The Photooxidation of Polymers.
II. Photolysis of Polystyrene

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Synopsis

In the vacuum photolysis of polystyrene films at 28°C. under 2537 A. radiation the only gaseous product is hydrogen. At the same time the polymer becomes insoluble and discolors. The intensity exponent of the reaction is unity, the quantum yield of hydrogen is 4.3×10^{-2}, the overall energy of activation is 2.9 kcal./mole, and the rate of photolysis is independent of molecular weight. No hydrogen is produced when 3650 A. radiation is used. These observations can be interpreted in terms of a simple reaction scheme in which the primary effect of the 2537 A. radiation is to liberate hydrogen atoms. The subsequent reaction of these and the polystyryl radicals simultaneously formed in a number of competing steps results in the appearance of hydrogen, the occurrence of crosslinking, and the production of carbon–carbon unsaturation in the main chain which ultimately leads to conjugation and color. These theories are supported by infrared and ultraviolet spectral measurements and by the observation that the rate of photolysis is accelerated by nitrogen.

I. INTRODUCTION

Since the oxidation reactions which are described in the third paper of this series were to be initiated photochemically it was clearly important to try to define the action of ultraviolet radiation in promoting oxidation. Taking a wider view it is of course also of interest to investigate the role which radiation by itself can play in the overall aging process.

II. EXPERIMENTAL

A. Preparation of Polymers

It was not known initially whether or not the chain length, impurities, or chain terminal initiator fragments would influence the photolysis or oxidation of polystyrene. For this reason a large sample of as pure polymer as possible was prepared thermally and without catalyst for the study of the effect of light intensity, oxygen pressure, temperature, and wavelength on the rate of the reaction. Smaller samples were prepared for the study of the effect of molecular weight, initiator fragments, etc.

Styrene (Forth Chemicals Ltd.) was washed several times with dilute

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KOH solution to remove inhibitor and several times with distilled water. It was dried over anhydrous magnesium sulfate and distilled under reduced pressure, the middle fraction (b.p. 68°C./15 mm.) being retained. After degassing by alternate freezing and thawing in vacuum, the monomer was distilled into a dilatometer (the first 10% being eliminated) and sealed off under vacuum. When initiator was used, the appropriate amount of azobisisobutyronitrile was added to the dilatometer before distillation of the monomer.

Polymerization was carried to 10% in a thermostat, the mixture thereafter being dissolved in benzene, the polymer precipitated by adding to methanol, and reprecipitated as a powder from chloroform solution. In this form it could be freed from chloroform by drying in air at room temperature and storing in vacuum for several days.

Molecular weights were measured osmotically. Details are given in Table I.

TABLE I

Polymer	Temperature of polymerization, °C.	Initiator concentration, % (w/v)	Molecular weight $\times 10^{-5}$
S1	90	0	4.93
1	60	0.002	3.3
2	60	0.01	2.14
3	60	0.1	1.86
4	60	0.2	1.59
5	60	0.4	1.5
SG3	60	0	15.1

B. The Photolysis Reaction

In order to achieve most effective elimination of oxygen, photolyses were carried out under vacuum in the apparatus described in Part I of this series[1] with the use of 2537 A. radiation unless otherwise mentioned. If volatiles are produced, pressure develops in the film side and the difference in levels on the manometer is related to the number of moles of products by the expression given in Part I.[1]

A film thickness of 0.0044 mm. was used and the apparatus evacuated to 10^{-6} mm. before irradiation.

Figure 1 illustrated that gaseous products are evolved linearly, and they were found to be completely noncondensible at $-196°C$. Blank experiments showed that these gases were genuine products of photolyses of the polystyrene.

