earlier) Toshiba filters used. >325nm UV35 >300nm UV33 >275nm UV31 >255nm UV29 >227nm UV27 >205nm UV25 235-410nm UV-D25		ESR IR		Methyl radicals Free radicals	>325nm Small broad singlet >300 to >275nm intensity of singlet increased-G=2.005. >227 to no filter showed 4 peaks of methyl radical 235-410nm also gave methyl radical. When warmed at 78°C from-196°C sharp singlet was observed-G(2.001) then decayed. This singlet was ascribed to alkoxy radical with G (2.005); formed via R-OO and R-O.	79
PP (Isotactic)	Vac. 77°K	Philips HPK 125w 253.7-578nm		ESR X-Band 100Kc Field Modulation (Japan Electron Optics Lab. Co.) Model JES-3B		Methyl radicals	After irradiation spectrum shows diffuse component and sharp component. Superposition abstraction of the abo from a 2 hr spectrum gives a sharp methyl radical spectrum. Production of free radicals may be due to impurities.	80
PP (Isotactic)	Vac. 170°K 260°K 10^{-4} torr	Co-60 0.5 Mrad/hr Total dose was 3 5 Mrad.		ESR		Methyl radicals	170°K region corresponds to γ-dispersion and 260°K as β-dispersion of PP. Free radicals trapped in polymer decay with small scale motion of the matrix polymer (twisted). Less twisted polymer decay with large scale motion of matrix Activation energy of decay was 11 kcal/mole at 170°K and 48 kcal/mole at 260°K.	81

Abbreviations as follows:

PP Polypropylene
PET· Polyethyleneterephthalate

Unsaturated Polyhydrocarbon

Material	Environ. Cond	Irradiation Source	Additive	Anal Method	Results: Phys. and Optical Effects	Results: Photolysis Products	Conclusions	Ref
Isoprene Isoprene-Silver Nitrate Solution	Vac 10^{-3} Torr 2 to 15°C	Co-60, 800 Curie 0.78 x 10^{6} r/hr Ferrous-Ferric Dosimeter		Hitachi UV Spectrometer IR	Insoluble Products	1,2 complex of isoprene-$AgNO_3$	Rate of polymerization increases in $AgNO_3$ solution 20-50 times as much as that of pure isoprene. Equilibrium constant K_f was found to be $K_f(1,2) > K_f(1,4)$ also IR verify 1,2 structure's presence in greater proportion	42
Polyisoprene (Crepe natural rubber)	Air, r.t.	1600w OSRAM Xenon Discharge quartz lamp 300-600nm 396nm max				330nm main chain photolysis 355nm : Methylenic bonds, H_2	Vulcanization residue as MBT and sulfur acts as protective agent. ZnO protects below 370nm and sensitizes at near visible. 369nm degrdn highly auto catalytic at the beginning of irradiation. 330nm beginning of photolytic relaxation. 500nm and higher initial increase in tension noted $\phi cs = 5.4 \times 10^{-2}$ 330nm $= 3 \times 10^{-2}$ 340nm $= 5.3 \times 10^{-2}$ 355nm	83

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Polyacrylonitrile

Material	Environ. Cond	Irradiation Source	Additive	Anal Method	Results: Phys. and Optical Effects	Results: Photolysis Products	Conclusions	Ref
Polyacrylonitrile a). 80 20 wt ethylene carbonate propylene carbonate soln b). In powder c). as film. glutaronitrile (model cpd.)	Vac. 10^{-5} torr	(given earlier) 253.7nm (95%)		Beckman DU Spectrophotometer B&L Spectronic 505 Beckman IR-5 Oswald-Fenske Viscometer	Powder form turned brown Film turned yellow in air and dark brown in vacuo. Decrease of $\bar{M}n$	HCN NH_3 Terminal olefin	Photodegrdn process in solution was random chain-scission process The rate depended on history of polymer Beer-Lambert's law is obeyed in chain-scission $\phi cs = 0.84 \times 10^{-4}$ after 40 hr irradiation Molecular-size distributions change during degrdn which affects viscosity	46

Polyvinylketones

Material	Environ Cond.	Irradiation Source	Additive	Anal. Method	Results: Phys and Optical Effects	Results: Photolysis Products	Conclusions	Ref.
Ethylene & Carbon monoxide copolymer in solution (2% in heptane), 12-tricosanone (model cpd)	Vac. 25°C 80°C 120°C H_2 atm	AH-6 1kw HP (100 atm) ME/D 250 w LP (30 atm) 313 nm Uranyloxalate actinometer 0-8.5x10^{-4} E/hr	2-hydroxybenzophenone	Desreux dilution Viscometer, PE 521 IR PE 800 GC Spectronic 505 UV	Decrease in mw	CO $\phi_I = 0.012$ $\phi_I = 0.018$ (120°C, H_2 atm)	(1) Cause of degdn. Norrish type II at 25°C-major cause (2) Type I occurs at higher temp. & activation energy increase of 5 kcal/mole (3) Carbonyl group with no adjacent hydrogen are more stable. (4) 2-hydroxybenzophenone stabilizes polymer by screening rather than by energy transfer	84
PMMA-MVK PS-PVK PPVK (Polyphenyl vinyl ketone), PE-CO	Vac 27°- 137 5°	313 nm (given earlier) Ferrioxalate actinometer		Water's Ana-Prep GPC (gel perm. chrom) Desreux dilution viscometer DSC PE DSC-1 calorimeter	Decrease in mw	ϕ at Tg PMMA-MVK ϕ_{cs} = 0 21, PPVK ϕ_{cs}= 0 14 PS-PVK ϕ_{cs}= 0 08 PE-CO ϕ_{cs}= 0.02	Norrish II reaction occurs at higher temp. PPVK type II decreases with increasing temp In Tg region Type II increase Radiationless process occurs at r.t and above.	85
PPVK (in Ben-Sols.) butyrophenone, benzophenone (model Cpds)	Vac r t	Philips HPK 125 5 x 10^{-7} E min incident intensity 365 nm benzophenone-benzhydrol actinometer	Naphthalene, isoprOH	Hitachi-PE 139UV PE 237 IR	Decrease in mw	PPVK ϕ_{cs}= 0 3, butyrophenone ϕ_{II}= 0 43 CO ϕ_I= 10^{-3}	Naphthalene and isoprOH does not inhibit Main chain scission is by Norrish Type II. Photochemical behavior similar to benzophenone	86
PPVK (B37), PVK-PS (B43), Fraction of above (B43f)	Vac 25°	313 nm (given earlier)	1-cis,3-cis-cyclo octadiene (COD) (Triplet quencher)	Desreux viscometer GPC	Decrease in mw	B43 ϕ_{cs}= 0 17, B37 ϕ = 0 25 B43f ϕ = 0 18 acetophenone, benzaldehyde	Major chain scission was Norrish Type II -acetophenone. Norrish Type I yielded benzaldehyde Apparent lack of styrene or phenyl vinyl ketone monomers suggests that chain unzipping is unfavored 93% of chain scission is quenched by COD Dissolved air did not effect quantum yield chain scission Quantum yield for copolymer was high in the order of 0.2	[illegible]
Poly(Methylvinyl ketone) (PMVK)	Vac. 25°	310 nm (given earlier)	Naphthalene, biacetyl	Varian aerograph auto prep 700 GC	Decrease in mw	ϕ_F PMVK 0 75 PMIPK 1 75	No definite trend observed in the model solvents. Fluorescence yield increase when α-hydrogen of acetone is replaced by alkyl group was confirmed Thus (1) PMIPK with fewer α-hydrogen reduces radiationless decay of singlet and increases fluorescence, (2) PMVK gamma hydrogen gives low singlet emission, (3) Length of chain contributes to increased density of vibrational state and steric hindrance to biradical formation. Naphthalene energy transfer to polymer ketone was found inefficient Energy transfer from polymer ketone to biacetyl was found efficient Efficiency of singlet energy transfer increases with increase in viscosity of solvent.	[illegible]
Poly(Methyl isopropenyl ketone) (PMIPK)				Bausch & Lomb Spectronic 505, Hitachi-PE-MPF-2A fluoresence spec				
Model Cpds. (1) 8 types of methyl substituted acetones (2) 14 types of ketones								
Copolymers (1) MMA-MVK (2 9%) (2) MA-MVK (3%) (3) Poly MVK	Air	250-w MP Hg Arc (313nm via interference filter)		Water's Anaprep GPC Ebulliometric, viscometry	Decrease in mw	MMA-MVK ϕ_{cs}= 0 2, ϕ_{II}= 0 0065 at 25°C= 0.12 at 86° PMVK ϕ_{cs}= 0 04, MA-MVK ϕ_{cs}= 0 2	(1) ϕ = 0.2 for vinyl copolymers with pendant methyl ketone group and molecular mobility high (2) The scission mechanism [illegible] of [illegible] c-c bond through an intermediate transition state of 6 or 7 membered ring abstracting the γ or δ-H atom. (3) chromophores should be located at adjacent position in the main chain to effect transfer of excitation energy	89

