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# Photodegradation of High Polymers in Solution

## Part 1 - Solvent Effects in the Photolysis of Poly( $\alpha$ -Methylstyrene)

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## ABSTRACT

The photodegradation of poly( $\alpha$ -methylstyrene) has been investigated in the presence and absence of air in a series of solvents under irradiation by a low pressure mercury lamp at about 25°C. Changes in the intrinsic viscosities of the solutions as well as spectral changes are used to follow the course of the degradation. Under most conditions, random scission is the major degradation reaction; no crosslinking is observed. Typical quantum yields for random scission in solution (1 gram/deciliter) are: benzene, 0.00005; dioxane, 0.0005; cyclohexane, 0.0006; methylene chloride, 0.005; chloroform, 0.16; and carbon tetrachloride, 0.17 scission per quantum absorbed by the solution. Values in the presence or absence of air are similar although the mechanisms may be different. As polymer concentration increases, the quantum yield decreases. Small amounts of ethanol in chloroform inhibit photodegradation. In the mixed solvents cyclohexane/dioxane and cyclohexane/methylene chloride, no changes in rates of scission are observed. In mixtures of cyclohexane and carbon tetrachloride, a large inhibiting effect is found by adding a small amount of cyclohexane to carbon tetrachloride; the carbon tetrachloride exerts a strong sensitizing effect at low concentrations in cyclohexane. Empirical comparisons of the ultraviolet spectral changes resulting from the irradiation of poly( $\alpha$ -methylstyrene), poly(styrene), and analogous hydrocarbons indicate that a free radical reaction occurs initially at the methylene group in the polymer backbone. Mechanisms are suggested.

## PROBLEM STATUS

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

## AUTHORIZATION

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## PHOTODEGRADATION OF HIGH POLYMERS IN SOLUTION

PART I - SOLVENT EFFECTS IN THE PHOTOLYSIS  
OF POLY( $\alpha$ -METHYLSTYRENE)

## INTRODUCTION

Previous reports (1) from this Laboratory have been devoted to investigations of the behavior of solid films of vinyl polymers under ultraviolet irradiation. Although the study of solid films was initiated for practical reasons, a considerable body of information relating to the mechanism of photodegradation in vinyl polymers was obtained as well. At the same time, it became apparent that many questions arising during those studies could not be answered effectively because of the very nature of the solid state. Inherent disadvantages in solid phase studies involve, for example, phenomena connected with diffusion of small molecules and polymer chain mobility. The proximity of polymer chains can, and often does, result in competition between scission and crosslinking during degradation with consequent difficulties in interpretation of experimental data. Finally, in the solid phase, relatively little control can be exercised over traces of dissolved gases and extraneous nonpolymeric molecules which could be essential in the inhibition or sensitization of photolysis.

In degradation work, many of these disadvantages can be circumvented through the use of dilute solutions of high polymers, although at the same time additional complications are introduced. The separation of polymer chains by "inert" solvent molecules should tend to decrease crosslinking without affecting scission, and therefore under favorable conditions the influence of each may be assessed. In a pure solid polymer, the effects of the direct absorption of radiation should be the main ones observed; with polymer solutions, problems of both practical and theoretical importance such as energy transfer and free radical attack may be more amenable to investigation. A detailed study of the photolysis of polymers in solution, coupled with solid phase work, should go far in giving us a better understanding of polymer behavior under irradiation.

Ionizing radiation has been utilized in most investigations of the degradation of high polymers in solution. This work has been thoroughly reviewed by Chapiro (2) and, to a lesser extent, by Charlesby (3). Much polymer radiolysis has been directed toward biologically important systems, but poly(styrene), particularly, and a number of other hydrocarbon polymers have also been examined. Although the energy of typical ionizing radiation is orders of magnitude greater than that of ultraviolet radiation, many analogies can be drawn between the effects of the two types of radiation on polymeric substances.

The photolysis of high polymers in solution has been reviewed by Jellinek (4). A thorough study of the photolysis of poly(methyl vinyl ketone) in dioxane and, less extensively, ethyl acetate solutions with 3130A radiation has been made by Guillet and Norrish (5). This polymer undergoes random chain scission with a quantum yield of about 0.025 scission per quantum absorbed; at the same time unsaturation appears in the polymer fragments along with readily rationalized gaseous degradation products. The photolysis was not strongly affected by the presence of air. Although no crosslinking was detected, polymer radical formation unaccompanied by chain scission did take place since irradiation of the polymer in the presence of certain monomers resulted in the formation of graft polymers (6). The photodegradation of poly(acrylonitrile) in ethyl carbonate/propylene carbonate solutions by 2537A radiation in the absence of air at 25°C has been investigated by Jellinek and coworkers (7,8). Random chain scission with a quantum yield of about  $10^{-4}$

was found, but the results appeared to be influenced by the history of the polymer sample. Poly(styrene) in benzene under 2537A radiation (9) and nylon-66 in formic acid under radiation from a high pressure mercury source (10) have also been studied. With the exception of poly(styrene) these photodegradations were carried out in transparent solvents, and in none of this work was the effect of the solvent, other than as a diluent, more than briefly considered.

Some work has been carried out with systems in which energy transfer or radical attack must play a prominent role. Notable among these is the report of Baxendale and Thomas (11) in which aqueous solutions of poly(methacrylic acid) were exposed to x-radiation or ultraviolet radiation in the presence of hydrogen peroxide; here the attacking species was the hydroxyl radical. Voelker (12) found that aqueous solutions of this polymer or of poly(acrylic acid), as well as their salts, could be degraded by either visible or ultraviolet radiation. From the standpoint of the present investigation, perhaps the most interesting work has been given in brief communications by Mönig and coworkers (13-15) in which the photolysis of poly(methyl methacrylate) in benzene, chloroform, and dioxane was reported; the rates of degradation of this polymer were markedly affected by both the solvent and 3,4-benzpyrene as an added photosensitizer in benzene in the presence of oxygen.

It is apparent from the results of radiolytic studies and the photolyses just discussed that the influence of the solvent, which is the major constituent of the reaction system, will be of primary importance in a large number of cases. In the work reported here, poly( $\alpha$ -methylstyrene), previously studied in this Laboratory in film form under both ultraviolet (16) and gamma (17) radiation, has been chosen for investigation in solution because of its demonstrated freedom from crosslinking in the solid and the fact that both this polymer and its homolog, poly(styrene), are strong absorbers at 2537A, so that the relatively monochromatic radiation from a low pressure mercury source can be utilized. A comparison between these two polymers under the same conditions is, of course, desirable on the basis of structure. In later reports in this series, this and other points, such as the influence of sensitizers, will be considered.

## EXPERIMENTAL PART

### Materials

The same poly( $\alpha$ -methylstyrene) which was used in earlier film studies (16) was employed in this work. It was purified by reprecipitation from benzene with methanol, freeze-drying from benzene, and exhaustive extraction with methanol until no material absorbing at wavelengths above 2300A were found in the extracts. The polymer was dried in a vacuum oven at 60°C. On the basis of its sedimentation pattern, the polymer was assumed to have a "most probable" molecular weight distribution; the intrinsic viscosity of the polymer in benzene indicated a number-average molecular weight of  $1.07 \times 10^5$ . Spectroscopic grade or highly purified solvents were used throughout this work. Changes in the ultraviolet absorption of the solvents during irradiation were negligible except in the cases noted.

### Apparatus

A U-shaped Hanovia 84A-1 low pressure mercury lamp was used as the radiation source throughout most of this work. About 90 percent of the emitted radiation from this lamp is at a wavelength of 2537A. This is the only photolytically active radiation, since shorter wavelengths (primarily the ozone-producing 1849A radiation) are absorbed by the quartz irradiation cell and longer wavelengths are not absorbed by the solutions used. Ferrioxalate actinometry (18) was employed, and the lamp output was continuously monitored with a photocell.

Irradiations were carried out in the cell shown in Fig. 1. The apparatus consists of a cylindrical quartz cell 2.5 cm in diameter and about 30 ml in volume, containing a glass-enclosed stirring bar. This cell is surmounted by a filter and capillary viscometer (running time for benzene is about 62 seconds at 30°C), a side arm for the polymer sample, and a cuvette for spectroscopic measurements. During irradiations, the cell was mounted at a distance of 8 inches from the source and the irradiations were carried out at ambient room temperatures, approximately 25°C.