C. Nature of Gaseous Products

Since these materials are all volatile at $-196°C$. they must consist of H_2 or CH_4 as products of photolysis, CO, an oxidation product, or N_2 or O_2 if the film contained appreciable residual air.
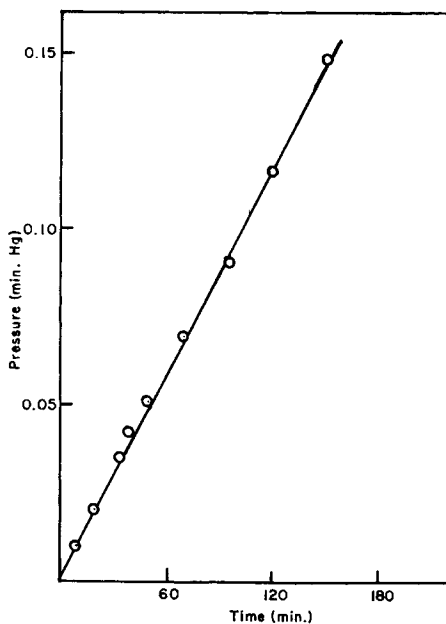
Fig. 1. Evolution of gaseous products of photolysis of polystyrene.

Experiments for the analysis of the volatile products were carried out in a modified apparatus incorporating a Macleod gage, a cold finger, and a quartz tube, which could be heated electrically to 300–350°C., containing cupric oxide. Thus H_2, CO, and CH_4 could be oxidized quantitatively to H_2O and CO_2.

With the cold finger immersed in liquid nitrogen, the Macleod gage indicated that during combustion the pressure returned to its preirradiation value, and there was no increase in pressure on replacing the liquid nitrogen by solid carbon dioxide—strong evidence that hydrogen was the only product. This was verified by gas–solid chromatography with the use of a Perkin-Elmer Fraktometer instrument and a column consisting of 1 m. of 0.25 in. diameter copper tubing packed with crushed Linde molecular sieves (type 5a), activated for 16 hr. at 180°C. in a stream of dry N_2. The column temperature was 60°C.

D. Effect of Radiation Intensity

The intensity of 2537 A. radiation incident upon the film was varied both by varying the film–arc distance and by the use of intensity screens interposed between film and arc. These screens consist of blackened copper gauze of various mesh sizes, the transmissions of which had been accurately determined by uranyl oxalate actinometry.[2]

Table II gives the relevant experimental data and from the slope of the log–log plot in Figure 2, a value of 0.978 may be deduced for the intensity exponent of the photolysis reaction.

TABLE II
Effect of Radiation Intensity on the Rate of
Photolysis of Polystyrene (0.0044 mm. Film at 28°C.)

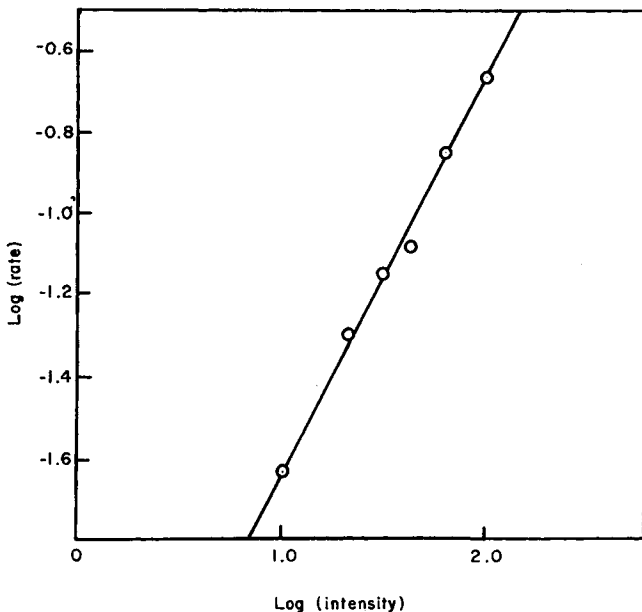| Film–arc distance, cm.	Transmission of screen	Relative intensity	Rate, μmole H_2/cc./sec.
7.375	100	100	0.216
9.250	100	64.3	0.141
11.125	100	43.2	0.0832
13.000	100	32.2	0.0700
7.375	21.7	21.7	0.0505
7.375	10.1	10.1	0.0230

Fig. 2. Intensity exponent of photolysis of polystyrene.

