FINAL REPORT

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Study of Photosensitized Decomposition of Hydroperoxides

By: Gerald Oster (Principal Investigator)

In Collaboration With:

Kiyoshi Futaki
Mark Goodman
Robert Lu
Michael Mullins
Nan-Lo Young
Anne Zelechow

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I. ABSTRACT

The motivation for the research of Grant NGR-33-006-017 was to provide a source of molecular oxygen which could be regulated by light. In particular it was hoped that oxygen could be produced photochemically by a system other than that of the photosynthesis of the living plant. The research was prompted by our discovery that chlorophyll in solution will sensitize (for red light) the photodecomposition of organic hydroperoxides (see Sec. III). This is accompanied by the evolution of oxygen. The effect has been studied for organic peroxides where transient species of chlorophyll are observed. In order to obtain a background of the kinetics of decomposition of peroxides, a review has been prepared (Sec. II).

Chlorophyll-sensitized decomposition of hydroperoxides is postulated to take place in the living plant. In connection with this, it was found that hydroperoxides are formed on irradiation of chloroplasts with red light (Sec. IV). Chloroplasts which had been inactivated with heat do not show this effect.

Manganese (as Mn^{++}) has been implicated in the oxygen evolution mechanism of photosynthesis. Manganese chelates were used as substrates for photosensitized reactions (Sec. V).

Tetrazolium salts undergo photoreduction to produce the corresponding formazans (Sec. VI).

Suspensions of zinc oxide flushed with carbon dioxide produce on irradiation oxygen and formaldehyde (Sec.VI). The reaction variables are not known, however.

A review has been prepared on the various ways free radicals produced by light will initiate polymerization of vinyl monomers(Sec.VIII). The polymerization method is the most sensitive for the detection of free radicals and has many applications to photochemistry.

II. DECOMPOSITION OF PEROXIDES (A Review by Robert Lu and Gerald Oster)

A. Thermal Decomposition

1. Benzoyl Peroxide

The dissociation energy of the oxygen-oxygen bond in organic peroxides is about 30-40 Kcal/mole and, above about 80°C, these compounds undergo homolysis at appreciable rates giving alkoxy and/or acyloxy radicals[1,2].

The thermal decomposition of benzoyl peroxide was apparently first clearly described as a homolytic reaction by Hey and Waters[3].

$$\phi\text{-}\overset{O}{\overset{\|}{C}}\text{-O-O-}\overset{O}{\overset{\|}{C}}\text{-}\phi \longrightarrow 2\phi\text{-}\overset{O}{\overset{\|}{C}}\text{-O}\cdot \qquad (1)$$

In dilute solution, or in the presence of suitable radical scavengers, the induced decomposition of the peroxide can be suppressed and this primary unimolecular homolysis has an activation energy of about 30 Kcal/mole.

With iodine[4] in moist carbon tetrachloride, benzoic acid is formed almost quantitatively, presumably through the homolysis of benzoyl hypoiodide

$$\phi\text{-}\overset{O}{\overset{\|}{C}}\text{-O}\cdot + I_2 \longrightarrow \phi\text{-}\overset{O}{\overset{\|}{C}}\text{-O-I} + I\cdot \qquad (2)$$

$$\phi\text{-}\overset{O}{\overset{\|}{C}}\text{-O-I} + H_2O \longrightarrow \phi\text{-}\overset{O}{\overset{\|}{C}}\text{-OH} + HOI \qquad (3)$$

The benzoyloxy radical may be trapped similarly by the highly-colored 1,1-diphenyl-2-picrylhydrazyl radical, enabling

the rate of the dissociation of benzoyl peroxide to be measured photometrically[5]. The benzoyloxy radical can also act as an initiator for vinyl polymerization[6].