Abbreviations as follows

PMMA-MVK	Polymethylmethacrylate-methylvinylketone
PS-PVK	Polystyrene-polyvinylketone
PE-CO	Polyethylene-carbonmonoxide copolymer
MMA-MVK	Methylmethacrylate-methylvinylketone
MA-MVK	Methacrylic acid-methylvinylketone

Polyvinylchloride 1

Material	Environ Cond.	Irradiation Source	Additive	Anal Method	Results		Conclusions	Ref
					Phys and Optical Effects	Photolysis Products		
PVC(Sicron 548)	Vac 10^{-5} mm Hg 80° to 130°C	^{60}Co γ rays, 0 81 rad/sec Fricke dosimeter C(Fe^{3+})= 15.6		IR mw determination UV & visible with Unicom SP800 Spectrophotometer (200-700nm)	Discoloration red to violet	HCl Polyene gel fraction	Presence of HCl accelerates kinetics and acts as catalyst Rate dependent on temp & ir the proportion of the rate contribution due to irradiation when HCl is removed a). Constant length distribution occurs b) Total unsaturation increases linearly with time c) Cl abstracts methylene hydrogen to form free radical, thus the formation of double bond	90
PVC(Resin Q-1812),Gulf Chem. Canada,med high mw	Air	Rayonet RS RPR-208 8 lamps RVL-300nm, 85w, UV-simulating sunlight phosphor	THF (280nm λ max) Dichloroethane (190nm λ max)	Unicom SP800 200nm to 7000nm	Color development 280nm, Stiff insoluble polymer	Decreased mw gelation	THF & $C_2H_4Cl_2$ enhance uv degdn 253 7nm degrdn faster than 300nm PVC with residual solvent possess good uv stability. Chain scission is the controlling factor in early stage of degdn and crosslinking, the later stage	91
PVC(Opalon-660) Monsanto	Vac & Air	1 MeV Van de Graaff generation ~ Mrad/min, total 8 Mrad.	Butylated Hydroxytoluene 0.025% (BHT)	Cary 14 Spect ESR	Post irradiation color formation	HCl Polyene	Optical density of vac. molded PVC a). Absorption increases. b). Air treated material also increases in absorption Concentration of radicals did not change in all samples, on storage absorption max stays same but intensity increase BHT surpresses conjugated unsaturation Delocalization produces singlet electron spin resonance	92
PVC	Air N_2 Atm 273K to 333K	(given earlier) Potassium ferroxalate actinometry, 3 6x10^{16} quanta cm^{-2} sec^{-1}		Metrohm combititrator 30			Rate of dehydrochlorination increase ē temp-c=14 kJ/mole and constant after 1 hr Rate also depends on intensity but for an hour After 1 hr the change is controlled by availability of HCl and not a chemical process	93
PVC (Geon 101EF) B.F Goodrich	Air 40± 2°C	Rayonet chamber, 253 7nm 5 7x10^{16} ev/sec/g PVC	Ferrocene (Fc), Copper salicylate Benzene Copper phthalocyanine (CUP)	X-ray fluorescence Cary Model 14 Intrinsic viscosity	Gel (CUP)	Gel fraction	Pure PVC crosslink Gc = 0.29, $\alpha/_{\beta}$ = 0.10, Gs = 0 06 PVC Derivatives; CUP Gc = 0 40, Gs = 0.26; CUS Gc = 0.72, Gc = 1 38; Fc Gc = 3 1, main chain scission Gs = 6 2/100 ev, $\alpha/_{\beta}$ = 1 0 Crosslinking is enhanced due to chain-transfer followed by coupling.	94
PVC-PVisoBu ether	Air	(given earlier) 1 32x10^{4}/cm (absorption coeff.)		UMC-1 type 1963y f-m Eluro computer IR	Gel	Gel fraction isobutyl group	Gel content increases ē increase in dose. Gel content increased-ē for crosslinking decreased Rate of crosslinking is greater than scission. Side group splitting depends on intensity	95

Polyvinylchloride 2

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref.
					Phys. and Optical Effects	Photolysis Products		
PVC (Geon 121)	Vac.	γ-ray 1500c, ^{60}Co 0.3 Mrad/hr UV GE UA-1 Med. press 3.2×10^{-5} quanta/cm^2/sec 220 - 400 nm uranyl oxalate	3-5% residual MEK.	Cary 14 Spect.	After long irradi-ation-dark red-brown	HCl Polyenes	Residual solvent acts as sensitizer. Absorption from 210m to 650m after irradiation causes discoloration. IR showed no structure change i.e. C-Cl bond (14.5μ) or trans C=C (10.4μ). φ (HCl) independent of λ for all λ < λ_c (controversial difference found in uv source). 10 Mrad is equivalent to 1 hr uv. Trace impurities are cause of uv absorption and degrdn.	96
PVC/PVisoBu ether (See Ref.95)	Air 30°C	Med press ASH-400 Uranyloxalate 2.97×10^{16} photons/cm^2 / sec, formed λ=0.25μ		IR Zeiss UR-10 Griffin & George MK IIB GLC		HCl Cl isobutoxy gel fraction polyene	Rate of $\frac{\phi d}{\phi c}$ = 0.28-0.13 = φ Rate of crosslink was higher than scission Dose of 4.25×10^{10} to 12.75×10^{10} erg/cm were associated with oxidation. IR method for identification of syndiotactic (615cm^{-1} band) and isotactic (634cm^{-1} band) configuration was made.	97
PVC PMMA Methylene terephthalate (PET) PS PnBUMA	Vac.	GEUA-3 med press Hg lamp		Model A-100 Rame Hart Goniometer, FMIR spectra IR, KRS-5 prism Consol. Electrodynamic Corp. Model 21-103C, mass spec.		PS H_2O,CO_2 cis cinnamic or 2,4-diphenyl alkanoic acid.	PS, PBMA & PET contact angle did not change on irradiation. <u>PS:</u> Polar liquid changes contact angle on irradiation and carbonyl group formed. Angle change due to low mw acidic product or oxidized material. <u>PVC</u> Carbonyl formation removed by irradiation which improved contact angle. In air carbonylation and unsatn. occured. <u>PBuMA</u>: Produce acidic material. Small rate of chang with polar liquid. <u>PMMA</u>: Contact angle c̄ hexadecane increases unlike others. Surface attacked by polar solvents. <u>PET</u>: OH-stretch increase on irradiation. Contact angle becomes constant on increased irradiation.	98
PVC	Vac or Air 100°C	Co-60, 1000 curies		ESR	Gel	20 Mr in Vac or air no gelation 10 Mr in Vac then heated to 100°C-gelation occur Precaired rimed sample does not gel	Free radical determines the rate and PVC is only slightly cross-linked at r.t since Tg= 80°C. If radical is quenched during reaction c̄ O_2, crosslink will not occur. Crosslinking does not occur because thermal H-atom is accelerated. Activation energy of recombination of radicals is 35 kcal/mole.	99
PVC	Air, r.t.	UV Hg vapor lamp	1) Hexamethylene tetramine (HMTA) 2) Di-β-naphthyl/ p-phenylenediamine (DNPA) 3) Resorcinol (R) 4) Basic lead carbonate (BLC)		Decrease in viscosity then reaches constancy	HCl	HMTA: 0.2% addition gave the most severe degrdn. The rates of dehydrochlorination are similar under inert and oxidative condition. DNPA: It behaves as a decomposition catalyst and more so at inert than oxidative condition. R: Under inert condition it becomes an unstable system. Under oxidative condition it shows stability of the system. BLC. 180 min. lapses before HCl evolves. Rate and extent of dehydrochlorination under oxidative condition is less than inert condition. Pretreatment by washing PVC will enhance stability. Grafting also enhances stability. Thermal degradation causes more deterioration than photodegradation.	100

Abbreviations as follows:

PVC: Polyvinylchloride
PMMA: Polymethylmethacrylate
PS: Polystyrene
PnBuMA: Poly n-butylmethacrylic acid.