E. Determination of Quantum Yield

In Table II, the full intensity rate of 0.216 μmoles H_2/cc./sec. corresponds to 9.5×10^{-11} moles/cm.^{2}/sec. Since polystyrene has an optical density of 0.89 at 2537 A., 87.2% of incident radiation is absorbed. The quantum flux of 2537 A. radiation at the film[1] is 2.54×10^{-9} einsteins/sec./cm.^{2}. The number of quanta absorbed by the film is therefore 2.21×10^{-9} einsteins/cm.^{2}/sec., and the quantum yield is $9.5 \times 10^{-11}/2.21 \times 10^{-9} = 4.3 \times 10^{-2}$.

F. Effect of Molecular Weight and Initiator Fragments

In view of the influence which the nature of molecular chain ends has on some thermal degradation processes, the influence of molecular weight
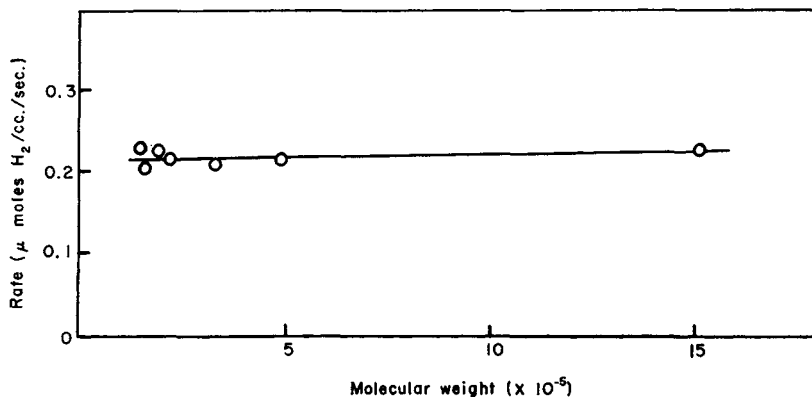
Fig. 3. Effect of molecular weight on rate of photolysis of polystyrene.

(concentration of chain ends) and initiator fragments on the photolysis of polystyrene was investigated by studying the rates of photolysis of the materials in Table I under otherwise identical conditions. The data in Figure 3 indicate that within experimental error the rates are independent of both these factors. For molecular weights below 10^5, films were too brittle to handle.

G. Effect of Temperature

Rates of evolution of H_2 were obtained under otherwise identical conditions over a range of temperatures. From the log rate versus $1/T$ plot
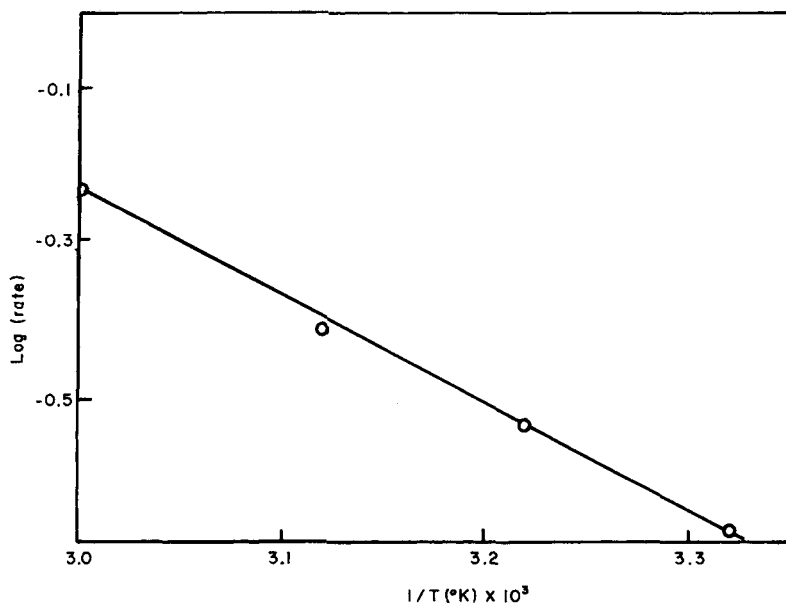