If the radical scavenger is absent or is inefficient, the benzoyloxy radicals break down partially or completely to phenyl radicals and carbon dioxide, and the phenyl and benzoyloxy radicals (and any radicals derived from their attack on the solvent) may induce decomposition of the benzoyl peroxide; the rate of decomposition increases and its order becomes greater than unity.

$$\phi\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\cdot \longrightarrow \phi\cdot + CO_2 \qquad (4)$$

If the medium contains aliphatic C-H bonds, the benzoyloxy and/or phenyl radicals usually react by hydrogen abstraction:

$$\left.\begin{matrix}\phi\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\cdot \\ \phi\cdot\end{matrix}\right\} + RH \longrightarrow \left.\begin{matrix}\phi\text{-}\overset{\overset{O}{\|}}{C}\text{-}OH \\ \phi H\end{matrix}\right\} + R\cdot \qquad (5)$$

Diphenyl and phenyl benzoate may also be formed, probably by the cage recombination of radicals, since the yield is not reduced in the presence of the radical scavenger styrene[7,8].

Ring-substituted benzoic acids, $R\cdot C_6H_4\cdot CO_2H$, may be a major product of the thermal decomposition of benzoyl peroxide in solvent RH and RCl. Walling and Savas[9] have suggested that these acids are formed in an induced decomposition in which the addition of the radical R. to the ring is connected with homolysis of the O-O bond

$$R\cdot + \phi\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\phi \longrightarrow X + \cdot O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\phi \qquad (6)$$

The intermediate X may be a 2,5- or 2,4-cyclohexadienyl α-lactone which rearranges to a para- or ortho-substituted benzoic acid.

The initiation of styrene (and methylmethacrylate) polymerization by C^{14}-labelled dibenzoyl peroxide, when carried out in benzene, shows that both phenyl and benzoyloxy radicals add to these monomers[10]. Shih, Hey and William[11] have stated that the three main mechanisms proposed for arylation of aromatic hydrocarbons are: (i) abstraction of hydrogen by the phenyl radical followed by combination of radicals:

$$\phi\cdot + ArH \longrightarrow \phi H + Ar\cdot \qquad (7)$$

$$Ar\cdot + Ar\cdot \text{ (or } \phi\cdot) \longrightarrow Ar_2 \text{ (or } Ar\phi) \qquad (8)$$

(ii) simultaneous approach of the phenyl radical and removal of a hydrogen atom:

$$\phi\cdot + ArH \longrightarrow [Ar\overset{\phi}{\underset{H}{\cdots}}] \longrightarrow Ar\phi + H\cdot \qquad (9)$$

(iii) slow formation of an addition complex between the radical and hydrocarbon, followed by a rapid reaction probably involving attack by a further radical or oxidizing agent:

$$\phi\cdot + ArH \longrightarrow \left[Ar\begin{matrix}\phi\\ H\end{matrix}\right] \xrightarrow{R.} Ar\phi + RH \qquad (10)$$

The kinetics of the decomposition of benzoyl peroxide in many solvents appears to be the sum of a first-order reaction plus a reaction of another order[12]. The over-all rate of decomposition of the peroxide varies very greatly with the solvent and the products of decomposition are very different in diverse solvents[1].

The decomposition of benzoyl peroxide in all solvents is to be regarded as resulting from an initial homolytic cleavage of the molecule into radicals[3]. The radicals may attack the solvent, and both primary and secondary radicals may then attack the peroxide, effecting a radical-induced chain decomposition. The dismutation of the $C_6H_5COO\cdot$ radicals leads to the formation of carbon dioxide. Recombination of radicals results in the termination of the chain reaction.

There is a very large effect of solvent on the over-all rate of decomposition of benzoyl peroxide; the approximate order of increasing decomposition rate is[1]: highly halogenated solvent $<$most aromatic $<$most aliphatics $<$ethers, alcohols, monohydric phenols. There is no relation between the over-all rate of decomposition and the acidity or polarity of the solvent.

Typical inhibitors of free radical chain reaction will lower the over-all rate of decomposition of benzoyl peroxide in a solvent such as dioxane or acetic anhydride[13]. These inhibitors include oxygen, hydroquinone, para-t-butyl catechol, m-dinitrobenzene, picric acid, and vinylacetate or methylmethacrylate. In certain cases the inhibitors will completely suppress the induced decomposition of the peroxide so that the measured rate of decomposition in the presence of these inhibitors may be taken as equal to the rate of spontaneous cleavage. This method has been used as a quantitative measure of spontaneous cleavage rates by employing 3,4 -dichlorostyrene or methylmethacrylate[6] and 2,2-diphenylpicrylhydrazyl[5] as the inhibitors.