Polyvinylacetate

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref.
					Phys. and Optical Effects	Photolysis Products		
A PVAc B VAc/IPAc (BP) C VAc/IPAc (AIBN)	Vac -196 C 35 C $1\text{-}5\times10^{-5}$ torr	Co-60 γ source 0.43 Mrad/hr		Varian A60 and T60 NMR IR Brice-Phoenix light scattering photometer Consolidated Electro-dynamic Corp. 21-104	Gelation(2.9 Mrad) Branched polymer A&B gel dose o.5-0.7 Mrads	HAc at 100 Mrad PVAc G(x)-0.163	Radiation-induced fracture of appr 1/6th of the branch points in PVAc prior to gel point has been confirmed by mw measurement. Copolymers B and C High sensitivity towards radiation of isolated branched points. 3 -Me groups/1000 VAc unit affected by post irradiation. Annealing stabilizes photolysis. Concentration of trapped radicals unaffected by copolymerization, but structure and reactivity differs	101

Abbreviations as follows

PVAc: Polyvinylacetate
VAc: Vinylacetate
IPAc: Isopropenylacetate
BP: Benzoylperoxide
AIBN: Azobisisobutyronitrile

Polystyrene 1

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method.	Results		Conclusions	Ref.
					Phys and Optical Effects	Photolysis Products		
PS P-MeS PMA PMMA PMVK PisoPrK	Vac. 10^{-5} torr 25°C then heated to 120°C	Hanovia 93A-1 low pressure 153.7nm 5×10^{18} quanta/g/min. Ferrioxalate actinometer 1.2 MeV, Co-60 5.81×10^{7} r 5.47×10^{9} ergs/g		Consolidated Electro Dynamics Corp. Model 21-103C 'c Bendix Time-of-Flight Mass. Spect. PE Spectracord Model 4000 uv, Viscometry	Insoluble gelation	$\phi_g \times 10^4$ U.V. Vac H_2 1.1 CO 1.4 CO_2 0.15 Bzn 0.94 C_6H_{12} 0.94 HC≡CH 2.4 See text for UV-O_2 CO 98.5×10^4 CO_2 252×10^4 Bzn 2.2×10^4 -Vac H_2 20.5×10^4 CO_2 3.4×10^4 Acetylene 3.4×10^4	PS: Vac-uv Crosslinks, Air-uv scission plus crosslink. PS most stable compared to others shown and more stable than the α-Me analogue. Order of stability ć ter-H are C_6H_5 > $COOCH_3$ > COMe and same order ć Me homologs; PS stability is due to resonance stability and ter-radical formed.	32
P-MeS QN17.1 (Dow Chemical)	Vac. 10^{-5} Torr, 27°C, 115°C (in the dark)	GEUA-3 Med. Press Uranyloxalate 280.4, 275.3, 265.4 and 253.7nm		PE-Spectracord Model 4000 UV PE Model 21 IR Consolidated Electro Dynamics Model 21-103B Mass Spec., Ubbelohde Type Viscometer	Long exposure yellow color	ϕ_g 115° H_2 0.017 CO_2 0.016 CO 0.0068 Acetylene 0.0028 Ethylene .0024 Isobutene 0.0012 Methane 0.0012 Ethane 0.0008 Propene 0.0008 Butanes Branched 0.0004 Pentanes	In Vac UV at 27 to 115°C: ϕ, 27°C ϕ, 115°C Chain Scission 1×10^{-3} 2×10^{-2} Monomer formation 7×10^{-3} & 0.5 Initial degradation is a random scission. Zip length was 7 at 27°C and 25 at 115°C.	35

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Polystyrene 2

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref
					Phys. and Optical Effects	Photolysis Products		
PS/P-MeS (25%) PS/P-MeS (50%) (Dow Chemical)	Vac. 25 to 40°C	^{60}Co γ-Source. 2.35x10^{22} eV/l-hr G= 15.5 or 2.27 x10^{19} eV/ghr polymer Ferrous sulfate dosimeter		Stakin-type osmometer Brice-Phoenix Photometer (546nm at 40 to 135°) Ubbelohde viscometer Turbimetry	Gelation		G values for chain scission, G(S), and crosslinking, G(r), were determined for fractionated and unfractionated polymers having 75-25 and 50-50 mole G(S) G(r) 75-25% ~~0 10~~ ~~0 094~~ 50-50% 0 12 0 062 g' values = 0.79 and 0.72. Lack of preferential energy transfer is due to the --Me effect to the phenyl group.	102
PS. High & Low Density Polythene Poly vinylidene chloride	Air 25 to 100°C	Atlas Fadeometer K.3B Fugitometer both carbon arc type Heat treatment	Antioxidant carbon black	Hounsfield Tensometer (0.25 in/min.) Charpy impact test also Hounsfield impact test. Cambridge textile extensometer (grip/in/min.) Avery impact machine Izod impact test at 70° & 100°C for 12 months.	Brittleness, loss of elongation, impact strength and tensile strength.		Unpigmented, toughened PS has poor UV resistance at both natural and accelerated conditions. Pigment improves resistance, black and white providing best protection for U.V. HD polythene resists temperature up to 70°C with increase in impact strength With antioxidant stable at 100°C, without unstable. HD material not protected by antioxidant to natural U.V. but is completely protected by carbon black.	103

Abbreviations as follows

PS·	Polystyrene
P-MeS	Polyalphamethylstyrene
PMA	Polymethacrylic acid
PMMA	Polymethylmethacrylate
PMVK	Polymethylvinylketone
PisoPrK	Polyisopropylketone

Polyvinylnaphthalene

Material	Environ. Cond.	Irradiation Source	Additive	Anal Method	Results: Phys. and Optical Effects	Results: Photolysis Products	Conclusions	Ref.
PS (BDH) 1-vinyl naphthalene (Koch light) PS/1-vinyl naphthalene Copolymer	Air, 77°K	900W HP Ze Arc broad band center 265nm	Naphthalene	Cary 14 Spect. 50 Hz phosphoroscope, Bausch & Lomb Tektronix 549 Oscilloscope.		Phosphorescence	Copolymer system (polymer/quencher) quenching efficiency was not enhanced relative to adding quencher. The reason for this was not established.	104
Poly 1-vinyl naphthalene (PVN) P-2-VN PIVN/PMMA PIVN/PS 1-ethyl naphtalene (1EN) (Model Cpd.)	Air, 77°K	(given earlier) 290nm		Aminco-Bowman Spectrophosphorimeter		Phosphorescence Fluorescence Naphthalenic carbonyl	Three spectral regions of PIVN, P2VN, PIVN/PMMA and model IEN. 325-375nm biphotonic in origin, delayed fluorescence due to triplet-triplet annihilation either free or at traps. 375-450nm: biphotonic in origin, delayed exciplex fluorescence due to defects or chain impurities. 500-600nm· monophotonic in origin, naphthalenic phosphorescence or short lived impurity traps.	105
PS PV Napthalene PMMA								

Abbreviations as follows:

PS·	Polystyrene
P-1-VN:	Poly 1-vinylnaphthalene
PMMA:	Polymethylmethacrylate
P2VN:	Poly 2-vinylnaphthalene

