

NRL Report 6328

Photodegradation of High Polymers in Solution

Part 2 - Solvent Effects in the Photolysis of Polystyrene

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October 21, 1965



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Washington, D.C.

Previous Report in This Series

"Part 1 - Solvent Effects in the Photolysis
of Poly(α -methylstyrene)," R.B. Fox and T.R.
Price, NRL Report 6120, Aug. 1964

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ABSTRACT

Polystyrene photolysis in solution under ultraviolet irradiation by low-pressure and medium-pressure mercury lamps has been studied in the presence and absence of air at about 25°C. Both intrinsic viscosity and ultraviolet spectral changes were followed during the exposures. In the absence of air, crosslinking is a major process; a measurable decrease in viscosity occurred only in dioxane and carbon tetrachloride and, at sufficiently high doses, insoluble material was formed. In the presence of air, viscosity decreases were observed in all solvents; apparent quantum yields for random scission (ϕ_s^P) ranged from 0.0002 in cyclohexane to 0.11 in carbon tetrachloride. In the latter solvent, ϕ_s^P decreased with increasing polymer concentration and intensity of absorbed radiation. Carbon tetrachloride sensitized the degradation in cyclohexane, and small amounts of cyclohexane acted as an inhibitor in carbon tetrachloride solutions. Spectral changes were similar to those observed earlier for poly(α -methylstyrene). Mechanisms are suggested.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

NRL Problem C04-04
Subproject RR 001-02-43-4801

Manuscript submitted July 20, 1965.

PHOTODEGRADATION OF HIGH POLYMERS IN SOLUTION

Part 2 - Solvent Effects in the Photolysis of Polystyrene

INTRODUCTION

In practice, most polymers contain varying amounts of nonpolymeric materials such as plasticizers and other modifiers which have been purposely added and catalyst fragments and impurities whose presence is adventitious. To study the effects of these and other extraneous materials on the course of the photodegradation of a polymer, it is necessary to know accurately the composition of the system. For very small amounts of nonpolymeric additives, such information is often difficult to obtain from a film. When complete removal of dissolved gases is required, concomitant removal of other volatile materials at varying rates may also occur. To surmount such problems, the study of the photodegradation of a polymer in solution may be of value. The first report in this series described the photolysis of poly(α -methylstyrene) in dilute solution (1), and in this report, earlier work in polymer solution photolysis was briefly reviewed.

Since polystyrene has long been known for its relatively high stability to ionizing radiation (2,3), it is of particular interest. Degradation of this polymer by γ radiation in a number of solvents in the presence and absence of air has been shown (4-6) to be solvent-dependent and strongly influenced by the presence of oxygen. In the relatively small amount of literature on polymer photolysis in solution (7,8), little appears on polystyrene. A single investigation (9) of the photolysis of this polymer in benzene by 2537A radiation showed that the degradation proceeded by a random chain scission process having a rate proportional to the radiation intensity.

Recent work in our Laboratory (10) on the photolysis of polystyrene films has shown that simultaneous random chain scission and, especially in the absence of air, crosslinking occur; in addition, rapid discoloration takes place. It is evident that in dilute solution, crosslinking will be decreased through interposition of solvent molecules. Thus, several purposes are fulfilled in the study reported herein: (a) a partial separation of the scission and crosslinking processes in the photolysis of polystyrene is made; (b) a comparison between polystyrene and its homolog, poly(α -methylstyrene), under similar degradation conditions is possible; and (c) a step toward the original objective, an understanding of the influence of nonpolymer molecules on the photolysis of polymers, is made through a study of the effects of solvents on the course of the photodegradation of polystyrene in solution.

EXPERIMENTAL METHOD

Materials

Two samples of polystyrene, designated PS-1 and PS-2, were prepared in the absence of air by heating 60 ml of degassed purified monomer with 1 and 0.5 g, respectively, of benzoyl peroxide at 50°C for three days. These polymers were purified by reprecipitation from tetrahydrofuran solution with methanol followed by exhaustive extraction with methanol and vacuum drying at room temperature for three days. The intrinsic viscosities were determined in benzene at 30.00°C using an Ubbelohde dilution viscometer with a running time for benzene of about 170 seconds. Number-average

molecular weights of 5.3×10^4 and 9.1×10^4 were calculated for PS-1 and PS-2, respectively, from the intrinsic viscosities, based on the equation (11)

$$[\eta] = 1.97 \times 10^{-4} \bar{M}_n^{0.72}.$$

Apparatus

A U-shaped Hanovia 84A-1 low-pressure mercury lamp was used in most of this work. From this source, 90% of the emitted radiation is at 2357Å. The effect of other wavelengths produced by this source is negligible; the shorter wavelengths (primarily 1849Å) are absorbed by the quartz irradiation cell, and longer wavelengths are not absorbed by either the polymer or the solvents.

A General Electric UA-3 medium-pressure lamp was used where a higher intensity source was desired. While this source emits radiation at many wavelengths, only those in the 2200-3000Å region need be considered here. Knowing the spectral distribution of the radiation from this source and the absorbance of the polymer and solvents used, the amount of energy absorbed by a given solution per unit time could be determined from actinometric measurements.