Fig. 4. Energy of activation of photolysis of polystyrene.

in Figure 4 a value of 2.9 kcal./mole for the overall energy of activation was obtained.

H. Effect of Wavelength

The Osram lamp, whose output characteristics are described in Part I,[1] gives no significant radiation at wavelengths below 3650 A. The quantum flux in the region 3650–3663 A. is approximately seven times that of the 2537 A. radiation concerned in the above experiments. No significant amounts of hydrogen could be detected after several hundred hours irradiation, however. It seems likely, therefore, that the threshold energy required for the production of hydrogen is in excess of that associated with 3650 A. radiation (77.8 kcal./mole). If this energy were indeed sufficient to break the C–H bond, a rate of production of approximately $^1/_{80}$ of that produced by the 2537 A. radiation would be expected, since this is the ratio of absorption of 3650 A. quanta to that of 2537 A. quanta with the lamps described. This assumes, of course, that the transfer of absorbed energy to the bonds to be dissociated is equally efficient in both cases.

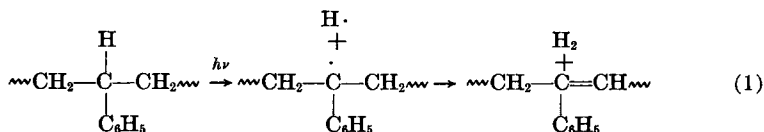## III. REACTION MECHANISMS

A. Hydrogen Production

Although the primary step in the production of hydrogen must be fission of C–H bonds, the 2537 A. quanta will be initially absorbed by the benzene rings and the energy subsequently transferred to the dissociating bonds.

The dissociation energies of the three types of C–H bonds in polystyrene, namely those in the benzene ring, and the secondary and tertiary chain bonds are 104, 76, and 71 kcal./mole, respectively. The last of these will be reduced, however, by the resonance stabilization of the resulting radicals, making the tertiary C–H bonds the weakest in the molecule by a considerable margin. The energy associated with 2537 A. quanta (112 kcal./mole) is sufficient to break all of these bonds, provided, of course, that it can be transmitted from the benzene rings. It seems most likely, however, that tertiary C–H scission will predominate, although the low quantum yield ($\simeq 4 \times 10^{-2}$) for hydrogen production indicates that the dissociation of C–H bonds affords only a small dispersion route for absorbed energy. No evidence for C–C bond fission was obtained from either product analysis or molecular weight measurements. Since the reaction is occurring in the condensed phase it is much more likely that the absorbed energy is dissipated by such quenching reactions as recombination and collisional deactivation.

Since the low quantum yield and the intensity exponent of unity appear to preclude a chain process, there seem two possible routes to the appearance of molecular hydrogen. Either the primarily formed hydrogen atoms combine in pairs or they abstract hydrogen atoms from the polymer structure. In either case, two chain radicals are formed for each hydrogen
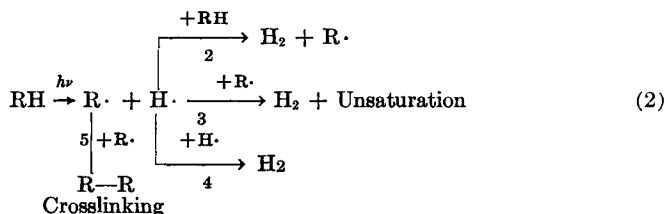
molecule. While the mobility of these radicals is low, in the latter case the radicals are likely to be formed close to one another so that bimolecular combination leading to crosslinking would be concomitant with hydrogen production.