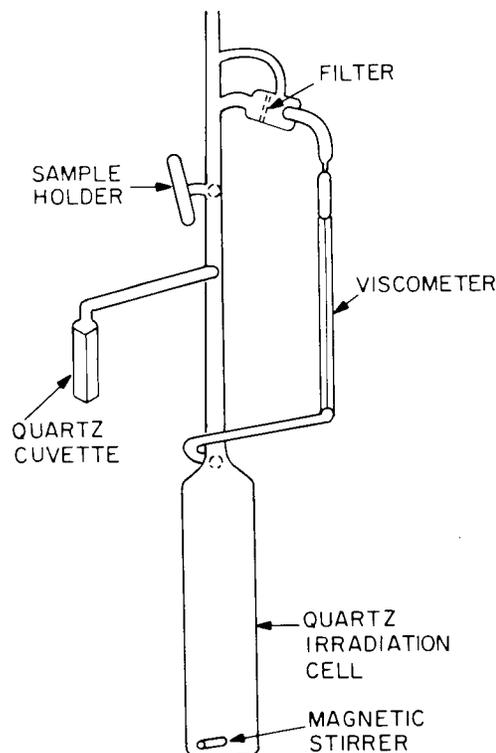


Fig. 1 - Irradiation cell

Intrinsic viscosities determined by dilution were run in Ubbelohde-type dilution viscometers having a running time of about 170 seconds for benzene at 30°C, the temperature at which all viscosity measurements were made.

#### Procedure

Approximately 20 ml of polymer solution was used in each run. For exposures in air, pre-prepared polymer solutions were used or air-equilibrated solvent was added to the polymer sample in the cell and the concentration determined by weighing. Single-solvent runs in the absence of air were carried out with a weighed sample of polymer in the side arm; degassed solvent was distilled into the irradiation cell on the vacuum line. After sealing off the apparatus, the ultraviolet spectrum of the solvent as well as its running time in the viscometer were measured; solution was then effected simply by mixing polymer and solvent. Where mixed solvents were used, the solvent mixture was added directly to the cell and degassed in place. Each system was evacuated to a pressure of  $10^{-3}$  torr during the degassing operation. After each exposure, ultraviolet spectra of the solutions were measured as appropriate, and relative viscosities determined.

## Evaluation of Quantum Yields for Scission

On the assumption that scission occurs at random points along the polymer chain, two kinds of information are required for a determination of the quantum yield. These are the number of scissions occurring in an average polymer chain and the number of quanta which must be absorbed to produce those scissions.

The number of scissions ( $s$ ) per polymer molecule were calculated on the basis of viscosity data in the same manner as in the film work reported previously (16). For a "most probable" molecular weight distribution before and after degradation, it is assumed that  $\bar{M}_v = \bar{M}_w = 2\bar{M}_n$ , referring to viscosity-, weight-, and number-average molecular weights, respectively. From the empirical relation between the molecular weight and intrinsic viscosity,  $[\eta] = K\bar{M}_n^\alpha$ , the number of scissions is given by:

$$s = \frac{\bar{M}_{n_0}}{\bar{M}_n} - 1 = \left( \frac{[\eta_0]}{[\eta]} \right)^{1/\alpha} - 1 \quad (1)$$

where the subscript zero refers to the initial polymer molecule. Intrinsic viscosities were derived from the single-point relative viscosities through a modification of the Huggins equation (19):

$$[\eta] = (\sqrt{2}/c) \sqrt{\eta_{sp} - 1n\eta_r} \quad (2)$$

where  $c$  is concentration and  $\eta_{sp}$  and  $\eta_r$  refer to specific and relative viscosities, respectively. Equation (2) gave viscosities within 1 percent of those obtained by the usual dilution and extrapolation procedure.

In general, the exponent  $\alpha$  in Eq. (1) was not available for the solvents or solvent mixtures used in this work. Since  $s$  is not particularly sensitive to small variations in  $\alpha$ , this parameter could be satisfactorily estimated by the method of Meyerhoff (20) on the assumption that  $\alpha$  for poly( $\alpha$ -methylstyrene) is 0.5 and 0.71 in cyclohexane and benzene, respectively (21,22). A plot of  $[\eta]$  for our sample against these values of  $\alpha$  gives a line from which  $\alpha$  can be estimated from the experimentally determined  $[\eta]$  in any other solvent. Intrinsic viscosities measured by dilution viscometry in Ubbelohde viscometers. Table 1 gives the values of  $\alpha$  so estimated.

The number of quanta absorbed to produce a given change in molecular weight is dependent on the amount of energy ( $I_0$ ) incident to the cell during time  $t$ . Quantum yields for scission may be based on the energy absorbed by the polymer only or on the energy absorbed by the entire solution. For solutions of poly( $\alpha$ -methylstyrene) at  $c > 0.1$  g/dl in transparent solvents, essentially all energy at 2537A is absorbed at the path length used here; this is equal to  $I_0 t$ , the quanta absorbed per ml determined by the actinometry. The proportion of this energy absorbed by the polymer ( $E_p$ ) in quanta per gram of polymer is determined from the absorption spectra of the polymer and solvent. The quantum yield based on absorption by the entire solution  $\phi_s^{s \circ 1n}$  is equal to  $\phi_s^p E_p$ , where  $\phi_s^p$  is the quantum yield based on absorption by the polymer only. Obviously  $\phi_s^{s \circ 1n}$  and  $\phi_s^p$  differ significantly only where the solvent absorbs at the wavelength of the incident radiation.

These quantum yields were evaluated from a plot of the number of scissions (Eq. (1)) against the number of quanta absorbed per gram of polymer ( $I t$ )

$$\phi_s^p = \left( A/\bar{M}_{n_0} \right) [([\eta_0]/[\eta])^{1/\alpha} - 1] / I t \quad (3)$$

Table 1  
Estimated Values of  $\alpha$   
for Poly( $\alpha$ -methylstyrene)  
in Various Solvents\*

Solvent	$\alpha$
Cyclohexane	0.5
4% CCl <sub>4</sub> in Cyclohexane	.52
4% Dioxane in Cyclohexane	.53
4% CH <sub>2</sub> Cl <sub>2</sub> in Cyclohexane	.54
20% CCl <sub>4</sub> in Cyclohexane	.62
Dioxane	.68
Benzene	.71
Methylene chloride	.72
Chloroform	.76
Carbon tetrachloride	.76

\*Concentration in percent by volume.

or against the number of quanta absorbed per cc of solution

$$\phi_s^{s \circ 1 n} = \left( cA / \bar{M}_{n_0} \right) \left[ \left( [\eta_0] / [\eta] \right)^{1/\alpha} - 1 \right] / I_0 t \quad (4)$$

where A is Avogadro's number and c is the polymer concentration in g/cc.

Examples typifying such plots on the basis of Eq. (3) are shown in Fig. 2. Generally, these plots were linear, i.e.,  $\phi_s^P$  was constant with dose. However at low polymer concentrations or where total absorption increased significantly,  $\phi_s^P$  tended to decrease as the dose increased; in such cases, initial slopes were used to evaluate the quantum yields.

## RESULTS AND DISCUSSION

### Molecular Weight Changes

It is evident from Fig. 2 that a range of quantum yields is encountered when different solvents are used. If the number of scissions depends only on the energy absorbed by the polymer, the quantum yield for chain scission should be independent of the solvent and, except for dilution effects, might be expected to be similar to that found in solid films. Since such is not the case, other processes must be involved, and quantum yields based on the total energy absorbed by the solution are probably more correct.

A summary of the quantum yields for random chain scission of poly( $\alpha$ -methylstyrene) at one concentration in pure single solvents is given in Table 2. These values have been obtained from data such as those shown in Fig. 2; they have been calculated on the basis of polymer absorption (Eq. 3) and solution absorption (Eq. 4) for the purpose of comparison.