Polyacrylates 1

Material	Environ. Cond.	Irradiation Source	Additive	Anal Method	Results		Conclusions	Ref.
					Phys. and Optical Effects	Photolysis Products		
PMMA-1 (Kallodoc) ^{14}CPMMA-2 (4.8 μc/g) ^{14}CPMA-2 (5 μc/g) PMA-1 (A. Light & Co.) PVAc PS PMeOS PAN	Vac. 10^{-4} torr	Co-60 at Harwell 2.5×10^{21} eV/g BEPO atomic Pile 2.3×10^{21} eV/g	5% Benzoquinone 18.6% α,α'-diphenyl picrylhydrazyl (DPPH)	Mass Spect Solubility test Viscometry Radioactive Assay	Insoluble material PMMA and PS did not discolor at 4.8 pile units and at 2 pile units respectively. PMA-1 did not discolor PMA-2 became yellow on exposure PMeOS and PVAc became light yellow after 2 units PAN changed from pale yellow to deep amber	PMMA-1, ϕ cpd — 100°C — 25°C PMMA — 1.1 — - Bzn — 0.1 — - Methylal — 6.0 — 1.9 MeFormate — 14.2 — 6.0 ME_2O — 2.3 — 2.1 CO_2 — 15.7 — 21.0 MeOH — 1.7 — 0.4 CH_2O — 3.0 — - CO — 30.5 — 41.1 H_2O — - — 2.5 CH_4 — 13.1 — 15.6 H_2 — 11.7 — 9.5 PMA-1, ϕ cpd — 100°C Bzn — 1.3 $(MeO)_2CH_2$ — 1.7 MeAc — 0.2 MeFormate — 4.1 Me_2O — 1.0 CO_2 — 12.1 MeOH — 3.8 CH_2O — 1.8 CO — 38.9 CH_4 — 20.1 H_2 — 15.0	Mass Spect. evaluation of PMMA-1 heated at 100°C and at 25°C, the ϕ of product indicate that at 100°C diffusion of photo-degraded product took place, and its product was not due to thermolysis. Also the products have derived from $COOCH_3$ group From PMA-1 heated at 100°C, no monomer evolved, the above rationale also apply to PMA 1. Incorporation of benzoquinone or DPPH did not affect the nature of products although some reduction was noted Little reliance was placed on the results of the remaining polymers studied PMMA containing p-benzophenone or DPPH gave 3% soln overnite. Others were insoluble. Protection was not proportional to the concn of additive	106
PMMA (purified)	Vac. and air, 25°C	GE [illegible] MP Hg Lamp [illegible]ranyl a[illegible]ometry		Bendix Time-of-Flight Mass. Spect Viscometry	Decrease in viscosity no gelation	CO CO_2 H_2 CH_4 HCOOMe-major no monomer.	The quantum scission, ϕs, was found to be 3.2×10^{-2} at [illegible] and 1.4×10^{-2} in air It is significant that an apparent induction period seems to occur during degradation in air. PMMA UV absorption below 250nm at 25°C leads to rapid decrease in mw, some due to O_2. However, O_2 does not appear to be involved in the formation of new chromophores during degradation.	107

Polyacrylate 2

Material	Environ Cond.	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref
					Phys. and Optical Effects	Photolysis Products		
PMMA-94 PMMA-139	Air, r.t.	Hanovia 88 A45 Hanovia 84A1 Low pressure. 253.7nm, Ferrioxalate actinometer	O_2 Aromatics Bzn, Naphthalene, pyrene Dienes: 1,3-Cyclohexadiene Ketones: Benzophenone, Biacetyl Nitro Cpds: Nitromethane 4,4,4-trinitro-butyric acid (TNBA)	Viscometry			Two solvents were used in this study CH_2Cl_2 and dioxane. O_2 Reduced photolysis rate to some extent in both solvents. Transfer of PMMA triplet absorbed energy to the ground state. O_2 triplet energy could be the degrdn. rate reducing without involving peroxide. Aromatics Energy transfers from benzene triplet to PMMA. Naphthalene triplet was an effective O_2 quencher. Dienes 1,3 cyclohexadiene was an effective inhibitor in air or degassed solution. Ketones Benzoquinone is an exception to the postulate that the increasing inhibitory effectiveness parallels the decreasing triplet level of the ketone. Competing reactions as hydrogen abstraction and presence of O_2 will change rate of degradation. Secondary reactions takes place with biacetyl. Nitro Cpd: Presence of O_2 completely nullified the inhibiting effect of nitromethane and TNBA. Nitromethane and TNBA were completely ineffective in dioxane due to formation of charge-transfer complexes. The active part of TNBA may be the carboxyl group then the nitro group.	108
PMMA	Vac. and air 25°C, 2-mm Hg	GE UA-3 MP Hg Lamp (Polychromatic) Uranyl oxalate Actinometry		Ubbelohde Viscometer Consolidated Electrodynamics, Model 21-620, Mass Spect PE Spectracord Model 4000	Viscosity decreases	Cpd φ CH_4 - H_4 - CO - CO_2 - CH_3COOMe 0.14 MeOH 0.48 C=CMeCOOMe 0.20	Polymers undergo random scission without extensive depolymerization. Rate of degradation in air is lower than in Vacuo. Primary photolytic process a. Major reaction is the random homolysis of main chain C-C bonds. b. Minor reaction is the disproportionation to give $COOCH_3$ radicals and terminal olefins.	38
PMMA	Air, r.t. CH_2Cl_2 Solution	Philips TUV 30 (Monochromatic) Philips BioSol (polychromatic) Co-60, 2400 c 110 Krad/hr 1.33 + 1.17 MeV		Viscometry		γ-ray at high temp. (150-200°C) COOMe CO, CO_2, CH_4 and H_2 per main chain break and at G = 1.6 (62 eV per break).	UV At r.t. random main chain fracture occurs. At higher temp depolymerization occurs. Energy absorbed per main chain fracture is about 550 eV. γ-Ray At r.t. fracture same as in UV which does not propagate to significant extent. At pyrolysis temperature (150-200°C) chain reaction and monomer evolution occur. In both cases the number of fractures were proportional to dose and radicals formed are identical in character. No special contribution was made by any ionic or highly excited species. Thin Film With TUV the average energy absorbed per monomer per hour exposure is 0.97×10^{-2} eV (0.18×10^{-4} main chain break) energy absorbed per break, E=540eV. With Biosol, E=510eV. Thick Film With TUV the number of breaks induced per monomer per unit dose r, $P_o = 0.046 \times 10^{-4}$ and E = 570eV. With Biosol, $P_o = 0.19 \times 10^{-4}$ and E = 2820eV. The precise significance of UV absorption spectrum has not been elucidated	4

Polyacrylate 3

Material	Environment	Irradiation Source	Additive	Anal. Method	Results: Phys. and Optical Effects	Results: Photolysis Products	Conclusions	Ref.
PMMA Film / Thickness cm A [illegible] B 0 1[illegible] C 0 [illegible] D 0 [illegible]65	Air, r t	Seven 30w GE LP Hg Lamps Corning H9863 filter 100 253 7nm Eppley Thermopile 550μw cm²		Cary Model 11 Spectrophotometer Cannon-Fenske Viscometer	Viscosity decreases, yellowing may be due to high energy irradiation		Quantum yield, φs, for random scission was found to be 2 [illegible]x10^{-3} Theory of experimental dose-effect was correlated with intrinsic viscosity-good fit except for D in benzene solvent Film A absorption of 253 7nm was 32% initial and [illegible] after 142 hr Film [illegible] absorbed 100% initially exhibits apparent decrease in scission efficiency with increasing exposure The 195nm peak may be associated with ketonic or aldehydic carbonyl group in A and B film	109
PMMA	Air, r t	Van de Graaff Generator-2MeV, 0 5 Mrad/hr Blue cellophane Dosimeter, four Westinghouse Sterilamps, Uranyl Oxalate Actinometer 6 1x10^{-4}w cm²	Pyrene, p-t-phenyl Xylene Benzene Pb Ac	Beckman DU spectrophotometer Cannon-Fenske viscometer	Discoloration at 1 5 6 5 Mrad		UV Irradiation Lucite φs = 0 032 for main chain scission at 253 7nm Pyrene protects PMMA as a light filter Excited PMMA, exciton, transfers energy to the scintillators and then back to the chain for C-C scission Electron Irradiation φs = 9 8x10 for main chain scission The G value is 1.56 Pyrene showed little discoloration per dose Positive charge transferred to the additive whereby neutralization occur An excellent protective agent for Lucite is a scintillator with low ionization potential such as a neg ion which would be stable after loss of an electron	110
PMA Model compds Propionic acid Trimethylaceticacid	Vac	LP Hg lamp, 5x10^{-4}E 1-min Siemens Constant Potential x-ray Tube 140kv and 12mA Ferrous sulfate Dosimeter	H_2O_2	U-Tube Capillary Viscometer	UV Irradiation OH 62 5 X ray Irradiation H_2 7 58 CO_2 [illegible] 2[illegible] Isobutene 0 15		Presence of air decreases the degdn rate Degdn in absence of air is known that it is due to peroxide group in the polymer and when these are removed by heating degrdn stops. This was found not to be true Presence of H_2O_2 in higher concentration enhances degrdn in x-irradiation. In UV irradiation the primary photolysis is the scission of the carboxylic group The H radical from H_2O_2 abstracts hydrogen from CH_3 group	111
MMA/MA copolymer Molar ratio A 11[illegible] 1 B [illegible] 1 C [illegible] 1 D [illegible] 1	Vac 170 C	(Given earlier) 253 7nm		Mechrolab Osmometer			Photolysis and thermolysis are compared. In photolysis there was no direct evidence of crosslinking as in thermolysis Rate of chain scission not dependent on MA content but a random scission Rate of volatilization retarded by increasing MA content-depropagation process is blocked In all these aspects photo-reaction is identical with thermal reaction The main difference found were 1 Zip length in photolysis greater than thermolysis. 2 The 1 1 ratio between CO_2 and chain scissions in thermolysis does not apply to photolysis. 3. Monomer liberation in photolysis (1 10) is smaller than thermolysis (1 4).	112