Ferrioxalate actinometry (12) was employed with both lamps; lamp output was continuously monitored with a photcell. Irradiations were carried out in the cell shown in Fig. 1. The apparatus consisted of a square quartz cell, of 2.5 cm path length and about 30 ml volume, containing a glass-enclosed stirring bar. Degassing of the solutions was carried out in a Pyrex sidearm since the square quartz irradiation cell was unstable to thermal shock. A filter, a capillary viscometer (whose running time for benzene was about 116 seconds), and a cuvette for spectroscopic measurements were also attached. During exposures, the cell was mounted 8 inches from the low pressure mercury lamp or 15 inches from the medium pressure lamp.

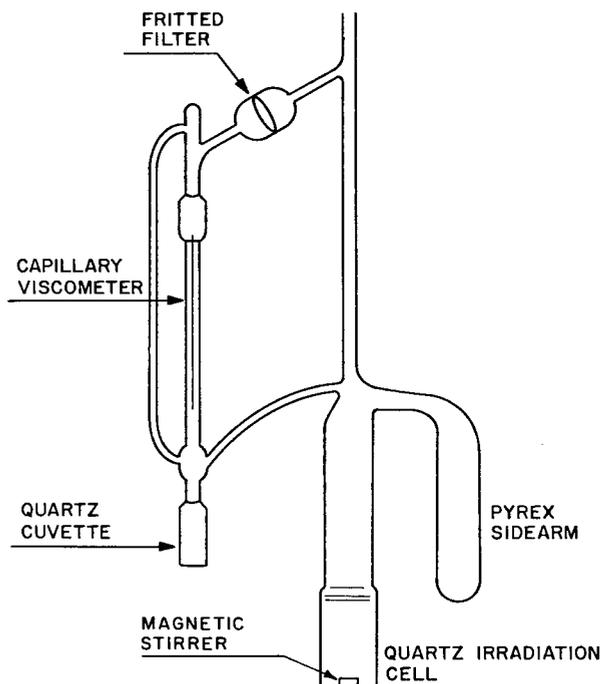


Fig. 1 - Irradiation cell

Procedure

Approximately 20 ml of polymer solution was used in each run. Preprepared polymer solutions were used and the concentration determined by weighing the apparatus at the end of an exposure series. For runs in the absence of air the system was evacuated to about 30 microns during degassing (three freeze-thaw cycles) and the system sealed. The running time of the solution in the viscometer was then measured and the ultraviolet spectrum obtained. After suitable intervals of irradiation, the viscosity of the solution and the ultraviolet spectrum were measured. At the conclusion of the irradiation the degraded polymer was recovered by precipitation with methanol, filtration, and vacuum drying.

Evaluation of Quantum Yields for Scission

If a random scission process is assumed to occur, the quantum yield can be calculated from the number of scissions produced by a given number of quanta. The number of scissions per polymer molecule is

$$s = \left(\frac{\bar{M}_{n_0}}{\bar{M}_n} \right) - 1$$

where \bar{M}_n is the number-average molecular weight and the subscript zero refers to the initial state. If a "most probable" molecular weight distribution is assumed for the polymer, then

$$2\bar{M}_n \approx \bar{M}_w \approx \bar{M}_v$$

where \bar{M}_w and \bar{M}_v are weight-average and viscosity-average molecular weights, respectively. From the relationship between molecular weight and intrinsic viscosity,

$$[\eta] = K\bar{M}_n^\alpha$$

then

$$s = \left(\frac{[\eta_0]}{[\eta]} \right)^{1/\alpha} - 1$$

where $[\eta]$ is intrinsic viscosity and K and α are constants for a given polymer-solvent system. The method of Meyerhoff (13) was used to estimate values of α for the various solvents and mixtures with the assumption that for polystyrene α is 0.50 and 0.72 in cyclohexane and benzene respectively (11,14). Since s is insensitive to small variations in α , this method of estimation is sufficiently accurate. The values of α estimated in this manner are listed in Table 1. Intrinsic viscosities were derived from relative viscosities at a single concentration through a modification of the Huggins equation:

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

where c is concentration and η_{sp} and η_r are specific and relative viscosities, respectively.

The quantum yield for random scission, Φ_s^i , based on the number of scissions per quantum absorbed by the species i can be calculated from the equation

$$\Phi_s^i = \left(cA/\bar{M}_{n_0} \right) \left[\left(\frac{[\eta_0]}{[\eta]} \right)^{1/\alpha} - 1 \right] / I^i t$$

Table 1
Estimated Values of α for Polystyrene
in Various Solvents

| Solvent | α |
|---|----------|
| Cyclohexane | 0.50* |
| 1% Carbon tetrachloride in cyclohexane | 0.51 |
| 20% Carbon tetrachloride in cyclohexane | 0.58 |
| 40% Carbon tetrachloride in cyclohexane | 0.62 |
| 80% Carbon tetrachloride in cyclohexane | 0.70 |
| 90% Carbon tetrachloride in cyclohexane | 0.70 |
| 96% Carbon tetrachloride in cyclohexane | 0.71 |
| Carbon tetrachloride | 0.71 |
| Dioxane | 0.67 |
| Methylene chloride | 0.69 |
| Benzene | 0.72* |
| Chloroform | 0.76 |

*Taken as reference points to determine the other values of α .

where c is concentration, A is Avogadro's number, \bar{M}_{n_0} is the initial number-average molecular weight, I^i is the radiation intensity absorbed by i , and t is time of irradiation. Plots of the number of scissions against the quanta absorbed per milliliter of solution, as shown in Fig. 2, were generally linear. Where departures from linearity occurred the initial slopes were used in the calculation of quantum yields. Quantum yields calculated on the basis of energy absorbed by the polymer alone (Φ_s^P) differ from those based on energy absorbed by the solution (Φ_s^{soln}) only when the solvent is a strong absorber.