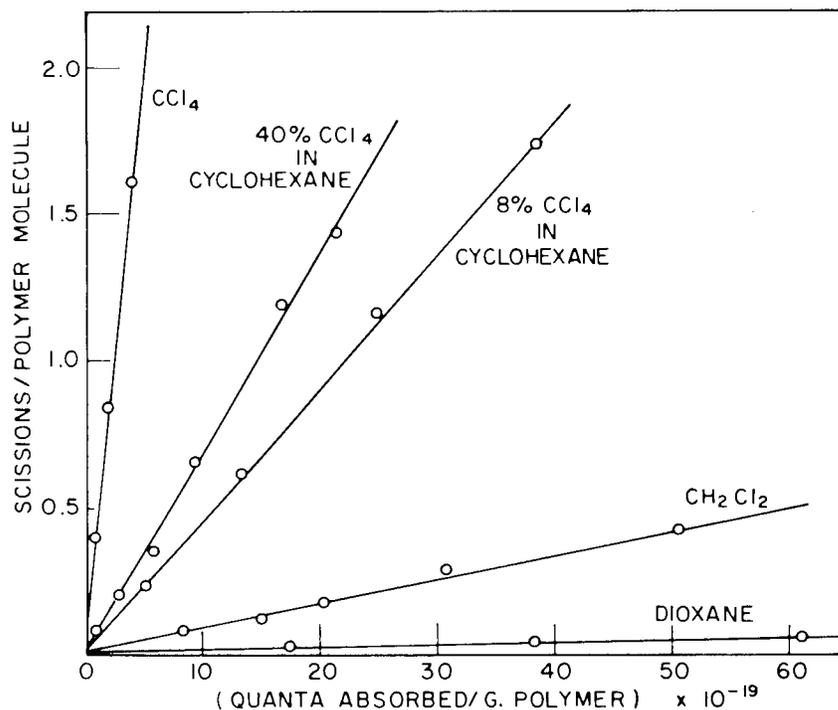


Fig. 2 - Photolysis of poly( $\alpha$ -methylstyrene) in various solvents

Table 2  
Quantum Yields for Scission of Poly( $\alpha$ -Methylstyrene) in Solution\*

Solvent	$\phi_s^P \times 10^4$		$\phi_s^{soln} \times 10^4$	
	Air	Solvent Vapor	Air	Solvent Vapor
Benzene	95	-	0.53	-
Dioxane	4	5	4	5
Cyclohexane	-	6	-	6
Methylene chloride	50	50	50	50
Chloroform	1600	-	1570	-
Carbon tetrachloride	2110	1850	1680	1460

\*  $c = 1 \text{ g/dl.}$

Two negative features of these data are of interest; neither the absorption coefficient of the solvent at  $254 \text{ m}\mu$  nor the so-called polymer-solvent interaction coefficient  $\alpha$  (Table 1) appear to correlate with the rate of scission. Of these solvents, benzene has the largest absorption coefficient at  $254 \text{ m}\mu$  and, on the basis of solution absorption, the lowest quantum yield for scission is observed in this solvent. This is not solely the result of the action of an optical filter is seen in the fact that in the solvent with the next highest absorption coefficient at  $254 \text{ m}\mu$ , carbon tetrachloride, the highest quantum yield is found. The lack of

correlation of  $\alpha$  with the rate of scission in these data, may not be meaningful since other factors may well be overriding. The phenomenon of concern here is the influence of the compactness of the molecular coil in solution, which could in turn give rise to interactions between neighboring groups during irradiation; at best, these effects may be weak compared to energy transfer or attack by solvent radicals.

A very important point brought out by the data in Table 2 is the absence of any appreciable difference between the quantum yields found in the presence or absence of air in any given solvent. At this time it cannot be said with certainty whether oxygen plays only a minor role in the photodegradation of poly( $\alpha$ -methylstyrene) under these conditions or whether the mechanisms of degradation in the presence or absence of oxygen are quite different and the similarity of the rates of scission is coincidental. Spectroscopic evidence indicates that in carbon tetrachloride the mechanism of photodegradation in the absence of air is quite unlike that in the presence of air.

This behavior is in marked contrast to that found with poly(styrene) in solution under similar conditions (23). In the absence of oxygen, viscosity changes indicate poly(styrene) to be many orders of magnitude more stable than poly( $\alpha$ -methylstyrene). This could be a reflection of crosslinking overcoming the effect of scission, since poly(styrene) films in vacuum have been observed to undergo extensive crosslinking under ultraviolet irradiation (24). In the presence of air, irradiation of poly(styrene) solutions produces viscosity changes corresponding to an apparent rate of scission of the same order of magnitude but somewhat smaller than that found with the  $\alpha$ -methyl homolog. This effect probably resides in the presence of the tertiary hydrogen atoms in the backbone of the poly(styrene). This cannot be the entire story, since no change due to oxygen was detected in the photolysis of dioxane solutions of poly(methyl vinyl ketone) (5), whose backbone also has tertiary hydrogen atoms on alternate carbon atoms.

The solvents listed in Table 2 are readily divided into two groups based on the values of the quantum yields for scission in poly( $\alpha$ -methylstyrene). A point on which to base the division is  $10 \times 10^{-4}$ , the quantum yield for random scission of solid films of this polymer in vacuum (16).

Those solvents in which higher quantum yields are observed are, in a sense, sensitizers for the degradation reaction. It is seen that these are halogenated solvents, and the order of increasing quantum yields is also roughly the order of increasing ease of homolytic cleavage in these solvents as exemplified by chain transfer constants in radical reactions or by general photolytic reactions. This suggests that the processes occurring during the degradation of this polymer by ultraviolet radiation are analogous to those proposed for the so-called "indirect" processes taking place during the radiolysis of many polymers in these and similar solvents (2). The most obvious of these reactions is attack of the polymer by free radicals formed by photolysis of the solvent. A less obvious, but possibly more important process in such solvents is energy transfer without decomposition of the solvent. A study of these two phenomena in polymer degradation is in progress.

By inference, it appears that the predominant processes taking place in the remaining solvents must represent photolysis of the polymer itself, analogous to the so-called "direct" reaction in solution radiolysis. This is based on the qualitative similarity between the quantum yields for scission of poly( $\alpha$ -methylstyrene) in these solvents and that found in the solid film. The very low value observed in benzene, much lower than that in the film, may tentatively be ascribed to an energy transfer from the polymer to the solvent, the reverse of the "indirect" effect in the halogenated solvents. Benzene is not known to produce significant amounts of radicals under 254 m $\mu$  irradiation (25) in the doses used here although it is the major absorber in this system. Neither cyclohexane nor dioxane are strong absorbers at this wavelength, and these solvents would not be expected to undergo significant photolysis under our experimental conditions. It is of interest, however, that poly(methyl methacrylate) has been reported to undergo photolysis (13) and radiolysis (26)

more rapidly in dioxane than in chloroform solutions. Poly(styrene) in solution undergoes radiolysis (27) with G-values for chain breaks in various solvents following the same qualitative order as those reported here for poly( $\alpha$ -methylstyrene). Such results again point to energy transfer as the predominating process in these solvents, since there is little reason to expect dioxane to form radicals more readily in the presence of one pure polymer than in another (note that poly(methyl methacrylate) is well known for the ease with which it can form peroxides; if such were present, comparisons with other polymers are invalid).

Cyclohexane was selected for a solvent in this work not only because of its transparency to ultraviolet radiation at the wavelengths used here, but because it is a theta solvent for poly( $\alpha$ -methylstyrene) at 34°C (21). This means that under our experimental conditions, the undegraded polymer was near the point of incipient precipitation. It was anticipated that a very small amount of crosslinking during irradiation in this solvent would result either in a rapid increase in viscosity or in outright precipitation. Actually, no gelation but rather a very slow decrease in viscosity, linear with absorbed dose, was observed. It is therefore assumed that crosslinking is not a significant reaction during the photolysis of poly( $\alpha$ -methylstyrene) in 1-percent solutions in the absence of sensitizers.\*

At several points in this report, reference has been made to the possibilities of energy transfer being responsible for some of the observed effects. If such occurred to a significant extent, a relatively small proportion of a substance acting as an energy sink would be expected to function as an inhibitor for any reaction which otherwise might have occurred. Conversely, any substance which absorbs energy from a source outside the system and is able to transfer that energy by some means to the polymer where a reaction can take place can be said to have acted as a sensitizer.