Polyacrylate 4

Material	Environ Cond	Irradiation Source	Additive	Anal. Method	Results Phys. and Optical Effects	 Photolysis Products	Conclusions	Ref.
(PMMA (PEMA (PnBMA (PLMA (PMA (PEA (PnBA (PisoBA (P2EHA	Air, r.t.	Toshiba GL-15 LP Hg Lamp		Hitachi-Perkins Model 115 Osmometer Japan Spectroscopy Co Model FRM, Spectrophotometer IR GPC	Yellowing (due to double bonds)	Gel fraction Methacrylates: CO_2 Monomer Acrylates: CO_2 Acid	Reduction of weight by volatilization increases linearly with increase in irradiation time Volatilization increases with increasing side chain length, except for PnBMA. Gel fraction of PnBA becomes constant with exposure time (60 hrs) while that of Pi-BA decreases. No gel fraction noted in other polymers. (PnBMA small amount). Crosslinking and decomposition occur simultaneously except for PMMA. Increase in side group chain length *increases crosslinking*	113

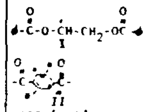
Abbreviations as follows:

PMMA-1	Polymethylmethacrylate-1
^{14}CPMMA-2	Radioactive polymethylmethacrylate-2
PMA-1	Polymethacrylic acid-1
^{14}CPMA-1	Radioactive polymethacrylic acid -2
PVAc	Polyvinylacetate
PS	Polystyrene
PMeOS	Polymethoxystyrene
PAN	Polyacrylonitrile
PEMA	Polyethylmethacrylate
PnBMA	Poly n-butylacrylic acid
PLMA	Polylaurylmethacrylate
PEA	Polyethylacrylic acid
PnBA	Poly n-butylacrylic acid
PisoBA	Polyisobutylacrylic acid
P2EHA	Poly(2-ethylhexyl)acrylic acid

Polyesters 1

Material	Environ Cond.	Irradiation Source	Additive	Anal. Method	Results: Phys and Optical Effects	Results: Photolysis Products	Conclusions	Ref
Polyethylene terephthalate (PET) (1) ICI-Melinex S (2) DuPont Mylar L (3) DuPont Mylar	Air 20°C 65	Atlas C-arc Fade-ometer FDA-R Atlas Xe-arc Weather-ometer 600-WR	Unknown, stabilizers	Wilks #9ATRKRS-5 crystal, Beckman IR8, Instron TTC, Farrand spectro-fluorometer (Mark I) Cannon-Ubbelohde	Film 3-80% elongation after 300 hr. Gelation not obverved Brittle.	-OH COOH Increase in fluoresence with Zenon	All showed basic pattern of degdn. and only on degree/unit irradiation time Film 3 degr'ed faster than 1 & 2. Xenon arc is more damaging than carbon arc. Damaging rays 315 to 350nm COOH production is due to photochemical not thermolysis or hydrolysis, Zenon arc causes faster rate of fluoroscence appearance	47
PET (2L) DuPont Mylar	Vac and air	Osram super-pressure Hg lamp (SP 500 W); CS-7-5-4 225-420nm CS-7-5-4 / CS-D-54 300-420nm Eppley thermopile 2..8 & 35.4 m-w/cm^2		Cahn RG electro balance, mass spec., Hewlett-Packard 5750GC Beckman IR8, UV Spectrometer		ϕ = (x10^4) 300-420 Vac Air CO 6.1 8.7 CO_2 1.1 8.7 COOH 17.2 18.3 H_2 CH C_2H_6 225-420 Vac Air CO 8.5 12.8 CO_2 3.6 28.3 COOH 13.9 20.3	(1) Initial reaction leading to COOH formation independent of λ and environment, occurs via Norrish Type II photo-elimination. (2) CO formation also independent of λ and environment and consists of primary photolytic chain scission sequence. (3) CO_2 formation due to photooxdn in the presence of air via hydroperoxide formation. (4) Hydroperoxide decomposition mechanism secondary reaction involved in formation of fluorescent product. (5) photo-oxdn cause non volatiles at long λ nonvolatile photo-chemically degraded to give additional CO+CO_2 at shorter λ	49
PET PCDT. (1,4-cyclohexylenedimethylene terephthalate)	Vac. and air	Hanovia 54A-10 med. press. Hg arc 253.7nm (filtered)		Aminco-Bowman spectrofluorometer			Blue fluorescence occured intensifying on increased irradiation. Excitation / Emission Initial fluorescent product 340nm 459nm Second fluorescent product (120hr) - 435nm. Fluorescent product reduced under N_2. Hydroxylation occurs via reaction with -OH or -OOH radicals in air	50
(1) Poly(tetramethylene-decanedioate-CO-4-oxo heptanedioate, (DMKP) (2) Copolymer 5-oxomonanedioate (DMKA) (3) Copolymer 6-oxo-hendecanedioate (DMKH) Each monomer later was used as model cpd.	Air	AEI Type ME/D Med. Press. arc 313nm, 3 x 10^{-6} einstein/in.		NMR Varian A60 60 MHZ PE model 800 GC		ϕ chain scission (1) 0.014/36 hr/ 1 x10^{-3} Einstein (2) 0.012/85 hr/ 4.5x10^{-3} (3) 0.013/77 hr/ 6.4x10^{-3} Einstein Methyl propanoate (ϕ=0.4), dioxanyl dioxane, 1,5-di-carbomethoxy-3-pentanal, ϕ=0.12	Photochemistry depended on n (-CH_2-) from carbonyl group. 1. n=2 Norrish Type I photo reduction (DMKP) 2. n=3 Norrish Type II with higher than normal quantum yield. (DMKA) 3. n=4 Norrish Type I and II occur (DMKH) 4. n=5,6,7, etc. will behave qualitatively as DMKH but with reduced quantum yields due to mw effect. Quantum yield for scission is reduced by 0.01 when ketone is in polymer chain compared to the model cpd.	114