The over-all decomposition of benzoyl peroxide as the sum of a

spontaneous cleavage and a radical-induced chain reaction was put forth independently by Bartlett and Nozaki[13] and by Cass[14]. Bartlett et al. showed that the disappearance of peroxide can be expressed as follows:

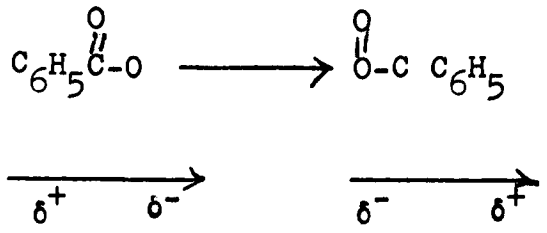
$$-\frac{d(P)}{dt} = k_d P + k_i P^x \qquad (11)$$

where $-\frac{d(P)}{dt}$ represents the rate of decomposition of the peroxide, k_d the specific rate of spontaneous cleavage, k_i the specific rate of induced decomposition, and x the order of the induced reaction which may vary between 0.5 and 2.0.

Bawn and Mellish[5] employed diphenylpicrylhydrazyl (DPPH) as an inhibitor to study the rate of spontaneous decomposition of benzoyl peroxide in various solvents. The stable radical DPPH combines directly and stoichiometrically with the radical produced in the spontaneous cleavage of benzoyl peroxide. The rate of spontaneous cleavage of the peroxide can therefore be measured by following the disappearance of the inhibitor; since DPPH is highly colored, its disappearance can be conveniently followed by a photometric method.

It was found[1] that electron-repelling substituents on one or both of the phenyl rings increase the rate of unimolecular spontaneous decomposition, whereas electron-attracting groups retard the reaction. The stability of the radicals formed after cleavage is not an important factor in determining the rate of spontaneous cleavage of the substituted benzoyl peroxides. The explanation is that the two benzoate groups in benzoyl peroxide are dipoles which are attached to one another in such a way as to

repel each other[6].



The peroxide cleaves into free radicals because this relieves the electrostatic repulsion between the two benzoate groups.

2. Tertiary-butylhydroperoxide

The thermal decomposition of t-butylhydroperoxide has been studied in both the gaseous and the liquid phase[15]. It has been carried out at 260°C in the presence of an excess of cyclohexene. The products found included acetone, t-butyl alcohol, methane, methanol, carbon monoxide, water and a 13% yield of cyclohexanol. The most reasonable way is the cleavage of the O-O linkage followed by an addition of the hydroxyl radical to the cyclohexene.

The over-all reaction mechanism as postulated by Bell et al.[15] is:

$$(CH_3)_3COOH \longrightarrow (CH_3)_3CO\cdot + \cdot OH \quad (12)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \quad (13)$$

$$X\cdot + (CH_3)_3COOH \longrightarrow XH + (CH_3)_3COO\cdot \quad (14)$$

$$R\cdot + (CH_3)_3COO\cdot \longrightarrow (CH_3)_3COOR \quad (15)$$

$$(CH_3)_3COOR \longrightarrow (CH_3)_3CO\cdot + RO\cdot \quad (16)$$

$$2(CH_3)_3COO\cdot \longrightarrow 2(CH_3)_3CO\cdot + O_2 \quad (17)$$

where X = RO·, HO·, $(CH_3)_3CO$·, CH_3·, and R = CH_3· or a radical derived from the solvent.

The combination of two RO_2· radicals to give two RO· radicals and molecule oxygen is particularly noteworthy.

Decomposition of the vapor of t-butylhydroperoxide at 195°C is very slow, but the addition of di-t-butyl or di-t-amylperoxide accelerates the reaction[16]. The products identified were similar to those obtained at 250-300°C, with the addition of carbon monoxide and ethane, which are due to the decomposition of acetyl radicals and the recombination of methyl radicals.

The kinetics of the decomposition of t-butylhydroperoxide in a number of solvents at 73.5°C were studied by Stannett and Mesrobian[17] who found that reaction is most rapid in those solvents capable of forming a radical on abstraction of hydrogen, i.e., alcohols, phenols, esters and vinyl monomers. In benzene, no appreciable amount of decomposition occurs until radical-forming compounds (e.g., α-α'-azoisobutyronitrile) are added.