Bearing in mind the proposed radical mechanism for the elimination of hydrogen chloride from poly(vinyl chloride), abstraction of a hydrogen atom from the carbon atom adjacent to the radical center [eq. (1)] seems energetically favorable,

$$\text{www}CH_2\text{—}\underset{\underset{C_6H_5}{|}}{\overset{\overset{H}{|}}{C}}\text{—}CH_2\text{www} \xrightarrow{h\nu} \text{www}CH_2\text{—}\underset{\underset{C_6H_5}{|}}{\overset{\overset{\overset{H\cdot}{+}}{\cdot}}{C}}\text{—}CH_2\text{www} \rightarrow \text{www}CH_2\text{—}\underset{\underset{C_6H_5}{|}}{\overset{\overset{\overset{H_2}{+}}{C}}{}}=CH\text{www} \qquad (1)$$

in which case unsaturation, in conjugation with benzene rings, would appear.

The mechanism may thus be summarized as shown in eqs. (2),

$$RH \xrightarrow{h\nu} R\cdot + H\cdot \begin{array}{l} \xrightarrow[2]{+RH} H_2 + R\cdot \\ \xrightarrow[3]{+R\cdot} H_2 + \text{Unsaturation} \\ \xrightarrow[4]{+H\cdot} H_2 \end{array} \qquad (2)$$

$$\underset{\text{Crosslinking}}{R\text{—}R}$$

and the rate of production of hydrogen must clearly be proportional to the light intensity as found experimentally.

The mechanism also predicts that crosslinking will be concurrent with hydrogen evolution. In fact, insolubility and embrittlement of the polymer occurred after relatively short periods of irradiation.
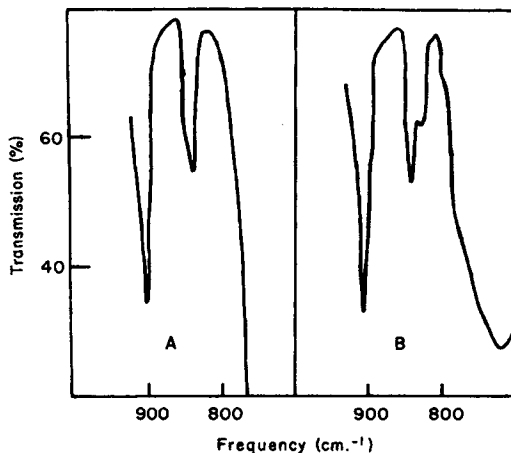

Fig. 5. Effect of irradiation on the infrared spectrum of polystyrene: (A) unirradiated; (B) irradiated in vacuum for 10 hr.

B. Spectroscopic Evidence

1. Infrared.   Infrared spectra of polystyrene films undergoing photolysis showed, as in Figure 5, that a shoulder gradually appears at 825 cm.$^{-1}$ on the band at 840 cm.$^{-1}$.   Absorption in this region can be attributed to the out-of-plane vibration of the C–H bond in a trisubstituted ethylene[3] as in the unsaturated structure proposed in eq. (1):

$$\text{\textasciitilde\textasciitilde CH}_2\text{—C} \overset{*}{=} \text{CH—CH}_2\text{\textasciitilde\textasciitilde}$$
$$\underset{\text{C}_6\text{H}_5}{|}$$
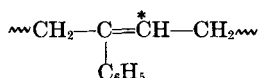
A quantitative interpretation of the formation of this structure in terms of its infrared absorption is extremely difficult in this instance because of the band overlap.   Ultraviolet spectra prove to be more amenable.

2. Ultraviolet.   During irradiation of polystyrene there is a general increase in absorption in the region 2300–3500 A.   Rates of increase are relatively much greater in the 2400 and 2900–3000 A. regions, however, as shown in Figure 6.