Impurities in the solvents used may therefore assume considerable importance in determining the rate of scission of the polymeric solute. A case in point is that of chloroform, which normally is obtained commercially with about one percent of ethanol added as a "preservative." The function of the ethanol as a degradation "inhibitor" is not entirely clear. Qualitatively the results of the degradation were similar to those found by Durup (28), who studied the radiolysis of poly(styrene) in these solvents. As seen in Table 3, small amounts of ethanol in two halogenated solvents drastically reduces the rate of scission of the polymer. The observed linearity in the plots of scission against quanta absorbed in these experiments implies that the ethanol was not being consumed; however, runs at very low ethanol concentrations were not carried out. Irradiation of dilute solutions of hexane, heptane, or cyclohexane in chloroform containing ethanol in the absence of air always gave acetaldehyde and hydrogen chloride as major initial products. This indicates that ethanol may function as a hydrogen atom donor to scavenge chlorine atoms resulting from photolysis of the chloroform.

Three other solvent systems were examined. All involved cyclohexane, which in many respects seemed to be the most photolytically inactive of the solvents used. The addition of 4 percent by volume of either dioxane or methylene chloride to cyclohexane had little discernible effect on the quantum yield for scission in either the presence or absence of air. Quantum yields, based on energy absorbed by the polymer, obtained in mixtures of

\*Crosslinking can take place under certain undefined conditions with poly( $\alpha$ -methylstyrene), however. This is based on the observation of turbidity in preliminary experiments in which solutions of this polymer in methylene chloride were irradiated in the absence of air. The solvent batch itself was not responsible for the effect, since after two repetitions of the experiment, no further turbidity was observed under any conditions, even with the same solvent batch. The cause of the phenomenon is unknown.

Table 3  
Effect of Ethanol on the Scission of Poly( $\alpha$ -Methylstyrene) in Air\*

Solvent	$\phi_s^P \times 10^4$	$\phi_s^{soln} \times 10^4$
Freshly distilled spectrograde $\text{CHCl}_3$	910	895
$\text{CHCl}_3$ , washed ten times with water	1600	1570
$\text{CHCl}_3$ , with 2% by volume of ethanol added	590	580
Carbon tetrachloride	2100	1850
Carbon tetrachloride with 2% by volume of ethanol added	155†	123†

\*  $c = 1\text{g/dl}$ .

† Values are the same in the absence of air.

carbon tetrachloride and cyclohexane are shown in Fig. 3. Sensitization by carbon tetrachloride and inhibition by cyclohexane are apparent from the s-shaped curve, since simple dilution should give a linear gradation in scission rates. The effect must be more than mere competition between the polymer and the cyclohexane for radicals derived from the carbon tetrachloride, for even low concentrations of carbon tetrachloride greatly increase the rate of scission.

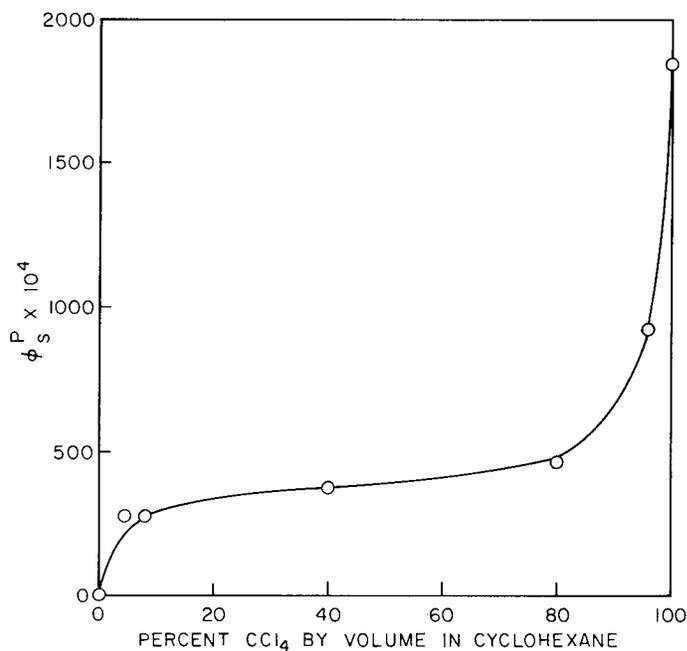


Fig. 3 - Photolysis of poly( $\alpha$ -methylstyrene) in mixtures of carbon tetrachloride and cyclohexane in the absence of air

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The influence of polymer concentration on the rate of scission in carbon tetrachloride in the absence of air was investigated briefly. As expected, the rate of scission decreased with increasing polymer concentration: at 0.46, 0.98, and 5.64 g/dl,  $\phi_s^{s_0 1n} \times 10^4$  was 1740, 1460, and 1310 scissions per quantum absorbed, respectively. This result undoubtedly reflects the decreasing mobility of polymer molecules in a more viscous medium, as well as the lower production of solvent radicals or decreased energy transfer at lower solvent concentrations. In all cases, hydrogen chloride was present after irradiation, indicating solvent radical attack since the polymer was the only source of hydrogen in the system.

The photolysis of carbon tetrachloride by ultraviolet radiation has long been known to yield chlorine atoms and trichloromethyl radicals (29), with the subsequent formation of hexachloroethane and, when other molecules are present, the products of their reactions with atomic chlorine. It was of interest, therefore, to observe qualitatively the effect of chlorine itself on both poly( $\alpha$ -methylstyrene) and poly(styrene) in carbon tetrachloride solutions in the absence of air. The consumption of chlorine in such solutions is readily followed by means of spectrophotometric measurements at about 327 m $\mu$ .

In these preliminary experiments, the contrast between the two polymers was quite remarkable. In neither case was chlorine consumed in the absence of light. With poly( $\alpha$ -methylstyrene), even the light from an ordinary 100-watt tungsten bulb at a distance of several feet is sufficient to initiate a fairly rapid reaction with chlorine. As the chlorine is consumed, the intrinsic viscosity of the polymer rapidly decreases; no attempt was made to evaluate a quantum yield for scission during this reaction, but it obviously is many orders of magnitude greater than that given in Table 2 for carbon tetrachloride. Poly(styrene), on the other hand, consumes chlorine more slowly than poly( $\alpha$ -methylstyrene) and to obtain a rate approaching that for the latter, it was necessary to use the 2537A source. In spite of the obvious reaction between poly(styrene) and chlorine, no concomitant intrinsic viscosity decrease was found. On the assumption that the major initial reaction between these polymers and chlorine consists of a hydrogen atom abstraction by a chlorine atom, it is apparent that the stability of the resulting free radical is crucially important in regard to subsequent scission of the polymer. A more detailed study of these reactions is outside the scope of this report.

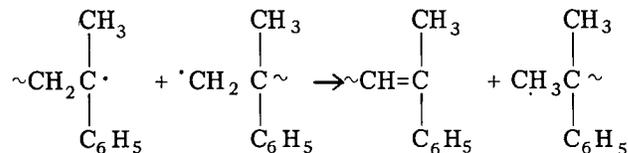
### Spectral Changes

At the radiation doses used in this work, spectral changes in either the polymer or its solutions are slight in the ultraviolet region and almost nonexistent in the infrared. In some solvents, such as dioxane, the effect of charge-transfer complexes with molecules such as oxygen (30) must be considered in any interpretation of spectral changes. Similar complexes may also be formed with the polymer itself (31). In this work, molecular weight changes or spectral changes in the polymer traceable to such complexes were not observed.

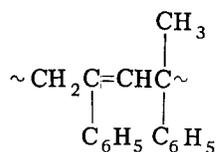
A general increase in absorption at wavelength below 350 m $\mu$  in poly( $\alpha$ -methylstyrene) solutions in all solvents occurs during irradiation. In most cases there is some evidence of band formation as a small shoulder in the spectrum in the 290-300 m $\mu$  region. This absorption was observed in cyclohexane, dioxane, and methylene chloride solutions irradiated in the absence of air and in chloroform solutions in air. The origin of this absorption is unknown, but it is of interest that while  $\alpha$ -alkylstyrenes (including the monomer  $\alpha$ -methylstyrene) have no pronounced maxima above 250 m $\mu$ ,\* both  $\beta$ -ethylstyrene and

\*Commercial  $\alpha$ -methylstyrene, which undoubtedly contains small amounts of oxidation products, does exhibit a small absorption maximum at 289 m $\mu$  as well as a very slight inflection at about 280 m $\mu$ . These are absent in the pure material.