Polyesters 2

Material	Environ Cond	Irradiation Source	Additive	Anal Method	Results Phys. and Optical Effects	 Protolysis Products	Conclusions	Ref.
PET film Mylar DuPont,21	Vac and air	Carbon Arc Atlas Fadeometer type FDA-R Corex D Globe,35°C,no humidity control Zenon Arc Atlas Weather-ometer model 600-WR,Pyrex filter system, 60 C 30% RH, Ostram Super-pressure Hg lamp (SP 500W) corning filter CS-7-5-4) 300- CS-0-54) 420nm	No additive	Instron tensile tester Type II-C,21° 65% RH,viscometer, acid-base titrimeter Farrand spectro-fluorometer (Mark I) GLC-Mass Spec	Brittle,fragile, slight reduction in yield load,increase in break load and reduction in elongation.Decrease in mw,absent in gel	Chain scission,COOH end group increase in fluorescence due to -OH formation CO,CO_2 90%	Zenon gives shorter than carbon thus,provides more energy CO and COOH production are independent of O_2 presence They occur as simple photolytic reaction. CO_2 production is due to photooxidative mechanisms,both light and O_2 involved Primary bond breaking reaction due to Norrish Type II giving COOH and CO_2 and fluorescence material; Norrish Type I gives CO	115 116
Same as above	Vac and air							
isophthalic phenolphthalein (F-1 polyacrylate) terphthalic-9,9'-bis (4-OH-phenyl) fluorene(CD-9 polyacrylate)	Air	PRK-2 lamp 8 9x10^{-8} E cm^{-2} sec^{-1} (UPHM-11 actinometer)		Varian V4502-10 Spectrometer (DPPH ref)	Discoloration	Gel	Parameters of crosslinking of F-1 and D-9 was calculated in relation to UV exposure Max Density is reached then little changes takes place in time mw distribution occurs to its most probable distribution on exposure.	117
Mylar DuPont (.00 25 cm thick)	Vac 10^{-4}mm Hg	^{60}CO 0 3-0.5 Mrad/hr,thermolysis at 60°, 80°, 100° and 120°C		ESR Varian V4502-10		 $\phi-\overset{O}{C}-O-\dot{C}H-CH_2-O\overset{O}{C}-\phi$ I II unassigned III	Disappearance of free rad in amorphous PET is due to mobility of segment even below Tg For crystalline polymer at above Tg to near m p , radical site hopping by hydrogen atom transfer is the cause of free rad disappearance. Amorphous polymer contains radall and III, III increase on heating Crystalline polymer contain rad I.	118 119
Same as above								
(1) Phthalic-neopentyl glycol-maleic NPC (2) isophthalic-neopentyl glycol-maleic (3) phthalic-3 butylene glycol (4) styrene added to above, 40 (5) styrene 21 -PMMA 17 added to above	Air	Atlas Weather-ometer Emmaqua Exposure,Ariz. Kingsport Exposure,Tenn	Mono-t-bu-hydro-quinone, 0 01% 2-OH-4-dodecyl oxbenzophenone,0.25%	Visual appearance Gardner glossmeter Gardner auto Color Diff. meter	Discoloration gloss reduction		NPG/PA/MA resin gave best results overall Color & gloss retention.	51

Polyethers

Material	Environ. Cond.	Irradition Source	Additive	Anal. Method	Results Phys. and Optical Effects	 Photolysis Products	Conclusions	Ref
ED-5 Epoxide tar coating	Air	PRK-2 lamps		JEM-5 electron microscope, UV spectrophotometer	Before irradiation fibrous-like structure. 1.5 hr exposure cause globular structure	Carbonyl (1685 cm^{-1} after 1 5 hr) NH group (3370-3340 cm^{-1})	Degrdn due to multistage process involving destruction of globular structures of asymmetric structural elements. Structural changes of super-molecules from the destruction of the macromolecules Mechanical and thermophysical change depends on the change of the super-molecule during the aging process.	60
Polyoxymethylene A) Hydroxyl terminated B) Acetyl terminated	Vac. and Air, 160°C	Hanovia "chromatolite" 30W lamp 253 7nm Osram 125 WMB lamp 320nm		PE Model 131R		H_2 CO Carbonyl -OH(A smaller than B) Carbonate Anhydride	Molar ratio of H_2/CO=3.5-4.0. Immediately hydroxyl and carbonyl forms. OH forms 100x more at 253.7nm than 365nm. Carbonyl-253.7nm "steady state" carbonyl production-i.e. at this energy it also destroys. At 365nm absorption increased autocatalytically-carbonate and anhydride increase linearly Polyoxymethylene thermally stable at 160°C No formation of H_2O shown.	59

Polyamides 1

Material	Environ. Cond	Irradiation Source	Additive	Anal. Method	Results: Phys and Optical Effects	Results: Photolysis Products	Conclusions	Ref
Nylon 6 (yarn) scoured (NS) scoured & absorber (NST) scoured & absorber & scoured (NSTS)	Terr (India)	Carbon arc Fade-ometer 65% RH, Daylight	2,2'-dihydroxy-4,4'-dimethoxy-benzophenone, 0.2%	Oswald u-tube, Beckman DB Spec IR-PE	Tensile loss Decrease in mw	Pyrrole, malonic acid	(1) Random scission of C-N bond (2) Poly chain not affected-since IR indicates no structural change despite preparation (3) No appreciable change in tensile strength and M_v (4) Degdn proceed by free radical leading to formation of peroxide-decomposed to form pyrrole and on prolonged exposure malonic acid formation. (5) H_2O soluble degrdn product obtained (6) Benzophenone uv absorber decreases degrdn (7) Scouring reduces photo-degradation	120
Poly 4,4'-bis(p-aminophenyl) 2,2'-bithiazoleisophthalamide (BTA) Poly 1,3-bis(3-aminobenzamido) benzene terephthalamide (M3P) DuPont Nomex	Air	Hanovia 900w HP Zenon Arc		Jarrell Ash F16 3 Plane Grating 0.75 meter spectrograph Microdensitometer Mark III B, Cary Model 14, spectrophotometer	Tensile loss discoloration BTA: yellow-brown to dark purple M3P: yellow		BTA discolored by visible light, 414nm Most damaging radiation lies at 370-500nm Secondary inflection at 440-470nm M3P and Nomex discolored and degraded at 370-360nm-tensile loss. M3P and Nomex discolored and degraded at the same wavelength but the mechanism may be different	12
Nylon 66 DuPont 330 (yarn)	Terr (Florida) 21,000 Langleys, Air 145°F 35% RH	Nuclear (inside core) Nuclear (outside core) Uva-test Hg lamp, 253 7nm Laser (N_2), Atlas Fade-ometer 300-400nm	Dyes CI 151+159 (yellow) CI 25 (blue) CI 226 (226) metal Manganese stabilizer, Merpol HCS	Instron (70°F, 65% RH)	Tensile loss		2 hr laser exposure equivalent to 200 hrs or Fade-ometer, a factor of 100 1 Other mentioned sources were not very useful as accelerated sunlight source. Suggestions have been made concerning further studies.	121
(1) Polyhexamethylene-α-Truxillamide (poly 6α) (2) Polynonamethylene-α-Truxillamide (poly 9α) (3) Polyhexamethylene-δ-Truxinamide (poly 6δ) (4) Polynonamethylene-δ-Truxinamide (poly 9δ)	Air	450w-HP, Hg lamp		JASCO CRM-FA Spectr Irradiator TGA & DTA Shimazu MTG 12 Viscometry, NMR	Brittle at 224nm	Transcinnamide 272nm Cinnamyl group 224nm Trans-stilbene 320nm	Photodegradable polymer. Poly - degrades faster than poly δ due to steric effect at 224nm. No effect of aliphatic chain length on depolymerization rate has been detected Poly-δ gives two types of scission a. Symmetrical-gives rise to two cinnamyl groups -272nm b. Asymmetrical-gives rise to one trans-stilbene and one f[illegible]amide linkage Thermal study revealed polyamide stability to 350°C.	122
Nylon 66 (yarn 210 filament, 6 den)	Air, 20-160°C	Hanou Zero-Test, 400nm Filtered with Dow Corning filter glass Nos 0-53, 0-54, 0-52, 3-73		Beckman Model DU Spectrometer Cary Model 11UV	Dis[illegible]ion [illegible] in terms of [illegible]ance unit/gr strength loss	ROOH, (160-170ppm after 120 hr exposure)	Photodecomposition by photon attacking the amide linkage abstracting H from carbon α to NH. α-carbon radical reacts with atm. O_2 to form peroxide. Rate of peroxide formation is dependent on wavelength of uv radiation. Peroxide decompose at 100°C. Occurrence of thermal degrdn. during irradiation was demonstrated. Traces of iron salt in yarn sensitizes photodegrdn	123