Absorption in the 2400 A. region is characteristic of compounds having a carbon–carbon double bond in conjugation with a benzene ring.   Styrene, for example, has an absorption band at 2440 A.[4]   Figure 7 illustrates the increase in optical density at 2400 A. as a function of time of irradiation. Clearly, double bond formation is concomitant with the appearance of hydrogen.
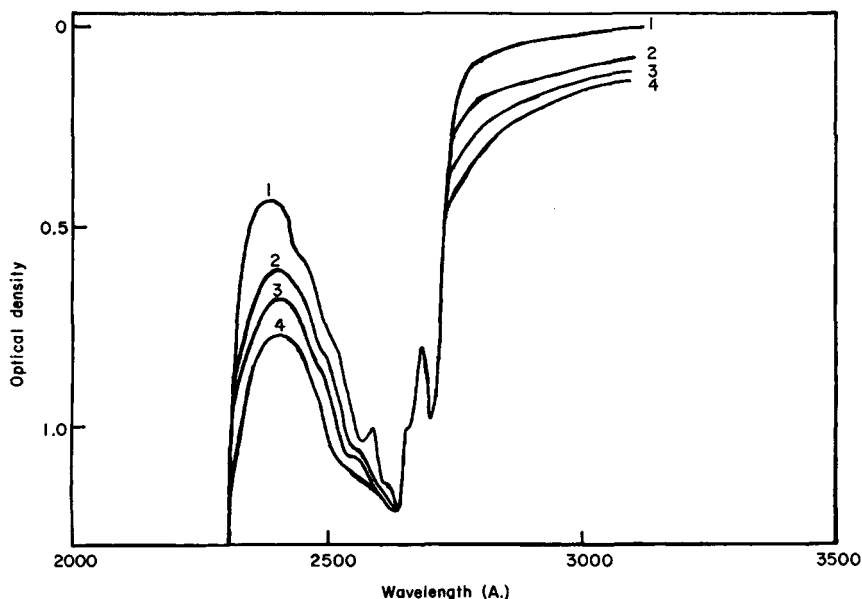

Fig. 6. Effect of irradiation on the ultraviolet spectrum of polystyrene: (*1*) unirradiated;   (*2*) 60 min.;   (*3*) 120 min.;   (*4*) 180 min.
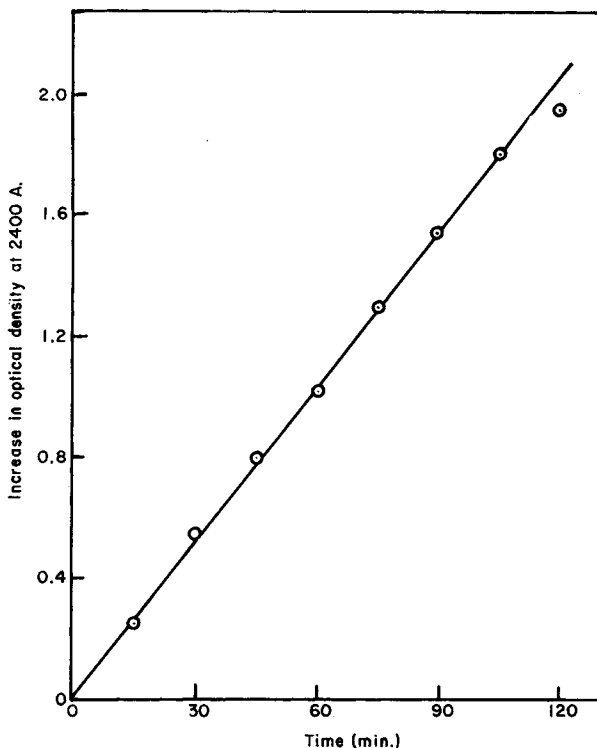
Fig. 7. Increase in optical density of polystyrene at 2400 A. with irradiation.