$\beta$ -methylstyrene do have maxima at 293  $m\mu$  (32). Scission of the main chain in poly( $\alpha$ -methylstyrene) would give two radical fragments which, if terminated by disproportionation, would lead to one chain end of the  $\beta$ -substituted styrene type



Without suggesting how such a reaction might come about, it might also be postulated that elimination of the elements of methane from the polymer chain would lead to a  $\beta$ -substituted styrene group without scission



Irradiation of carbon tetrachloride solutions of poly( $\alpha$ -methylstyrene) produces more distinct changes in both the ultraviolet and the infrared spectra of the solutions. In the case of the run in which a small amount of ethanol was added to a carbon tetrachloride solution and the irradiation carried out in the presence of air (Table 3), a liquid phase separation occurred after an absorption of about  $10^{20}$  quanta/ml. An infrared spectrum of the separated product showed the presence of bands ascribable to hydroxyl, carbonyl, aliphatic carbon-hydrogen, and aromatic linkages, but no carbon-chlorine absorption was observed. This product was not further identified, but it obviously involves the polymer and some oxidation products of either the polymer or the ethanol. Such phase separation was found only under these conditions; it did not occur in the absence of air or in the absence of ethanol.

Changes in the ultraviolet spectrum of carbon tetrachloride solutions of poly( $\alpha$ -methylstyrene) during irradiation in either the presence or absence of air are particularly interesting. While a structureless general increase in absorption takes place during irradiation of a one-percent polymer solution in air, a different situation prevails in the absence of air. In addition to a more rapid general increase in absorption, a band having a maximum at about 326  $m\mu$  appears (traces 2 and 3 in Fig. 4); any changes which may occur in the 290-300  $m\mu$  region appear to be masked. If the cell is opened to the atmosphere and shaken for 15 minutes to equilibrate the solution with air and atmospheric moisture, no change takes place in the spectrum. However, if irradiation of this solution is performed in air, a general decrease in absorbance at all wavelengths in the 280-350  $m\mu$  region takes place (traces 4 and 5 in Fig. 4). No such sequence of spectral changes was observed in cyclohexane solutions of the polymer and therefore carbon tetrachloride must be directly involved in the formation of the new chromophores.

The alterations in the spectra are the result of changes within the polymer structure itself rather than originating in small molecules generated during the photolysis. This was determined by twice precipitating a polymer which had been irradiated in carbon tetrachloride in the absence of air and observing the spectrum of one-percent solutions of the reprecipitated polymer in both carbon tetrachloride and in methylene chloride. The spectrum of the carbon tetrachloride solutions before and after reprecipitation were the same. In methylene chloride, the major absorption maxima of the polymer at 256 and 261  $m\mu$  were readily observed at a concentration of 0.01 g/dl; in this region, the spectrum was identical to that of unirradiated polymer. Infrared spectra showed differences between irradiated and unirradiated polymer only in the 7.5-8.5  $\mu$  region, and these changes were

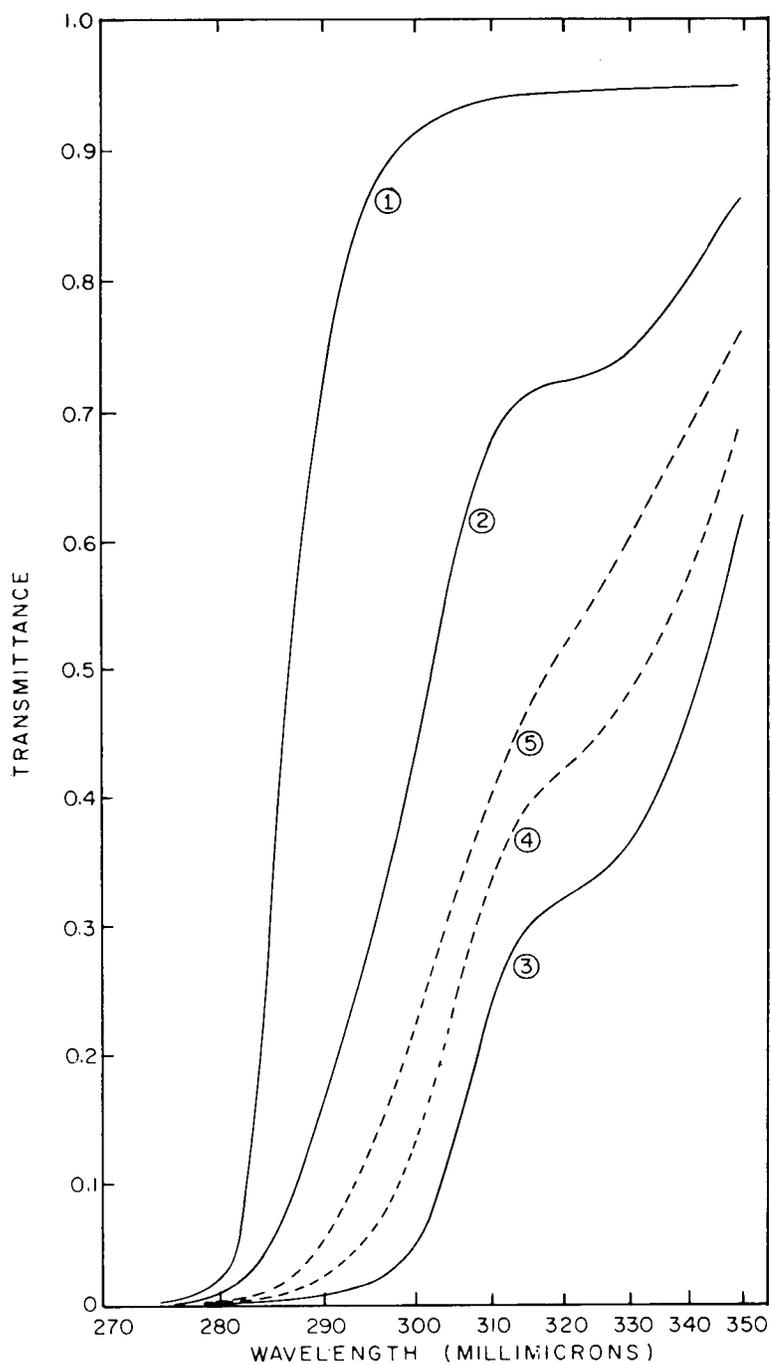
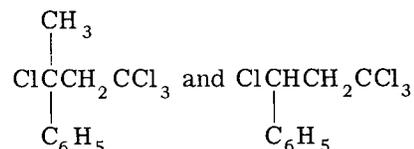


Fig. 4 - Spectral changes during the irradiation of poly( $\alpha$ -methylstyrene) in carbon tetrachloride ( $c = 1 \text{ g/dl}$ ): (1) unirradiated; (2) 15 min, no air; (3) 70 min, no air; (4) opened to air, irradiated 14 min; (5) 42 min additional irradiation in air

minor and difficult to interpret. For comparison, these infrared spectra are shown in Fig. 5 along with the same spectrum of the polymer separated after irradiation in carbon tetrachloride containing chlorine. These spectra, coupled with the fact that the 326  $m\mu$  band did not form in the chlorine experiment (which was carried out until all chlorine was consumed), indicates only that the spectral changes in carbon tetrachloride alone must be due to reaction with some entity other than chlorine, either molecular or atomic. A most likely source, of course, is the trichloromethyl group or some chromophore resulting from dehydrochlorination involving this group.

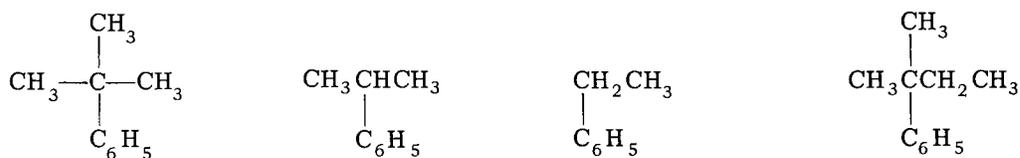
Further inquiry into the source of the 326  $m\mu$  absorption was made by irradiating various alkyl-benzenes and alkenyl-benzenes in carbon tetrachloride in the absence of air. The results are shown in Figs. 6 and 7. Under the same conditions no spectral changes occurred upon irradiation of carbon tetrachloride alone or of a one-percent solution of cyclohexane in that solvent, although in the latter solution, hydrogen chloride was present at the conclusion of the irradiation.