RESULTS AND DISCUSSION

Molecular Weight Changes

The determination of molecular weight changes by viscometric methods is valid only if random chain scission is the sole dissociation process occurring. Under these conditions the average length of the polymer molecules decreases but the solvent-polymer interaction exponent α would be expected to remain constant. The change in molecular weight then would be a function of the change in intrinsic viscosity. However, if the complication of crosslinking is introduced, the interpretation of molecular weight changes by viscometric methods becomes more difficult. Kilb (15) has investigated the effect of simultaneous chain scission and crosslinking and shown that the effect on intrinsic viscosity is a function of the ratio of scissions to crosslinks. Intrinsic viscosity tends to increase when this ratio exceeds 1.

In the present work no increases in viscosity were found to occur. However, under some conditions, to be described later, insoluble material collected at the solvent-vapor interface. This insoluble material was apparently highly crosslinked polystyrene. The

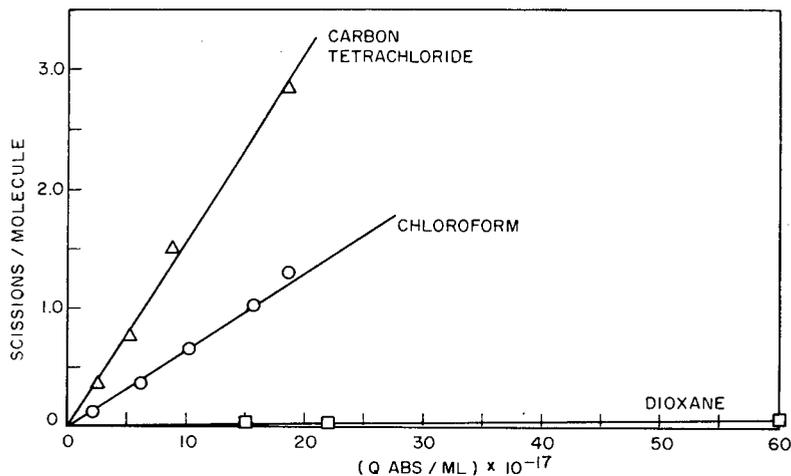


Fig. 2 - Photolysis of polystyrene in various solvents in the presence of air

formation of insoluble material was always associated with very small decreases in intrinsic viscosity. It is uncertain whether these small decreases in viscosity were due to simultaneous chain scission and crosslinking or to the decrease in polymer concentrations resulting from removal of crosslinked material.

Of particular interest is a study of the radiolysis of polystyrene in solution carried out by Henglein and Schneider (4). At 1% polymer concentrations in methyl ethyl ketone, dioxane, or ethyl acetate, the rate of degradation of polystyrene determined viscometrically was found to decrease with increasing time of irradiation. This was believed to indicate that crosslinking was occurring in addition to some random chain scission. Crosslinking apparently occurred to a greater extent in the absence of oxygen. Irradiation at polymer concentrations of 5% in the above solvents resulted in increased intrinsic viscosities and some turbidity due to the precipitation of crosslinked polystyrene molecules.

The quantum yields obtained in our work with 2537A radiation are summarized in Table 2. Values have been determined both on the basis of the energy absorbed by the polymer (Φ_s^p) and on the basis of energy absorbed by the solution (Φ_s^{soln}). As was the case with poly(α -methylstyrene) (1), these results are not readily correlated with either the absorption coefficients at 2537A or the Mark-Houwink exponents α of the solvents. Since optical filter effects and polymer-solvent interaction coefficients do not explain the solvent dependency of the chain scission process, other effects such as energy transfer and attack by free radicals produced from the solvent must be considered.

Cyclohexane was chosen as a solvent because it is transparent to 2537A radiation and is a theta solvent for polystyrene at 34°C (16). Since the theta temperature is the temperature of incipient precipitation it was necessary to warm the solution slightly in order to keep the polymer in solution. It was thought that any small amount of crosslinking that occurred in such a poor solvent should be readily detected by the formation of insoluble material or by increased viscosity. No crosslinking of the polymer was detected in this way when the solution was irradiated in air, but the low quantum yield, close to that determined for photolysis of polystyrene films in air (10), indicates that analogous processes are probably occurring.

The quantum yield determined in dioxane solution in the presence of air is somewhat higher than in cyclohexane solution, but the differences are not great enough to be considered significant.