Quantitative kinetic study[1] of the liquid phase decomposition of t-butylhydroperoxide in n-octane was made in the temperature range of 150-180°C. The reaction proved to be a combination of a unimolecular fission plus a chain process of higher order. The rate constant for unimolecular fission in the range of 150-180°C in n-octane was found to be:

$$k_d = 1 \times 10^{15} \exp \left\{-39.0^{Kcal./RT}\right\} \qquad (18)$$

The decomposition of t-butylhydroperoxide in chlorobenzene was

studied by Bell et al.[18]. Chlorobenzene is very resistant to radical attack. At 140°C a rapid chain decomposition of the hydroperoxide occurs to produce an almost quantitative yield of t-butyl alcohol and oxygen, as:

$$(CH_3)_3COOH \longrightarrow (CH_3)_3CO\cdot + \cdot OH \quad (19)$$

$$\left.\begin{matrix}(CH_3)_3CO\cdot \\ \cdot OH\end{matrix}\right\} + (CH_3)_3COOH \longrightarrow \left.\begin{matrix}(CH_3)_3COH \\ HOH\end{matrix}\right\} + (CH_3)_3COO\cdot \quad (20)$$

$$2(CH_3)_3COO\cdot \longrightarrow 2(CH_3)_3CO\cdot + O_2 \quad (21)$$

The decomposition rate of t-butylhydroxide in dodecane at 98.5°C is increased if the oxygen which is evolved is removed in a stream of helium (ref. 18, p. 170). Two factors may account for this: firstly, alkyl radicals derived from the solvent, which otherwise induce decomposition of the t-butylhydroperoxide, are rendered inactive by reaction with dissolved oxygen, to give a dodecanylhydroperoxide; secondly, this solvent-derived hydroperoxide would be analytically indistinguishable from the t-butylhydroperoxide and reduce its apparent rate of decomposition[19].

At higher temperatures in the gas phase or in solution, less oxygen is evolved and acetone and methanol are formed in appreciable amount, presumably by the breakdown of t-butoxy radicals[20,15].

B. Catalyzed Decomposition

1. Redox Reactions with Metal Ions

Organic peroxides, particularly the alkyl hydroperoxides, may decompose in a number of different ways when treated with ions of variable oxidation number (ref. 18, p. 170). Most of these

reactions can be rationalized on the basis of four initial reactions outlined in equations (22)-(25) below and are classified by reference to the electronic operation which the metal ion performs upon the peroxide.

$$+1e \quad M^{n+} + RO\text{-}OH \longrightarrow M^{(n+1)+} + RO\cdot + OH^- \tag{22}$$

$$+2e \quad M^{n+} + RO\text{-}OH \longrightarrow M^{(n+2)+} + RO^- + OH^- \tag{23}$$

$$-1e \quad M^{n+} + RO\text{-}OH \longrightarrow M^{(n-1)+} + RO\text{-}O\cdot + H^+ \tag{24}$$

$$-2e \quad M^{n+} + RO\text{-}OH \longrightarrow M^{(n-2)+} + RO\cdot O^+ + H^+ \tag{25}$$

A hydroperoxide can frequently be decomposed by the metal in both its higher and lower oxidation states; a small amount of the ion can then catalyze the decomposition of a large amount of the peroxide by a combination of the above reactions.

The classical example of this type of reaction is the ferrous ion induced decomposition of hydrogen peroxide. Haber and Weiss[21] proposed the following scheme to explain this reaction:

$$H_2O_2 + Fe^{++} \longrightarrow HO\cdot + OH^- + Fe^{+++} \tag{26}$$

$$HO\cdot + Fe^{++} \longrightarrow HO^- + Fe^{+++} \tag{27}$$

$$HO\cdot + H_2O_2 \longrightarrow H_2O + HO_2\cdot \tag{28}$$

$$HO_2\cdot + H_2O_2 \longrightarrow HO\cdot + H_2O + O_2 \tag{29}$$

The fact that radicals are produced in the reaction between hydrogen peroxide and ferrous ion was demonstrated by Evans and co-workers[22] who carried out this decomposition in the presence of water-soluble monomers such as acrylonitrile; a rapid polymerization of the monomer is induced.