At first sight, it appears in Fig. 6 that both poly( $\alpha$ -methylstyrene) and poly(styrene) give rise to nearly the same spectrum in the 280-350  $m\mu$  region, and that therefore similar chemical structures in the polymer are responsible for the spectra. Logical candidate model compounds would, of course, include the monomers corresponding to each of the polymers. The irradiation of  $\alpha$ -methylstyrene in carbon tetrachloride\* in the absence of air does indeed result in a spectrum very much like those of the two polymers. Styrene does not, under the same conditions, give a similar spectrum. The 1:1 adducts from these monomers and carbon tetrachloride would be expected to have the structures (33)



or possibly some dehydrochlorination product from these compounds.

Attention was then turned to model alkylbenzenes. The compounds



tert-butylbenzene    iso-propylbenzene    ethylbenzene    (1,1-dimethylpropyl)benzene

were irradiated as one-percent solutions in carbon tetrachloride in the absence of air to yield the spectra shown in Fig. 7 and in each of these experiments, the cell was opened to the atmosphere and the contents again irradiated. Since the polymers being irradiated are at least initially free of unsaturation, these model compounds give some indication of the position of attack by radicals present in these solutions. It would appear from Fig. 7 that attack of the side chain methyl group in poly( $\alpha$ -methylstyrene) is unlikely since tert-butylbenzene undergoes no significant spectral changes in this region under the same conditions as does the polymer. Ethylbenzene, isopropylbenzene, and

\* Monomers were irradiated as dilute solutions in tert-butylbenzene to simulate a small quantity of monomer found in the polymer; tert-butylbenzene does not give rise to spectral changes in the region of interest under these conditions.

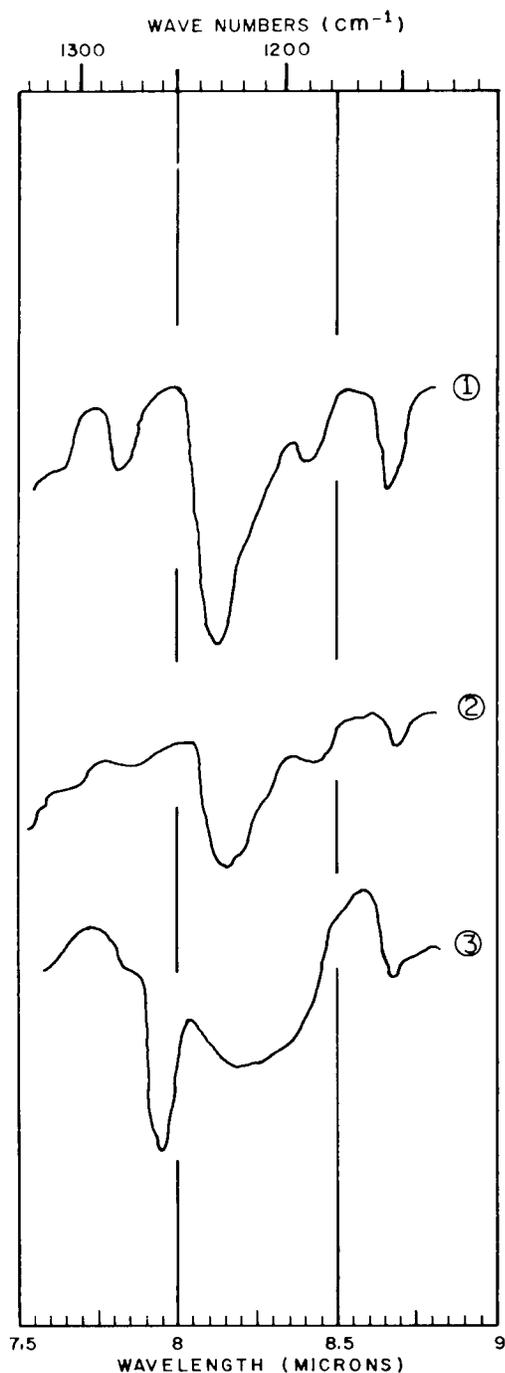


Fig. 5 - Infrared spectra of poly( $\alpha$ -methylstyrene) (KBr discs): (1) undegraded; (2) irradiated in carbon tetrachloride; (3) irradiated in carbon tetrachloride in the presence of chlorine

(1,1-dimethylpropyl)benzene, on the other hand, do indeed give rise to new absorption bands, albeit at wavelengths somewhat lower than 326  $m\mu$ . Isopropylbenzene was also irradiated in cyclohexane in the absence of air; no spectral changes similar to those in carbon tetrachloride were observed. It would seem from these results that reaction could take place through hydrogen abstraction from either the  $\alpha$ -benzylic carbon atom or the

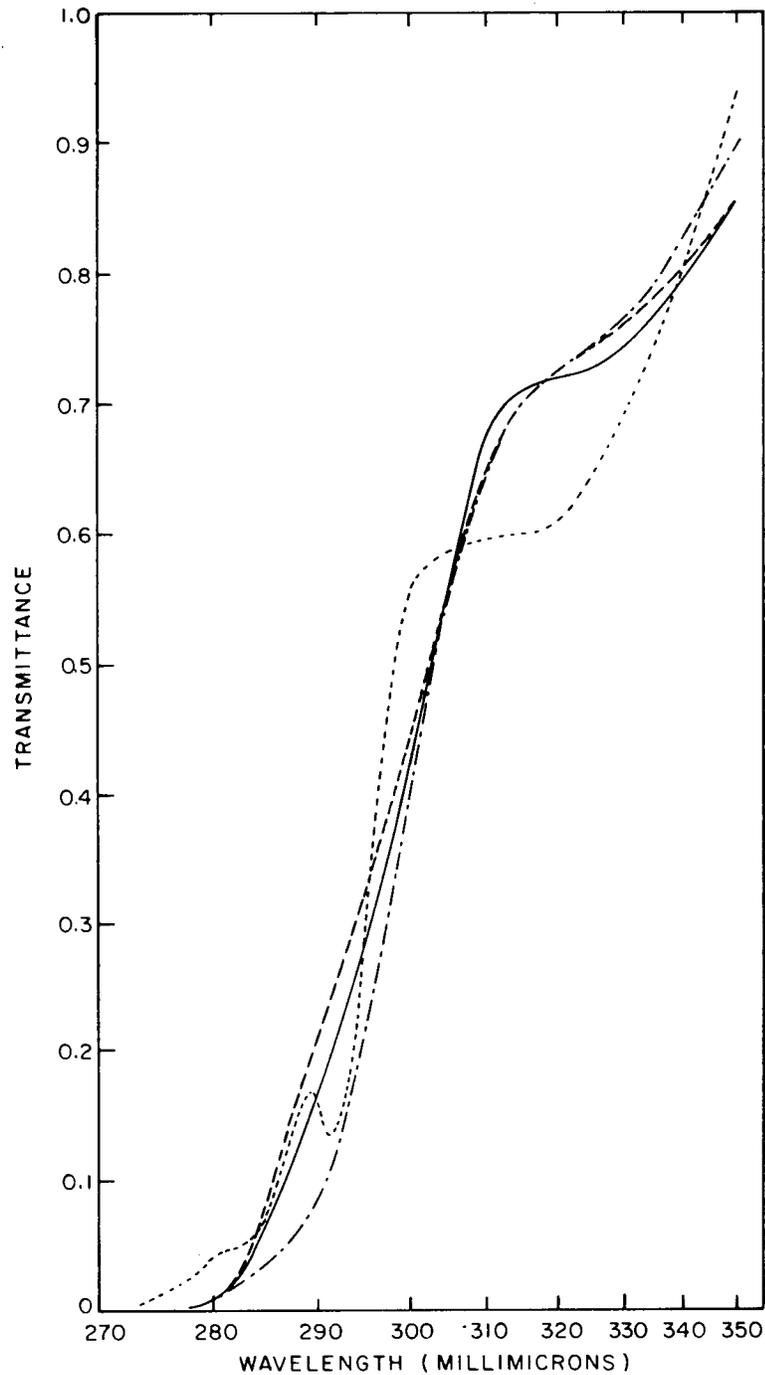


Fig. 6 - Spectra of solutions of polymers and monomers after irradiation in carbon tetrachloride in the absence of air: ——— poly( $\alpha$ -methylstyrene) (1%); - - - - - poly(styrene) (1%); - · - · -  $\alpha$ -methylstyrene (0.01%) plus tert-butylbenzene (1%); ······ styrene (0.01%) plus tert-butylbenzene (1%) (concentrations in percent by volume)