Table 2
Quantum Yields for Random Chain Scission of Polystyrene in Solution*

| Polymer Sample | Solvent | $\phi_s^P \times 10^4$ | | $\phi_s^{\text{soln}} \times 10^4$ | |
|----------------|--------------------------------------|------------------------|---------------|------------------------------------|---------------|
| | | Air | Solvent Vapor | Air | Solvent Vapor |
| PS-2 | Cyclohexane | 2 | - | 2 | - |
| | Dioxane | 7 | 9 | 7 | 9 |
| | Benzene | 34 | - | 0.3 | - |
| | Methylene chloride (c = 0.5 g/dl) | 44 | - | 44 | - |
| | Chloroform | 436 | - | 423 | - |
| | Carbon tetrachloride | 1134 | 7 | 936 | 6 |
| PS-1 | Methylene chloride | 24 | - | 24 | - |
| | Carbon tetrachloride | 1137 | † | 935 | † |

*2537A radiation from low-pressure mercury source. All concentrations 1 g/dl except as noted.

†No change in intrinsic viscosity.

Irradiated in the absence of air, a dioxane solution of polystyrene initially undergoes a decrease in viscosity, but further irradiation produces little change. According to Henglein and Schneider (4) such behavior indicates the occurrence of crosslinking; no insoluble material was seen in our experiment. The value of the quantum yield given in Table 2 is based on the initial viscosity change.

In benzene solution the quantum yield for chain scission of polystyrene (ϕ_s^{soln}) is lower than the value reported for chain scission of polymer films in the presence of air (10). However, benzene is a very strong absorber, and after subtraction of the energy absorbed by the solvent, the quantum yield based on energy absorbed by the polymer (ϕ_s^P) is similar to that found in methylene chloride although higher than reported for films (10) or in cyclohexane and dioxane solutions. Similar results were found for the photolysis of poly(α -methylstyrene) in benzene (1). Chen (9) studied the photolysis of polystyrene in benzene solution in air by 2537A radiation and calculated a quantum yield of about 0.7×10^{-4} scissions per quantum absorbed by the solution. Jellinek (8) recalculated the quantum yield from Chen's data and gave a value of 0.17×10^{-4} . The value determined in the present research (0.3×10^{-4}) is in good agreement with the recalculated quantum yield.

The data of Table 2 show a very great difference between the quantum yields for the scission of polystyrene in the presence or absence of air in carbon tetrachloride solutions. This is in contrast to the behavior of poly(α -methylstyrene), for which the quantum yields in most solvents are generally unaffected by air (1). The rates of degradation of both poly(α -methylstyrene) and polystyrene in carbon tetrachloride or chloroform solutions in the presence of air were relatively high. However, since it proved difficult to free chloroform of the last traces of alcohol (added to commercial chloroform as a preservative), which has been shown to act as an inhibitor in solution photolysis of

poly(α -methylstyrene) (1), no further work was done with this solvent. The rate of degradation in methylene chloride solution was much lower than that determined in carbon tetrachloride and chloroform solutions. Agreement between the quantum yields determined for the scission of PS-1 and PS-2 in carbon tetrachloride solutions is good. In the absence of air the quantum yield for scission of the polystyrene in carbon tetrachloride is very low. Hydrochloric acid was a product of irradiation of polystyrene in carbon tetrachloride, chloroform, and methylene chloride solutions both in the presence and absence of air; in carbon tetrachloride solution, at least, the polymer is the only source of hydrogen for this acid.

A summary of the quantum yields for chain scission of PS-1 and PS-2 in several solvents irradiated by the medium-pressure lamp is given in Table 3. Under this source, the energy absorbed per unit time was about four times that absorbed from the low-pressure lamp. The results from the two sources are in good agreement for both polymer samples. This indicates that there is no apparent effect due to the wide spectral distribution of the radiation produced by the medium-pressure mercury source. Intensity differences evidently are not important here, although some significant intensity effects will be discussed later.

Table 3
Quantum Yields for Chain Scission of Polystyrene in Solution*

| Polymer Sample | Solvent | $\phi_s^P \times 10^4$ | | $\phi_s^{\text{soln}} \times 10^4$ | |
|----------------|----------------------|------------------------|---------------|------------------------------------|---------------|
| | | Air | Solvent Vapor | Air | Solvent Vapor |
| PS-2 | Cyclohexane | 17 | Crosslinks | 17 | Crosslinks |
| | Dioxane | 9 | 2 | 9 | 2 |
| | Carbon tetrachloride | 1192 | - | 940 | - |
| PS-1 | Dioxane | - | Crosslinks | - | Crosslinks |
| | Methylene chloride | 60 | Crosslinks | 60 | Crosslinks |
| | Carbon tetrachloride | 1156 | Crosslinks | 912 | Crosslinks |

*Medium-pressure mercury source; $c = 1$ g/dl.

No insoluble material formed in any of the irradiations in air. With the absorption of higher dosages of radiation from the medium-pressure source, polystyrene was found to crosslink in the absence of air in cyclohexane, dioxane, methylene chloride, and carbon tetrachloride solutions as shown by the formation of insoluble material at the solution-vapor interface. In general, there was a slight initial decrease in viscosity in the irradiations conducted in the absence of air. The rate of decrease in viscosity became slower as irradiation continued until finally the formation of insoluble material showed that some crosslinking had occurred. Whether a slight amount of chain scission takes place simultaneously with the crosslinking reaction is uncertain.