By studying the rate of reaction between hydrogen peroxide and ferrous ion in the presence of excess monomer, Baxendale, Evans and Park[22] were able to determine the rate constant for the elementary reaction (1):

$$k(Fe^{++}, H_2O) = 1.78 \times 10^9 e^{\left\{-10.1^{Kcal/RT}\right\}} \text{ liter mole}^{-1} \text{ sec.}^{-1} \qquad (30)$$

Good evidence that an alkoxy radical is formed as

$$Fe^{++} + RO\text{-}OH \longrightarrow Fe^{+++} + RO\cdot + {}^{-}OH \qquad (31)$$

is that the ferrous ion-hydroperoxide system can initiate the polymerization of a vinyl monomer, and the alkoxy group can then be detected as the end group of the polymer. If an excess of the monomer is present to absorb all the RO· radicals and prevent their inducing chain decomposition of the hydroperoxide, the reaction is found to be first order with respect to both hydroperoxide and ferrous ion[23,24].

If the radicals are generated in the presence of a molecule ZH which readily donates a hydrogen atom, the alcohol ROH is formed by hydrogen transfer

$$RO\cdot + ZH \longrightarrow ROH + Z\cdot \qquad (32)$$

This hydrogen abstraction occurs more readily with the t-butoxy radical and is probably general for the reactions of t-alkyl hydroperoxides.

In the absence of additives which will absorb the alkoxy radical or donate to it a hydrogen atom, three main types of reactions are apparently open.

Firstly, if the concentration of ferrous ion is high, the alkoxy radical may be reduced further to the alcohol by a non-chain-sustaining process

$$RO\cdot + Fe^{++} \longrightarrow RO^{-} + Fe^{+++} \qquad (33)$$

Secondly, the $R'_3CO\cdot$ radical may undergo elimination or rearrangement

$$R'_3CO\cdot \longrightarrow R'_2C{=}O + R'\cdot \ (\longrightarrow R'R' \text{ and } R'H) \qquad (34)$$

$$R'_3C\text{-}O\cdot \longrightarrow R'_2\dot{C} - OR \longrightarrow (R'_2C\text{-}OR)_2 \qquad (35)$$

Thus, t-butyl hydroperoxide may decompose to give acetone.

Thirdly, the alkoxy radical may induce decomposition of the hydroperoxide by a chain-sustaining process such as[25]

$$\phi\text{-}C(Me)_2\text{-}O\cdot + \phi\text{-}C(Me)_2\text{-}O\cdot OH \longrightarrow MeOH + \phi\text{-}\overset{O}{\overset{\|}{C}}\text{-}Me + \phi\text{-}C(Me)_2O\cdot \qquad (36)$$

In the absence of a reactive substrate, further reaction of the $RO_2\cdot$ radicals with M^{n+} ions gives molecular oxygen and a carbonium ion[26].

$$M^{n+} + RO\text{-}OH \longrightarrow M^{(n-1)+} + RO\text{-}O\cdot + H^{+} \qquad (37)$$

$$RO\text{-}O\cdot + M^{n+} \longrightarrow R^{+} + O_2 + M^{(n-1)+} \qquad (38)$$

This formation of a carbonium ion has recently been questioned, and it appears that a second peroxide molecule or radical may be involved in the evolution of oxygen[27,28].

$M^{(n-1)+}$ ions which are formed can also induce decomposition of hydroperoxide by a redox process, now at the O-O bond and by electron donation.

$$M^{(n-1)+} + RO\text{-}OH \longrightarrow M^{n+} + RO\cdot + {}^{-}OH \quad (39)$$

$$RO\cdot + M^{(n-1)+} \longrightarrow M^{n+} + RO^{-} \quad (40)$$

RO· radical can also induce decomposition of the hydroperoxide.

$$RO\cdot + RO\text{-}OH \longrightarrow RO\cdot + \text{alcohol} + \text{ketone} \quad (41)$$

Thus, the metal ion in either its M^{n+} or $M^{(n-1)+}$ valence state can be used. A small amount of the ion will suffice to decompose a large amount of hydroperoxide, but less than the stoichiometric amount of oxygen will be liberated.

The evolution of oxygen from hydroperoxide may be brought about in three different ways[26]:

(a) by treating the hydroperoxide with a powerful oxidant, e.g., Co^{+++}, capable of abstracting one electron;

(b) by treating tertiary hydroperoxide with alkali;

(c) by treating the hydroperoxide with an "additive", e.g., succinonitrile and alkali, at room temperature.