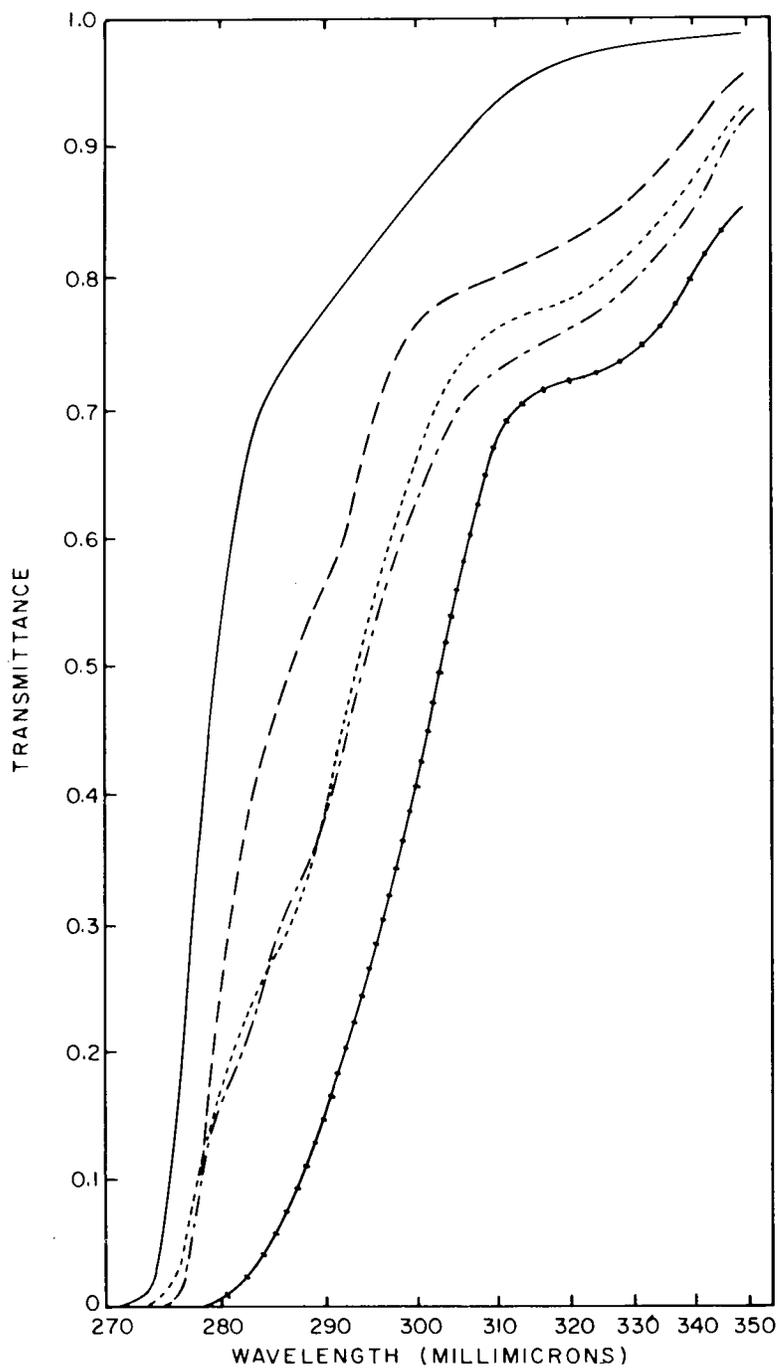
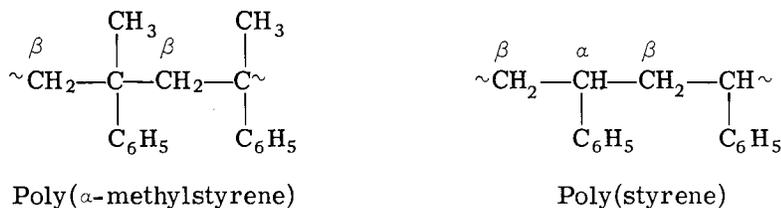


Fig. 7 - Spectra of 1% solutions of alkylbenzenes in carbon tetrachloride after irradiation in the absence of air: ——— tert-butylbenzene; - - - - - ethylbenzene; ······ 1,1-dimethylpropylbenzene; - · - · - isopropylbenzene; + + + + + poly( $\alpha$ -methylstyrene)

$\beta$ -methylene carbon atom. The latter is present in the backbone of both poly( $\alpha$ -methylstyrene) and poly(styrene), but only poly(styrene) possesses the  $\alpha$ -benzylic type of hydrogen



The spectral behavior of these solutions after they have been exposed to air and again irradiated now becomes of interest. While the new absorption resulting from irradiation in the absence of air is slightly reduced by irradiation in air of the ethylbenzene and isopropylbenzene solutions, the general increase in absorption throughout the entire spectral region rapidly masks the loss of this band. Since tert-butylbenzene shows no changes, it is assumed that this behavior does not involve the  $\alpha$ -methyl groups. With (1,1-dimethylpropyl)benzene and poly( $\alpha$ -methylstyrene), on the other hand, a large decrease in the new band is observed during the irradiation in air. Only  $\beta$ -methylene hydrogens are available in these two substances. On this admittedly weak evidence, it is tentatively concluded that the initial attack by carbon tetrachloride radicals on poly( $\alpha$ -methylstyrene) and possibly on poly(styrene)\* is at the  $\beta$ -methylene carbon atoms.

Examination of the infrared spectrum of the (1,1-dimethylpropyl)benzene/carbon tetrachloride solution in a 1 mm cell in the 1650-1950  $\text{cm}^{-1}$  region was revealing. The unirradiated solution had no bands of intensity greater than 1% transmittance in this region, but after irradiation in the absence of air, followed by irradiation in air, a sharp band of medium intensity at 1812  $\text{cm}^{-1}$  and a very weak band at 1690  $\text{cm}^{-1}$  were observed. Under the same conditions, carbon tetrachloride irradiated in air gave a sharp band at 1817  $\text{cm}^{-1}$  with a lower intensity than the 1812  $\text{cm}^{-1}$  band and showed no new absorption in the 1690  $\text{cm}^{-1}$  region; the 1817  $\text{cm}^{-1}$  band is one of the strongest in the phosgene spectrum. Since the 1812-1690  $\text{cm}^{-1}$  band combination is reasonable for the carbonyl absorption in an acid chloride, the solution giving this spectrum was stirred with hot water several hours to hydrolyze this acid chloride to the acid as well as to convert any phosgene to carbon dioxide and water. After separation and drying of the organic phase, this solution gave a spectrum in which the 1812  $\text{cm}^{-1}$  absorption was almost nil and in which the 1690  $\text{cm}^{-1}$  band was slightly increased; there was also a slight general increase in absorption in the 3300-3600  $\text{cm}^{-1}$  region. These finds are tenuous at best, especially in view of possible contamination with phosgene, but they do support the conclusion that the following series of transformations has taken place:



Further confirmation is noted in the fact that no additional absorption in the 280-290  $\text{m}\mu$  region of the ultraviolet spectrum was observed after irradiation in air. Such absorption would be expected from conversion of a dichloromethylene group to an isolated carbonyl group, while acid chloride carbonyl absorption is usually observed at wavelengths below 240  $\text{m}\mu$ .

\*Other workers (34) have assumed, on the basis of relative radical stabilities, that photo-chlorination of poly(styrene) in carbon tetrachloride results first in substitution at the benzylic carbon atom; no direct evidence for such substitution under free radical conditions has been offered.

## Mechanism

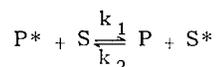
This investigation was intended primarily as an introductory survey of some of the possibilities of polymer photolysis in solution as a means of gaining insight into polymer degradation processes in general. As a consequence there are perhaps more questions raised than answered in this report. However, the picture of the processes in the degradation of poly( $\alpha$ -methylstyrene) is considerably clarified by this work. As expected, many of the mechanistic conclusions are analogous to those derived from the study of polymer solution degradation under ionizing radiation.