Vacuum irradiation is also accompanied by yellowish discoloration of the polymer. This could be attributed to the buildup of conjugated double bond sequences in the polymer backbone. Absorption in the 3000 A. region could similarly be accounted for. This, and other aspects of coloration are discussed in Part IV of this series.[5]

C. Irradiation in Nitrogen

Reactions 2, 3, and 4 in the mechanism of eq. (2) clearly all depend upon the mobility of the hydrogen atoms. In general, if the mobility is decreased, then the escape of hydrogen atoms from the polymer into the gas phase will be inhibited so that reaction 4 will be relatively less important and reactions 2 and 3 will be accelerated. The acceleration of reaction 3 should be reflected in the ultraviolet spectra of irradiated films.

In order to test this hypothesis, films were irradiated in various pressures of nitrogen. Nitrogen is not affected by 2537 A. radiation, but its presence should inhibit the diffusion of hydrogen atoms from the polymer. Figure 8 shows, as predicted, that the rate of formation of unsaturation is accelerated by the presence of nitrogen.

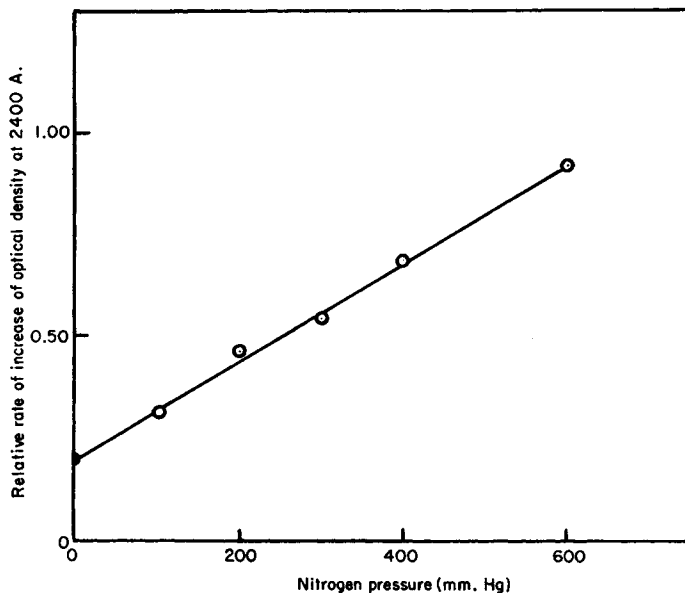Thus this simple photolysis mechanism accounts for a number of the

Fig. 8. Effect of nitrogen pressure on rate of development of unsaturation during irradiation of polystyrene.

more important experimentally observable features of the photolysis of polystyrene.

On the basis of a study of the γ-radiolysis of polystyrene, Wall[6] has suggested an alternative mechanism for crosslinking. According to this, the tertiary C–H structure effectively adds across a double bond in a neighboring benzene ring to form a substituted cyclohexadienyl structure, as shown in eq. (3).
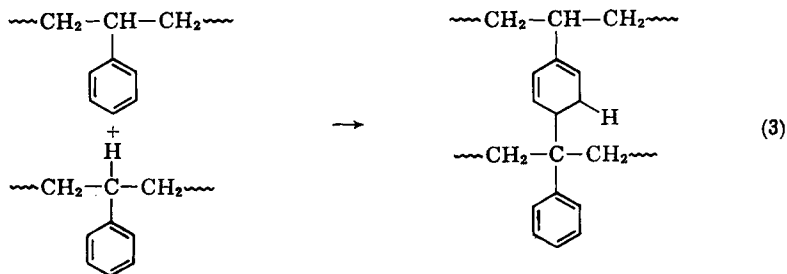
This reaction would be kinetically indistinguishable from the crosslinking reaction proposed above, and since the cyclohexadiene ring contains a tri-substituted ethylene group, this structure would account for the observed absorption at 825 cm.$^{-1}$. The cis-disubstituted olefin also appearing in the ring, however, should exhibit absorption in the 675–728 cm^{-1} region.[3] Despite the fact that there is intense absorption in this region by polystyrene itself, Kargin et al.[7] have observed a shoulder at 625 cm.$^{-1}$ on the

700 cm.$^{-1}$ peak following bombardment of polystyrene with high speed electrons, and this has been attributed to the *cis*-olefin shown above. Such absorption was sought but never observed in the present work.