Qualitatively, it appeared that absorption of less energy was required before the formation of insoluble material was noted in cyclohexane solutions of polystyrene than in the other solvents. The relative ease of crosslinking of polystyrene in solution in cyclohexane might be due to aggregation of the polymer molecules into micelles or into small particles. Cyclohexane is a very poor solvent for polystyrene, and at the temperature at which this irradiation was carried out (30°C) the polymer might not have been in solution. If the polymer molecules had been aggregated in some manner, the ease of crosslinking

would be increased on a statistical basis. A similar explanation was offered by Henglein and Schneider (4) to explain the relative ease of crosslinking of polystyrene in "poor" solvents when subjected to gamma irradiation.

The results of varying the concentration of polystyrene in dioxane are listed in Table 4. No concentration effect was observed in the presence of air, and it can be concluded that the small amount of chain scission occurring here is the result of the direct absorption of energy by the polymer. As would be expected, in the absence of air polystyrene in dioxane tends to crosslink more rapidly at higher concentrations.

Table 4
Quantum Yields for Random Chain Scission of Polystyrene in Dioxane
Solutions at Various Concentrations

| Polymer Sample | Ultraviolet Source | c (g/dl) | $\phi_s^P \times 10^{4*}$ | |
|----------------|-------------------------------------|----------|---------------------------|---------------|
| | | | Air | Solvent Vapor |
| PS-2 | Low-Pressure Mercury Source (2537A) | 0.5 | 6 | - |
| | | 1.0 | 7 | 9 |
| | | 3.0 | 7 | - |
| PS-2 | Medium-Pressure Mercury Source | 1.0 | 9 | 2 |
| | | 5.0 | - | Crosslinks |
| PS-1 | Medium-Pressure Mercury Source | 1.0 | - | Crosslinks |

* ϕ_s^P and ϕ_s^{soln} have approximately the same value.

Similar experiments on the effect of polymer concentration in carbon tetrachloride solutions are summarized in Table 5. The quantum yield for chain scission of polystyrene in carbon tetrachloride solutions calculated on the basis of energy absorbed by the polymer (ϕ_s^P) decreased with increasing polymer concentration. This might reflect the decreasing mobility of radicals in an increasingly viscous medium.

The effect of varying the intensity of radiation with carbon tetrachloride solutions in the presence of air was also investigated; the results are given in Table 6. Halving the intensity resulted in no significant change in the quantum yields for chain scission. However, at an intensity of about one-tenth the highest intensity the quantum yields were significantly higher. Durup (5,6) reported that polystyrene degraded more rapidly in chloroform or carbon tetrachloride solutions when irradiated with low-intensity gamma radiation than anticipated from the rate obtained with high-intensity radiation. He suggested that the higher yield of degradation was due to a contribution of the "post-effect" to the reaction resulting from the much longer times of radiation at the lower dose rates. The life of some of the radicals formed in the irradiation might be long enough that they are able to make a contribution to the degradation in the longer times available here. However, no change in viscosity was observed when a solution of polystyrene in carbon tetrachloride solution was allowed to stand for 12 hours after irradiation was completed. This means the radical lifetime must be short or the steady-state concentration of radicals is small. The lower quantum yields at higher intensities might also mean that some recombination of polymer radicals occurs under these conditions.

Table 5
Quantum Yields for Random Chain Scission of Polystyrene in Carbon Tetrachloride Solutions in Air at Various Concentrations*

| Polymer Sample | c (g/dl) | $\Phi_s^P \times 10^4$ | $\Phi_s^{\text{soln}} \times 10^4$ |
|----------------|----------|------------------------|------------------------------------|
| PS-2 | 0.5 | 1230 | 880 |
| | 1.0 | 1134 | 936 |
| PS-1 | 0.5 | 1267 | 912 |
| | 1.0 | 1137 | 935 |
| | 4.0 | 950 | 900 |

*Low-pressure mercury source, 2537A radiation.

Table 6
Quantum Yields for Random Chain Scission of Polystyrene in Carbon Tetrachloride Solution in Air at Various Radiation Intensities*

| Polymer Sample | Intensity (10^{13} quanta/sec-ml) | $\Phi_s^P \times 10^4$ | $\Phi_s^{\text{soln}} \times 10^4$ |
|----------------|--------------------------------------|------------------------|------------------------------------|
| PS-2 | 2.5 | 1620 | 1330 |
| | 2.5 | 1716 | 1410 |
| | 9.0 | 1155 | 949 |
| | 19.0 | 1122 | 920 |
| | 25.0 | 1175 | 964 |
| PS-1 | 3.5 | 1626 | 1335 |
| | 28.5 | 1137 | 932 |

*Low-pressure mercury source, 2537A radiation. All concentrations, 1 g/dl.