The oxidants which oxidize hydroperoxide to yield molecular oxygen fall into two classes:

(I) oxidants which give about one equivalent of oxygen based on the amount of oxidizing agent used, such as ceric salts and lead tetraacetate;

(II) oxidants, e.g., cobaltic acetate, which decompose hydroperoxides into oxygen by a chain reaction and which, therefore, need be present only in small amount.

$$ROOH + Co^{++} \longrightarrow RO\cdot + OH^{-} + Co^{+++} \quad (42)$$

$$ROOH + Co^{+++} \longrightarrow RO_2\cdot + H^+ + Co^{++} \quad (43)$$

$$RO\cdot + Co^{++} \longrightarrow RO^- + Co^{+++} \quad (44)$$

$$RO_2\cdot + Co^{+++} \longrightarrow R^+ + O_2 + Co^{++} \quad (45)$$

2. Decomposition Catalyzed by Alkali

In the alkali solution, the anion RO_2^- is the oxidant which attacks the undissociated molecule of the hydroperoxide.

$$2C_6H_5(CH_3)_2COOH \xrightarrow[\text{"additive"}]{NaOH} 2C_6H_5(CH_3)_2COH + O_2 \quad (46)$$

$$ROOH + NaOH \longrightarrow RO_2^- + Na^+ + H_2O \quad (47)$$

$$RO_2^- + \begin{matrix} R_1 \\ | \\ HC\text{-}OH \\ | \\ R_2 \end{matrix} \longrightarrow RO^- + \begin{matrix} R_1 \\ | \\ HO\text{-}C\text{-}OH \\ | \\ R_2 \end{matrix} \quad (48)$$

$$RO_2^- + ROOH \longrightarrow RO^- + ROH + O_2 \quad (49)$$

Thus no free radicals are involved; instead there is direct transfer of an oxygen atom.

The decomposition of peroxides by amines has been studied by Bartlett and Nozaki[13]. They found at 79.8°C that the decomposition of benzoyl peroxide by triphenylamine was of first order or lower with respect to amine.

There are two mechanisms which readily suggest themselves as explanations for the extremely rapid reaction between peroxides and amines[1].

First, the induced decomposition of peroxide by amino type

radicals may be an extremely rapid chain reaction.

Second, there may be a bimolecular reaction between the peroxide molecule and the amine molecule leading to peroxide decomposition. The bimolecular reaction would most probably be a one-electron transfer.

3. Decomposition Catalyzed by Acid

The acid-catalyzed decomposition of hydroperoxide was first reported by Hock and Lang[29], and later studied further by Kharasch and co-workers[30-32].

A hydroperoxide unstable to acid undergoes breakdown in preference to attacking another molecule which may act as a reductant.

No oxygen has ever been observed as a reaction product when hydroperoxides are decomposed by acids.

The over-all reaction for the acid-catalyzed cleavage of all the hydroperoxides studied is:

$$R_1R_2R_3COOH \xrightarrow{H^+} R_2R_3CO + R_1OH \qquad (50)$$

C. Photodecomposition of Peroxides

The photochemical decomposition of gaseous di-t-butyl peroxide at pressures less than atmospheric and temperatures from 25 to 75°C has been investigated by Dorfman and Salsburg[33]. Acetone and ethane are the major products of the photodecomposition, along with small amounts of t-butyl alcohol and methane. It is assumed that the primary quantum yield for fission of the O-O bond is unity since the wavelength used (250 mμ) has an energy of 100 Kcal/mole, whereas the bond strength is about 34 Kcal/mole. It was concluded

that at room temperature no chain decomposition of the peroxide occurs, but at higher temperature (75°C) there is the possible existence of short reaction chains.