Polyamides 2

Material	Environ. Cond.	Irradiation Source	Additive	Anal Method	Results: Phys and Optical Effects	Results: Photolysis Product	Conclusions	Ref.
Nylon 6 (polycaprolactam) I. methoxylated fiber II Methylene III. Methylene disulfide IV Alkylene sulfide cross-links	Vac. 10^{-4} mm Hg	Two GE G25T8 germicidal, low press. Hg Lamps 253.7mm, 2% visible, 48% heat, no energy below 200mm 6,000mw/cm^2 6.0x10^{-4} ergs/cm^2-sec		U.V., X-ray Viscometry	Gelation	Methylene groups are hydrolyzed to form formaldehyde. It is then reacted with chromotropic acid. The absorbancy gives estimate of crosslinking. Methoxyl group and Free sulfhydryl groups.	From calculated rate constant, the stabilities are in the order, Disulfide (k_2=0 025/hr) < methyl methoxy (k_2=0.01) ~ Methylene (k_2=0.01/hr) ~ alkaline sulfide.^{2} Irradiation causes decrease in orientation from decrease in internal stress due to scission-indicated by x-ray pattern	56
Nylon. 66: DuPont, Mylar C Dupont, PE (Marlex H density) Phillips Pet. Teflon: DuPont Acrilan 16 Chemstrand	Vac. N_2 Atm. r.t	GE A-H6, G30T8 Lamp, 90% 253.7mm, Epply thermopile 1 6 and 7.5 mw/cm^2		Instron	Initial gain and a gradual loss of tensile strength. Brittleness discoloration		(1) PE: Threshold value 3.2 eV or 74 kcal/mole. Deteriorates more rapidly in N_2 atm than in vacuo. It becomes brittle and amber colored (2) Mylar Threshold value 3.2 eV below which no damage is done Amber color forms and found no obvious embrittlement, Deterioration more rapid in N_2 than in vacuo. (3) Nylon Radiation causes darkening and gumminess of surface, deterioration more rapid in N_2 atm. than in vacuo Shorter wavelength caused greater damage. (4) Acrilan: UV light causes amber color quickly. Deterioration in N_2 atm not as great in vacuo compared with others. Tensile retention at high dose is better than other polymer retaining tensile strength at high dose (5) Teflon Degrdn. mor rapid in vacuo than in N_2 atm Threshold proton energy is same as PE and mylar Retains tensile [illegible] at high dose.	37
Nylon 6.6 (50% crystalline) Nylon 610 (max. λ 355mm) Polyoxamide (max. λ 508mm) Acrylic acid (radical scavenger)	Air -75 to 25°C	Van de Graaff Gen. 2-mev	Acrylic acid	Cary Model 11 Spec Viscometry	Transient discoloration which faded in the presence of O_2 Gelation Nylon 66 80 Mrads at 25°C polyoxamide 40 Mrads at -78°C		Absence of O_2 25°C Radiation dose increased relative-viscosity decreases [illegible] reaches max to a gel point; -78°C: Relative viscosity increase more rapidly with increasing dose than at r t. Less crystalline polymer crosslinks more readily even at -78°C Water containing yarn crosslinks more readily at 25°C than the conditioned yarns Acrylic acid containing polymer is much less susceptible to crosslinking, essentially zero	[illegible]

Siloxanes 1

					Results			
Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Phys. and Optical Effects	Photolysis Products	Conclusions	Ref
Polydimethylsiloxanes (DMS) DC 360 s 4' fluid (η)350 c' mw 10⁴ Methyl phenylsiloxane (MPS)	Vac. 10^{-5} torr	Xenon resonance lamp, 147nm $3.3 \pm 0.2 \times 10^{15}$ photon/sec Krypton lamp, 123.6 & 116.5nm $3.3 \pm 0.7 \times 10^{15}$ photons/sec.		Quadrupole Mass spec., McLeod gage-gas press. Dual trace oscilloscope recorder Viscometry	Viscosity increase	<u>DMS</u> <u>147nm Surface Mode</u> H_2 (0.009) CH_4 (0.020) C_2H_6 (0.033) <u>Immersion Mode</u> H_2 (0 021) CH_4 (0 087) C_2H_6 (Not detected) <u>123.6nm Surface Mode</u> C_2H_6 CH_4 H_2 C_2H_4 C_2H_2 H_2 <u>Immersion Mode</u> CH_4 (0 087) H_2 (0 049) <u>MPS</u> <u>147nm Surface Mode</u> CH_4 (0 001) no C_2H_6 H_2 (0.004) <u>Immersion Mode</u> Same as above	Mechanism illustrated <u>147nm</u> Surface mode Abstraction of H from CH_3 and Si-C cleavage to form CH_4. Immersion Mode and Surface Mode H_2 formed by abstraction Si-C change is more probable also primarily excited. <u>123 6nm</u> C-H bonds are primarily excited MPS indicated no long range energy transfer along the chain	63
Methyl siloxane Resin (from methyltrimethoxysilane and cyclic dimethylsiloxane)	Air	Atlas Weather-o-meter 6000w, Xenon Arc 281nm, Hg vapor lamp, GE-G4511-4w (Germicidal lamp)		PE-337 UV PE-137 IR		<u>Xenon-1524 hr</u> $SiCH_2Si$ (7 3μ) <u>Hg Vapor-355 hr</u> $SiCH_2CH_2Si$- (8.85 & 9.5μ) $Si-O_H$ (3.0μ)	<u>Zenon Arc</u> Gives wavelength greater than 281nm and energy greater than 103 kcal/mole. $SiCH_2Si$ linkages occur at 7 3μ band due to C-H and Si-C cleavage. <u>Mercury Vapor Lamp</u> (185-435nm, 66-155 kcal/mole) Si-OH formation indicated at 3.0μ band Also $SiCH_2CH_2Si$ formation showed 8 85 and 9 5μ bands Mechanism illustrated. Water was not removed from sample which could react to form Si-OH.	62

Siloxanes 2

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref
					Phys. and Optical Effects	Photolysis Products		
Polydimethylsiloxane (PDMS) Polydimethyldiphenylsiloxane (PDMDPS) (7 Mole % diphenyl units)	Vac. N_2O He Air N_2O/N_2 · 20%/80%,38°C	^{60}Co 5000c γ flux 2.6×10^5 r/hr		Vibrating Reed Technique	Discoloration PDMS Air-light yellow dose dependent vac-no change K_2O-orange He-no change N_2O/N_2 - light yellow PDMDPS Air-red brown Vac- light yellow N_2O-red brown He-no change N_2O/N_2-orange		Vibrating reed technique (20-100 cps) used to study rate of crosslinking. (1) Crosslinking rate, k, of PDMS is dependent upon the irradiation atm employed Order of rates. PDMS $k_{vac} \geq k_{Hc} > k_{N_2O} > k_{air} = k_{NO_2} + N_e$ PDMDPS similar except k_{air} slower than $k_{NO_2+N_2}$ (2) 20% NO_2/80% N_2 yielded identical rates and color at equiv exposure for PPMS as in air (3) PDMDPS discolored more than PDMS-mechanism not known (4) Crosslinking rate apparently controlled by the concn of N_2O and radiolylic by-products of N_2, O_2 + NO, O_2 + NO_2 depresses crosslinking N_2 is same as in vacuum. (5) Overall radiation stability can be significantly influenced by the stability of the end groups i.e. $-SiMe_s$ > $SiMe_2\phi$ > $Si\phi_2Me$ etc The source of color formation not explained	125
Arylmethylsiloxane Polydimethylsiloxane	Air, r.t.	GE Reasonant Transformer 1.5 Mev Dose rate 20 Mr/min.		Cannon-Manning Semimicro Viscometer Elbullicoscope $\bar{M}_n$.	Gelation	GX G gas $-SiMe_2O-$ 2.6 2.7 $-Si\phi Me-o-$ 0.25 0 0 $-Si\phi_2O-$ 0.13 0.02	In pregel region crosslink is temp-independent Parameter, Δ, represents the parallel displacement of the arrhenius (log - vs 1/T) viscosity curve. Therefore, ' is proportional to Thus G(LX) and R* can be calculated Conjugated aromatic substituents confer greater stability than singles aromatic. Homopolymer more stable than copolymer in aryl alkyl groupings	64
Dimethylsilicone Oil G.E.	Vac. N_2, r.t.	800kv electron source 100Mr/hr. 1.2Mr 1.4Mr 1.6Mr 1.7Mr		Viscometry, light scattering, osmometer	Gelation		Qualitative study of intrinsic viscosity study with irradiation. $(-)/(-)_o$ not very sensitive to 2 /- unless 1 < 2 /- < 10 Outside this range other methods should be used. Doses 1 2Mr and less were filtered through fine filter. $-(-)/(-)_o = 2.04$ 1 4Mr would go through coarce filter. 1.6 and above did not go through coarce filter $(-)/(-)_o = 2.24$	126

Poly(Alkylene Sulfides)