Degradation in Mixed Solvents

Since solvent effects are so important, the effect of varying the composition of a mixture of an active solvent, such as carbon tetrachloride, and a photolytically inactive solvent, such as cyclohexane, was investigated. In preliminary experiments it was found that the addition of small amounts of photolytically inactive dioxane (up to 4% by volume) had no effect on the rate of scission of polystyrene in cyclohexane in air. This may be contrasted to the quantum yields shown in Fig. 3, for chain scission of polystyrene in mixtures of cyclohexane and carbon tetrachloride under irradiation by the low-pressure source in the presence of air. While the addition of 1% carbon tetrachloride to cyclohexane increased the quantum yield considerably, addition of larger quantities, up to over 40%, produced little additional change in the quantum yields. On the other hand, as little as 4% cyclohexane in a carbon tetrachloride solution of polystyrene appeared to act as an inhibitor for the chain scission of the polymer. Simple dilution effects should

produce a linear relationship between the solution composition and quantum yields for the scission of the polymer. The S-shape of the curve of Fig. 3 indicates that the effects observed here are more complex than simple dilution. Neither free radical production nor energy transfer from carbon tetrachloride can alone explain the shape of the curve. A possible explanation may be in a combination of the two effects, with little transfer of energy occurring from carbon tetrachloride to cyclohexane but with considerable competition existing between polymer and cyclohexane for solvent free radicals. Since individual rates for the various processes are unknown, little can be said by way of rationalization at this time.

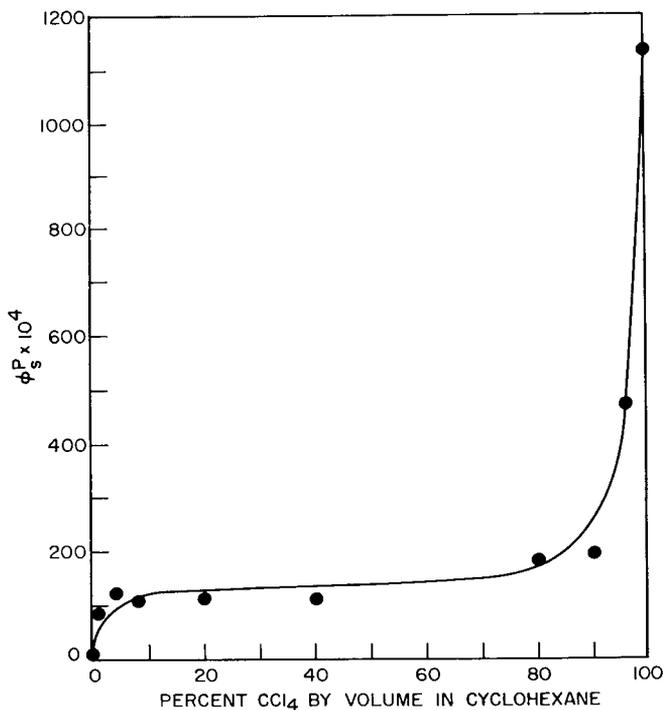


Fig. 3 - Photolysis of polystyrene in mixtures of carbon tetrachloride and cyclohexane in the presence of air

Spectral Changes

At the radiation doses used in this research practically no changes were observed in the infrared spectra of the polymer or its solutions. In the ultraviolet region a general increase in absorption occurred at wavelengths below $350 \text{ m}\mu$ in polystyrene in all solvents during irradiation. While only a general increase of this type was found when polystyrene was irradiated in solution in carbon tetrachloride in the presence of air, in the absence of air, a band appeared near $326 \text{ m}\mu$ as shown in traces 1 through 4 of Fig. 4. Opening the cell air and agitating the solution for 15 minutes to permit the solution to equilibrate with air brings about no change in the band at $326 \text{ m}\mu$. But if the solution is then irradiated in the presence of air, a general decrease in absorbance in the 280 to $350 \text{ m}\mu$ range takes place as shown in trace 5 of Fig. 4. No changes in the spectra below $350 \text{ m}\mu$, other than a general increase in absorbance, were found when polystyrene solutions in any of the other solvents were irradiated, showing that carbon tetrachloride must be