At the outset, the results seem to run counter to the idea of "weak links" being the source of scission in poly( $\alpha$ -methylstyrene) in solution. The weak link theory has been proposed and, to a considerable extent, demonstrated for the thermal degradation of poly(styrene) (35), but has not received very much attention in studies near room temperature. From the high dependence of the quantum yield for scission on the solvent and the fact that the quantum yield can be both smaller or larger in solution than in a solid film, it is clear that only in a photolytically inactive solvent could weak links in a polymer chain play a decisive role in its scission. The closest approach to such a solvent in this work appears to be cyclohexane.

In its broader aspects, the photodegradation of poly( $\alpha$ -methylstyrene) in solution can occur by one or more of the following routes: (a) absorption of radiation by the polymer, followed by bond breaking either in the main chain or in a pendant group; (b) absorption of radiation by either or both the polymer and solvent with transfer of energy in either direction, followed by bond breaking in the polymer; and (c) absorption of radiation by the solvent with subsequent formation of solvent radicals which in turn attack the polymer. The first route is the "direct" degradation process and the second and third, which cannot be distinguished in the present work, are the "indirect" processes referred to in work with ionizing radiation (1).

At present, little more can be added in regard to the first process over the conclusions given in the earlier report (16) on solid films of poly( $\alpha$ -methylstyrene). The major bond-breaking reaction appears to be random scission; crosslinking is negligible. Spectral results indicate the formation of unsaturation either in the polymer fragment ends or along the chain. Porter and Strachan (36) have shown that the order of bond strengths in rigid media (and therefore probably in liquids) is not the same as in the gas phase. For alkylbenzenes, the ease of homolysis by 2537A radiation follows the order  $C-H > C-CH_3 > C-C_6H_5$ . If this order holds in poly( $\alpha$ -methylstyrene) and poly(styrene), then the great difference in stability between the two polymers in the absence of oxygen in inert solvents or in the solid state is understandable. The radical most readily formed by C—H homolysis in poly(styrene) is a relatively stable tertiary disubstituted benzyl radical which would probably require additional excitation energy to give a C—C bond break which in this case is a main chain scission. The absorption of a second photon in the near vicinity of this radical is a statistically unlikely event, and in the present case, the rapidity with which poly(styrene) "yellows" indicates a preference for double-bond formation in comparison with poly( $\alpha$ -methylstyrene). Elimination of a hydrogen atom from the latter polymer gives a secondary radical on the main chain (or, less likely, an even more unstable primary radical from the side chain methyl group) which will require less additional energy to give a C—C bond break than did a tertiary radical. An alternative explanation involves a radical rearrangement such as that mentioned below.

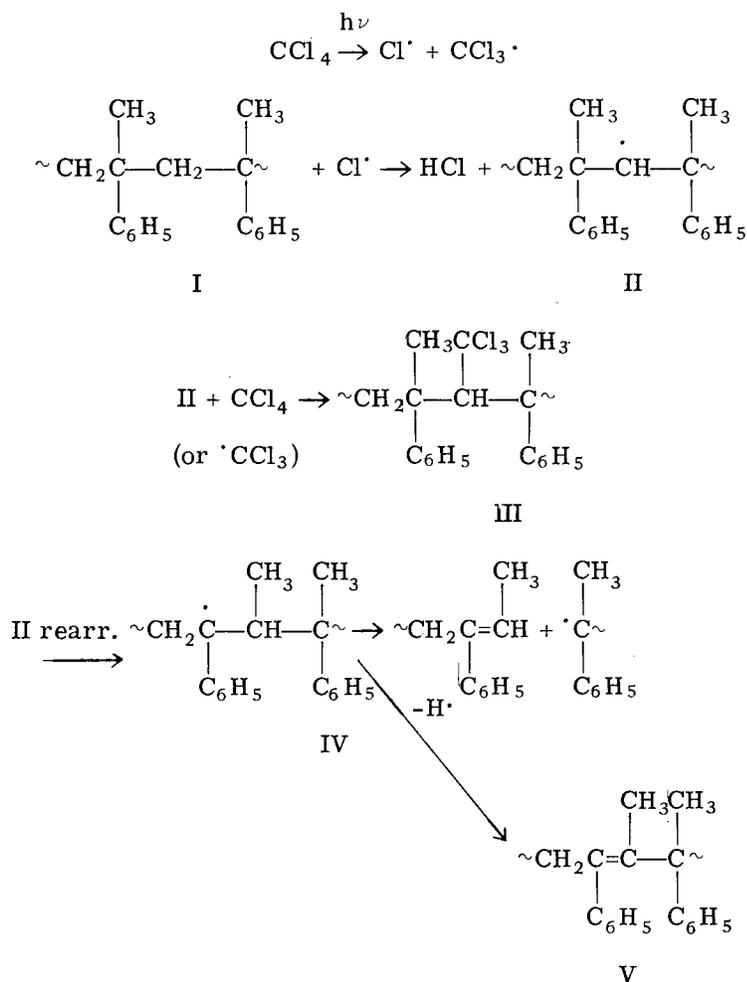
In view of the lower quantum yield for scission found in benzene compared to that in a solid film, it appears that in the energy transfer process



where P and S are polymer and solvent molecules, respectively, and the asterisk denotes an excited state,  $k_1 > k_2$  in benzene, and that this solvent can act as an energy sink. In the

other solvents studied in which the quantum yield was different from that in the film, either  $k_2 > k_1$ , solvent radical attack occurs, or both occur simultaneously.

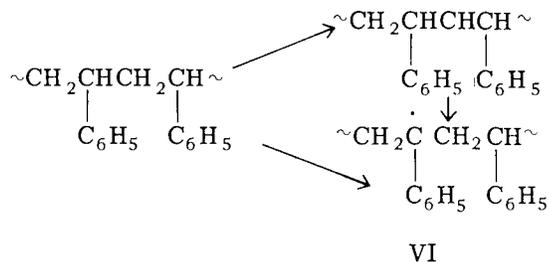
In solvents such as carbon tetrachloride, the formation of radicals under ultraviolet irradiation is well-established. It is possible that attack on the polymer by these radicals constitutes a major pathway in the degradation process, with energy transfer playing an unknown role. Direct photolysis of the polymer probably contributes only a minor part of the total number of bonds cleaved. The formation of hydrogen chloride and the spectral changes occurring in poly( $\alpha$ -methylstyrene) and in model compounds indicate that the reactions preceding or concomitant with chain scission may be as follows:



Obviously, the most important entity here is radical II. This radical could undergo scission by absorption of a second photon, or it could react with a second solvent molecule (this would mean a chain reaction which has not been demonstrated) or combine with a solvent radical to give an entity such as III. The latter is sterically hindered and if formed, probably would be easily cleaved. Finally, II may undergo rearrangement to yield a more stable radical such as IV which in turn would undergo cleavage or, less likely, expel a hydrogen atom to form an unsaturated main chain linkage.

The idea of a rearrangement such as  $\text{II} \rightarrow \text{IV}$  accounts for some of the difference between poly( $\alpha$ -methylstyrene) and poly(styrene) in regard to chain scission in the absence

of air. Poly(styrene) would form a tertiary radical (VI) (corresponding to IV) by abstraction of the tertiary hydrogen atom or by rearrangement of the secondary radical corresponding to II:



It is evident that IV is considerably more sterically hindered than VI and much more likely to undergo chain cleavage. This point may be clarified by determining the structure of the chlorination products from (1,1-dimethylpropyl)benzene.

A tentative explanation for the vast difference in behavior between poly(styrene) and poly( $\alpha$ -methylstyrene) in the presence and absence of oxygen may be offered. It is likely that peroxides or oxygen-headed peroxy radicals are formed at the same points in the chains where radicals are shown above. If such radicals are formed primarily by a rapid reaction between an already formed carbon radical and oxygen, then carbon radical formation will be rate-controlling and oxygen would have little effect on the overall rate of scission. Such may be the case in poly( $\alpha$ -methylstyrene) in which a secondary C—H is the most labile bond. Once oxygen-headed radicals are formed, their stabilities may be similar even though they may be based on a secondary or tertiary carbon atom. Thus, in air, it would be expected that the rates of scission for poly( $\alpha$ -methylstyrene) and poly(styrene) would be of the same order of magnitude and such has proved to be the case (23). Attack by chlorine, on the other hand, is equivalent to the formation of carbon-headed radicals found in solvent radical attack, and a disparity in scission rates between the two polymers is expected.

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