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results		Conclusions	Ref.
					Phys. and Optical Effects	Photolysis Products		
$-(CH_2-SS)-$ (PMDS) $-(CH_2-SSSS)-$ (PMTS) $-(CH_2-CH_2-SS)-$ (PEDS) $-(CH_2-CH_2-SSSS)-$ (PETS)	Vac. 5 °C 10^{-4} torr	Med. Press. Hg lamp GE UA-3 ($3x10^{14}$ quanta/sec-cm^2) 200-400nm range		Consolidated Eng. Co. Model 21-260 mass Spec., Glc	wt. loss brittle, cracking, curling. Rubbery yellow film from polytetrasulfide. Brown film from polycarbon monosulfide.	<u>PMDS & PMTS</u> H_2S } major CS_2 } CH_3SH) minor CH_2S) <u>PEDS and PETS</u> H_2S) major CS_2) minor H_2O and CO_2 was found with the above <u>Solids</u> Polycarbon monosulfide. Polyalkylene tetrasulfide.	wt. loss: PMTS 80% PETS 51% Degradation order tetrasulfide>disulfide;methylene polysulfide> ethylene polysulfide. Before and after,IR showed no change. Degraded sample remilled and exposed showed no change in wt. loss. Methylene polysulfides evolved the most H_2S. CS_2 was the major product of the methylene polymer only.	127
Abbreviations as follows: PMDS: Polymethylene disulfide PMTS: Polymethylenetetrasulfide PEDS: Polyethylenedisulfide PETS: Polyethylenetetrasulfide								

Binders and Pigments 1

Material	Environ. Cond	Irradiation Source	Additive	Anal Method	Results: Phys. & Optical Effects	Results: Photolysis Products	Conclusions	Ref
SR-82 (Polymethylphenyl, PMP) SR-112 (PMP) SR-119 (Polyester-PMP) SR-121 (Polyester-PMP) SR-125 (PMP) RTV-615 (PDMS) OI-650	Vac.	1000w Xenon Arc Lamp. 0.5-5.0 ESH	ZnS BNC Ta_2O_5 La_2O_2 HfO_2) High rate ZrO_2 } of degrdn. Cd_2O_3)	Spectroreflectometer	All SR series degrd at 100 ESH SR119 & 121 degrd less after 500 ESH. RTV 615 & OI650 no degrdn after 500 ESH		SR series degrade at 100 ESH after 500 ESH, then SR-82-112 800 ESH plus SR-119 & 121 less degrdn RTV 615 & OI650 stable at 100 ESH / 500 ESH -/ of ZnS = 0.016 / 0.067 -/ of BN(c) = 0.130 / 0.221 Heat of Formtn, kJ/mole / $\cdot c_s$ 500 ESH Ta_2O_5 -2092 / 0.106 & 0.120 La_2O_3 -1916 / 0.185 0.221 HfO_2 - 996 BN - 134 ZnS - 201 UV-Rad-induced degrdn of potential thermal-control coatings is strongly influenced by factors other than the standard heat of formation	128
PVC DCX2-6-0049 resin DC804 and 806A (Silicone resin urea-formaldehyde butyrate-(Beckamine P-196-60)	Vac.	Hanovia S4A-10 Hg vapor lamp 184.9-450nm 710 NRC Thermo 1 Control	ZnS Rutile Anatase ZnO	B&L Spectronic 20 375-700nm	Chalks Mill yellowed		ZnS pigmented PVC less susceptible to solarization than rutile Reason may be due to photoreduction of rutile at 420nm (3% decrease) All attempts to pigment silicones with ZnO have resulted in mill yellowing, DC-804 urea formaldehyde/half second butyrate (1 1) c ZnS was one of two best systems	129
Methyl Silicone Al_2O_3/PS S-13 TiO_2/MS TiO_2/PS	Vac $5x10^{-7}$ torr	Microware Rare Gas Resonance Lamp 105nm (cut off) Krypton 117-123.6nm → 270nm	Al_2O_3 ZnO TiO_2 Alzak	Beckman DK2A modified			High vac UV irradiation apparatus was successfully demonstrated. Lyman = radiation did not explain the rapid change in α_s of Al_2O_3/PS. 50x Lyman - intensity at 11-hr exposure caused larger change in α_s. ($\Delta\alpha_s$ = 0.0222 at 123.6nm irradiation. A-5 alzak for 233 hr at 1.3 solar constant showed $\Delta\alpha_s$ = 0.022).	130
Polymers (1) Vac/AA (15%) (2) PVAc/dibutyl phthalate (3) PA (4) Vac/fumarate (18%) (5) PVAc	Air 65-70% RH, 40°C	Zenon arc weatherometer Kipp-Zonen Pyranometer (Filter used and energy distribution of Zenon arc is given earlier)	TiO_2 (anatase) ZnO	Ashing	Chalking	1 & 5 with anatase contained 5% resin	The effect of radiation is not proportional to its intensity It also depends on diffusibility of O_2 and H_2O molecules to the surface of pigment. 1 & 4 + ZnO at low energy do not chalk but loose wt. due to partial oxdn. of binder	131

Binders and Pigments 2

Material	Environ. Cond.	Irradiation Source	Additive	Anal. Method	Results: Phys. & Optical Effects	Results: Photolysis Products	Conclusions	Ref
1. PS/2-Et-hexyl-acrylate/MMA/AcN 2. VCl/Ac (60% VCl) 3. VAc/fumàrate (18%) 4. VAc/Ac/Si (15% Ac & 5% Si 5. VAc/Ac (15%) 6 Ac Pure 7. VAc/dibutylphthalate	Air 30, 60 & 95% RH, 55°C	Zenon Arc Weatherometer Black body Temp 72° (RH 60%) 53° (RH 60%) Various filters	ZnO A&C (A from Zn metal waste, C from pure ingot) TiO_2 (Anatase)	Weight loss	Chalking	H_2O_2 (formation postulated)	Chalking decreased to 1/5 by lowering temp. from 55° to 37°C. 385nm to 445nm causes chalking for ZnO system 355nm to 415nm for TiO_2 system Resin 2-only TiO_2 caused total decomposition of the resin. At 30 to 95% RH rate of decomposition increased sharply. Resin 5-with TiO_2 and ZnO rate of decomposition rose c̄ with moisture also acceleration of crosslink noted with rise of RH. Resin 2- ZnO_2 did not cause total decomposition even at 95% RH. TiO_2 caused crosslink and decomposition. The water vapor pressure of 37° and 55°C increases chalking. Reaction mechanism 1. Contact of pigment and binder is not necessary, 2. Decomposition is highly dependent on partial water vapor pressure. Consequently, diffusion of O_2 and peroxide formation.	132
HDPE LDPE Impact PS Rigid PVC PP	Air, 55°C	GE RS-4 Sun Lamp 280-380nm 200w Flood lamp	ZnO, secondary additive. 1. Polygard [tri mixed-mono-and dinonyl phenyl) phosphite] 2. DLTDP (dilauryl thiodipropionate) 3. ZnS 4. Irganox 1076 5. Tinuvin P (organic absorber). 6. Ethyl Zimate		Time to failure 1. Flex break 2 Brittleness 3. Heavy pitting 4. Chalking 5. Severe cracking 6. Severe crazing 7. Edge crumble 8 Severe discoloration		HDPE ZnO-Polygard system 9X more efficient than organic stabilizer. LDPE ZnO same as organic UV absorber, 3X improvement. Secondary additive, ZnS, polygard, DLTDP gave 7X improvement. Impact PS-ZnO-Irganox 1076 gave physical property improvement, yellowed with RS-4 lamp exposure PVC-tin mercaptide-tin carboxylate and Ba-Cd-Zn phosphite epoxy system were resistant to degdn; PVC-ZnO at 30 p.h.r improved notch impact strength and color degrdn. RS-4 sunlamp caused exudation. PP-ZnO extend life in RS-4 lamp, 13X, 10 phr to 22X. 2 phr ZnO· 1 phr ethyl zimate gives 66X life expectancy in RS-4 lamp. Cyasorb UV 531 + PP becomes opaque on out door aging.	133

Abbreviations as Follows:

PVC	Polyvinylchloride
PS	Polystyrene
MS	Methylsilicone
VAc/AA	Vinylacetate/acrylic acid
PVAc	Polyvinylacetate
PA:	Polyacrylic acid
MMA	Methylmethacrylate
AcN	Acrylonitrile
AC	Acrylic acid
HDPE	High density polyethylene
LDPE	Low density polyethylene
PP	Polypropylene

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