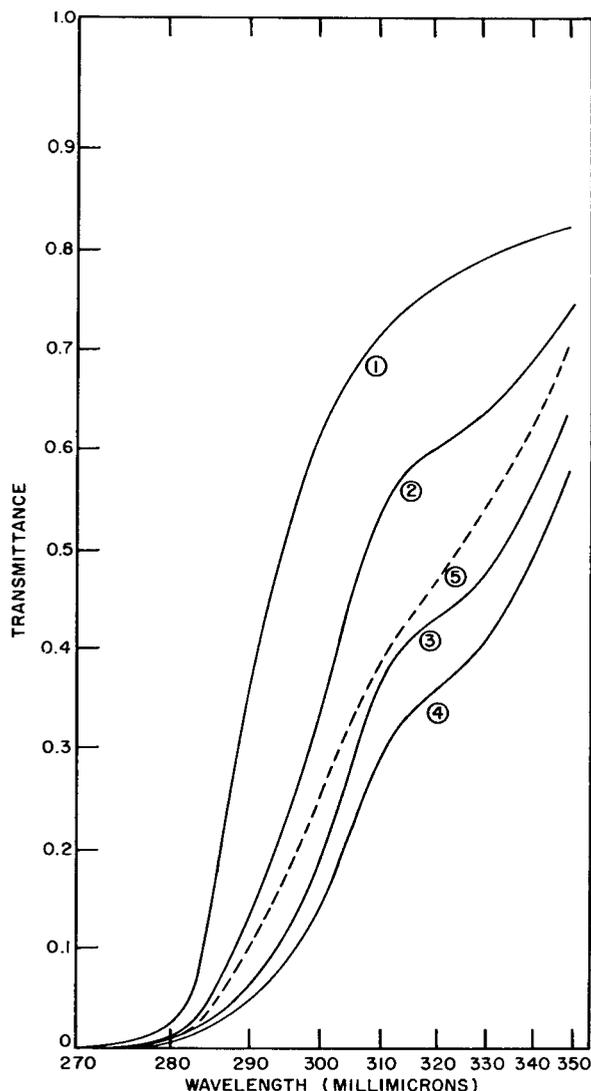


Fig. 4 - Spectral changes during the irradiation of polystyrene in carbon tetrachloride ($c = 1 \text{ g/dl}$): (1) unirradiated; (2) irradiated 30 min, no air; (3) irradiated 80 min, no air; (4) irradiated 100 min, no air; (5) irradiated 30 min, opened to air

involved in the formation of the new chromophore. Styrene monomer in carbon tetrachloride irradiated under the same conditions leads to new absorption at $312 \text{ m}\mu$ and is therefore unlikely to be responsible for the new absorption in the polymer solutions.

The new chromophore was incorporated in the polymer molecule and was not due solely to small molecules produced during the irradiation. A sample of polystyrene that had been irradiated in carbon tetrachloride solution in the absence of air was precipitated with methanol, recovered by filtration and vacuum dried at room temperature for 24 hours. In solutions of the recovered polymer the band at $326 \text{ m}\mu$ was still detectable.

Similar results have been reported for the irradiation of poly(α -methylstyrene) in carbon tetrachloride solution in the absence of air (1). In the poly(α -methylstyrene) work, it was shown by studies of model compounds that the most likely point of reaction in that polymer was the backbone methylene group. The same point of reaction appeared to be a possibility for polystyrene, also, although on the basis of radical reactivities the tertiary carbon is a more probable site of attack. It should be pointed out that Haas (17) has shown that substitution at the methylene group occurs when polystyrene is heated with benzoyl peroxide.

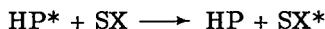
Mechanism

On the basis of this work, a few additions can be made to the extensively delineated mechanism for the radiolysis of polystyrene in the absence of air. Few qualitative differences between polymer radiolysis and photolysis have been reported.

While crosslinking is a major process in all solvents in the absence of air, only in dioxane, a poor absorber of 2537A radiation, and in CCl_4 , a fair absorber, is there an overall viscosity decrease. Where polystyrene is the major absorber in these solutions, any effect of solvent must come as the result of (a) the reaction of polymer free radicals with the solvent,



which would tend to decrease the rate of both scission and crosslinking, or (b) the transfer of energy from an electronically excited polymer molecule to a solvent molecule,



possibly followed by dissociation of the excited solvent molecule and reaction of the resulting radicals with the polymer. The latter reaction would lead to an increase in crosslinking of polymer radicals, and the decrease in the direct scission process and the increase in scissions due to attack by polymer radicals would tend to cancel each other. All of these solvent-dependent processes are superimposed on the direct process; their relative rates will determine the overall effect. The major point is that photolysis of the solvent itself cannot be a major contributor, even though in those cases where energy is absorbed by the solvent, the reverse of reaction 2 may take place if it is energetically possible.

In the presence of air, a much different mechanism must be involved. It has been suggested (18) that oxygen accelerates main-chain scissions without altering the crosslinking reaction in the radiolysis of polystyrene. Presumably, any of the radicals which form in the absence of air would, in the presence of air, yield the peroxy radicals $\text{POO}\cdot$, $\text{SOO}\cdot$, etc. While it has been proposed that the combination of $\text{POO}\cdot$ and $\text{SOO}\cdot$ will lead to a scission (5), it is not readily apparent how this can occur. However, the reaction



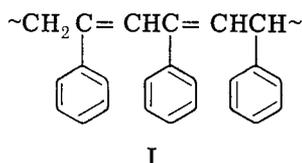
is possible and should be governed by the stability of $\text{S}\cdot$; combination reactions should lead to lesser amounts of other peroxides such as POOP and POOH . These peroxides can decompose by a reaction of the type



and the resulting highly reactive $\text{PO}\cdot$ radical should undergo further stabilization by conventional reactions to give a fragment ended by a carbonyl group and a polymer radical fragment. It would be expected that oxygen-headed radicals derived from primary,

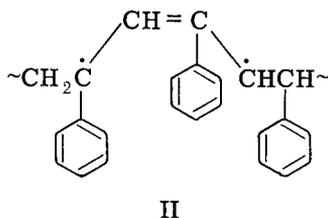
secondary, or tertiary carbon atoms would have more nearly the same reactivity than would the corresponding carbon-headed radicals. Thus may be explained the similarity in the photodegradation rates for polystyrene and poly(α -methylstyrene) in air.