There is also a serious objection to Wall's theory on the basis of ultraviolet spectra. The cyclohexadiene is essentially a substituted butadiene, and it is extremely unlikely that even the high degree of substitution would be sufficient to account for the very large bathochromic shift observed, the spectrum of irradiated polymer exhibiting high absorbance in the 2400–3500 A. region while butadiene has a maximum at 2170 A. It thus appears that this reaction, although possibly contributing to the crosslinking process, is of much less importance in the photolysis than in the radiolysis and electron irradiation of polystyrene.

References

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Résumé

Lorsqu'on effectue à 28°C et sous vide la photolyse de films de polystyrène par irradiation au moyen d'une longuer d'onde de 2537 A. le seul produit gazeux qui se dégage est l'hydrogène. Simultanément, le polymère devient insoluble et se décolore. Pour cette réaction, l'exposant affectant l'intensité lumineuse est l'unité, le rendement quantique de dégagement d'hydrogène est 4,3 × 10^{-2}; l'énergie d'activation totale est de 2,9 Kcal/mole et la vitesse de photolyse est indépendante du poids moléculaire. Si l'on effectue l'irradiation au moyen d'une longueur d'onde de 3650 A., il n'y a aucun dégagement d'hydrogène. Ces faits peuvent s'interpréter sur la base d'un schéma réactionnel simple dans lequel l'effet primaire du rayonnement de 2537 A. est de libérer des atomes d'hydrogène. La réaction ultérieure de ces derniers et des radicaux polystyryles formés simultanément, se traduit, à la suite d'une série d'étapes compétitives, par l'apparition d'hydrogène, par la formation de ponts et par la production d'insaturation carbone–carbon dans la chaîne principale; ceci crée finalement un système conjugué et se manifeste aux mesures spectrales infra-rouges et ultraviolettes et par le fait que la vitesse de photolyse est accélérée par l'azote.

Zusammenfassung

Bei der Vakuumphotolyse von Polystyrolfilmen bei 28°C mit einer Bestrahlung von 2537 A. tritt als einziges gasförmiges Produkt Wasserstoff auf. Gleichzeitig wird das Polymere unlöslich und verfärbt sich. Der Intensitätsexponent der Reaktion ist eins, die Quantenausbeute für Wasserstoff ist 4,3 × 10^{-2}, die Bruttoaktivierungsenergie beträgt 2,9 kcal/Mol, und die Photolysegeschwindigkeit ist vom Molekulargewicht unab-

hängig.   Bei Verwendung einer 3650-A.-Strahlung wird kein Wasserstoff erzeugt.   Diese
Beobachtungen können mit einem einfachen Reaktionsschema erklärt werden, bei wel-
chem der Primäreffekt der 2537-A.-Strahlung in der Freisetzung von Wasserstoffatomen
besteht.   Die Folgerreaktion der Wasserstoffatome und der gleichzeitig in einer Anzahl
kompetitiver Schritte gebildeten Polystyrylradikale führt zum Auftreten von Wasser-
stoff, zur Vernetzung und zur Bildung von C—C—Doppelbindungen in der Hauptkette,
welche schliesslich zur Konjugation und Farbbildung führt.   Diese Theorien werden
durch die Ergebnisse von Infrarot- und Ultraviolettspektralmessungen gestützt, sowie
durch die Beobachtung, dass die Photolysegeschwindigkeit durch Stickstoff hinaufgesetzt
wird.

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