The general processes just given may be made more specific for solutions of polystyrene in carbon tetrachloride. Oxygen itself reacts extremely slowly with polystyrene at room temperature, and therefore it is reasonable to assume that the same initial process may occur whether or not air is present. In films, as well as in solutions, a general increase in absorption occurs at wavelengths below 350 $m\mu$. If irradiation is extended sufficiently, changes in the infrared spectra occur which can be interpreted as due to double bond formation (19); the same result is obtained by irradiation with fast electrons (20). At this point, polystyrene probably contains structures of the following type:



In carbon tetrachloride solution, such a process should be accelerated through abstraction of hydrogen atoms by chlorine atoms. A further reaction in this solvent would be the addition of trichloromethyl radicals to the unsaturated linkages in I to give tertiary polymer radicals. The latter can undergo crosslinking by conventional reactions.

Further irradiation of I in the presence of air can result in a decrease in ultraviolet absorbance through a decrease in the backbone unsaturation. The usual oxidation processes for olefins may apply here, although it might be expected that crosslinking would continue if this were the case. An alternative explanation involves the excitation of I followed by crossover to the excited diradical triplet:



Such a transformation is typical of conjugated dienes. The resulting diradical is relatively stable but could be expected to react with oxygen to yield peroxy radicals or a peroxide (possibly a cyclic peroxide) having less absorption above 300 $m\mu$ than I. Further decomposition of the peroxidic structures may eventually lead to scission and an absorbing polymer fragment having a carbonyl end-group of the type envisioned by Wall and co-workers (21).

CONCLUSIONS

Polystyrene undergoes random chain scission with no detectable crosslinking up to an absorption of 600×10^{16} quanta per gram of polymer in carbon tetrachloride, chloroform, methylene chloride, dioxane, cyclohexane, and benzene solutions when subjected to ultraviolet radiation in air. The quantum yields for chain scission of polystyrene in carbon tetrachloride and chloroform solutions when irradiated in air are much higher than those obtained in the other solvents, and it is concluded that the degradation mechanism

involves interaction with the solvent and subsequent formation of peroxy or other oxygen-headed radicals which can undergo reactions leading to chain scission. In solution in methylene chloride few solvent radicals are produced; the quantum yield for chain scission of polystyrene in this solvent is relatively low and is probably the result of photo-oxidation. Photo-oxidation is probably also the principal reaction in dioxane and cyclohexane solutions in air.

Crosslinking of polystyrene is the principal reaction observed to occur during irradiation of all of the solutions in the absence of air.

Spectral evidence has been presented to show that the hydrogen substituent on the secondary carbon atom of the polystyrene chain might be subject to free radical attack, although the relationship between the formation of secondary radicals and the rate of scission is uncertain.

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

| | | | |
|---|--|--|-----------------------|
| 1. ORIGINATING ACTIVITY (Corporate author) U.S. Naval Research Laboratory Washington, D.C. 20390 | | 2a. REPORT SECURITY CLASSIFICATION Unclassified | |
| | | 2b. GROUP | |
| 3. REPORT TITLE PHOTODEGRADATION OF HIGH POLYMERS IN SOLUTION, Part 2 - Solvent Effects in the Photolysis of Polystyrene | | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Interim report on the problem | | | |
| 5. AUTHOR(S) (Last name, first name, initial) Price, T.R., and Fox, R.B. | | | |
| 6. REPORT DATE October 21, 1965 | | 7a. TOTAL NO. OF PAGES 20 | 7b. NO. OF REFS 21 |
| 8a. CONTRACT OR GRANT NO. NRL Problem C04-04 | | 9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6328 | |
| b. PROJECT NO. RR 001-02-43-4801 | | 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | |
| c. | | | |
| d. | | | |
| 10. AVAILABILITY/LIMITATION NOTICES Distribution of this document is unlimited | | | |
| 11. SUPPLEMENTARY NOTES | | 12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research) | |
| 13. ABSTRACT Polystyrene photolysis in solution under ultraviolet irradiation by low-pressure and medium-pressure mercury lamps has been studied in the presence and absence of air at about 25°C. Both intrinsic viscosity and ultraviolet spectral changes were followed during the exposures. In the absence of air, cross-linking is a major process; a measurable decrease in viscosity occurred only in dioxane and carbon tetrachloride and, at sufficiently high doses, insoluble material was formed. In the presence of air, viscosity decreases were observed in all solvents; apparent quantum yields for random scission (Φ_s^P) ranged from 0.0002 in cyclohexane to 0.11 in carbon tetrachloride. In the latter solvent, Φ_s^P decreased with increasing polymer concentration and intensity of absorbed radiation. Carbon tetrachloride sensitized the degradation in cyclohexane, and small amounts of cyclohexane acted as an inhibitor in carbon tetrachloride solutions. Spectral changes were similar to those observed earlier for poly(α -methylstyrene). Mechanisms are suggested. | | | |

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
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| | ROLE | WT | ROLE | WT | ROLE | WT |
| Polymers Photochemistry Ultraviolet radiation Solvent action Viscosity Molecular weight Spectra (ultraviolet) Radiation chemistry | | | | | | |
| Air Dissociation Polystyrene Scission Polymer degradation Crosslinking Quantum yields | | | | | | |

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