Frey[34] studied the photolysis of di-t-butyl peroxide by a medium-pressure mercury arc; it has been postulated that 11% of the peroxide undergoing photolysis follows the equation:

$$(CH_3)_3C\text{-}O\text{-}O\text{-}C(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3C\cdot + O_2 \qquad (51)$$

A light of wavelength shorter than 300 mμ is required. The following equation can then occur:

$$(CH_3)_3C\cdot + CH_3\cdot \longrightarrow (CH_3)_4C \qquad (52)$$

$$2(CH_3)_3C\cdot \longrightarrow CH(CH_3)_3 + (CH_3)_2C{=}CH_2 \qquad (53)$$

$$2(CH_3)_3C\cdot \longrightarrow (CH_3)_3C\text{-}C(CH_3)_3 \qquad (54)$$

$$CH_3\cdot + CH_3\cdot \longrightarrow C_2H_6 \qquad (55)$$

$$(CH_3)_3C\cdot + CH_3\cdot \longrightarrow CH_4 + (CH_3)_2C{=}CH_2 \qquad (56)$$

Volman et al.[35] suggested that the most reasonable expectation is that the absorption of light leads to a rupture of the O-O bond with primary photochemical efficiency of unity.

$$(CH_3)_3COOC(CH_3)_3 + h\nu \longrightarrow 2(CH_3)_3CO\cdot \qquad (57)$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2CO + CH_3\cdot \qquad (58)$$

The photochemical decomposition of dicumyl peroxide and cumene

hydroperoxide in solution has been carried out by Norrish[36]. The initial fission takes place at the O-O bond. Light of wavelength 313 mμ has been used. In the case of 313 mμ incident light the methyl radical formed is split off, acetophenone is formed and the free methyl radical must combine either with another methyl radical to form ethane or attack the solvent. When incident light was 254 mμ, however, it would appear that the carbon-carbon bond of the phenyl group was more readily broken, giving rise to acetone and a phenyl radical. Quanta from these wavelengths are : 313 mμ, 91 Kcal./mole; 254 mμ, 112 Kcal./mole, the difference being 21 Kcal./mole.

In the decomposition of cumene hydroperoxide by 313 mμ and 254 mμ no acetophenone was formed in the reaction and no oxygen was found in the decomposition products.

$$\phi(CH_3)_2COOH \longrightarrow \phi(CH_3)_2CO\cdot + .OH \qquad (59)$$

$$\phi(CH_3)_2CO\cdot + RH \longrightarrow \phi(CH_3)_2COH + R\cdot \qquad (60)$$

$$R\cdot + \phi(CH_3)_2COOH \longrightarrow ROH + \phi(CH_3)_2CO\cdot \qquad (61)$$

The alkoxy radical can either decompose into a ketone or abstract hydrogen and form an alcohol[37]. This hydrogen can either be provided by the surrounding solvent or by another peroxide. Abstraction of hydrogen from a peroxide molecule can occur in two ways: first, the hydrogen may come from the alkyl group, a process which in the case of di-t-butyl peroxide has been shown to lead to the formation of isobutylene oxide [38]; or alternatively, the hydrogen abstracted may be the one attached to the oxygen in a hydroperoxide. In the latter reaction a radical of the type ROO· will be formed; this can

either first react with an alkyl radical and then break into alkoxy radicals [16] or break directly into an alkoxy radical and oxygen[15].

The photodecomposition of hydrogen peroxide by ultraviolet has been studied by Schumb[39]. The rate of decomposition by 320-380 mμ was 0.25% per hour, which was about 70-fold that observed in the absence of radiation under otherwise the same conditions. Dainton and Rowbottom[40] indicated that for light intensities up to about 10^{17} quanta/l. sec. and concentrations up to 20 molar, the rate of decomposition is directly proportional to the hydrogen peroxide concentration and to the square root of the intensity. Volman[41] studied the photodecomposition of hydrogen peroxide vapor, in which hydrogen peroxide vapor initially at a pressure of 1.23 mm. mercury was illuminated with 254 mμ radiation. The quantum yield was found to be 1.7 ± 0.4, independent of the hydrogen peroxide pressure, and independent of temperature over the range of 25-50°C. The initial photochemical act has been assumed (ref. 40, p. 462) to be

$$H_2O_2 + h\nu \longrightarrow 2 \cdot OH \qquad (62)$$

followed by reaction in the solvent cage to form H_2O and O; thus

$$2 \cdot OH \longrightarrow H_2O + O \qquad (63)$$

For the chain propagation, Haber and Willstätter[42] have postulated the reactions

$$\cdot OH + H_2O_2 \longrightarrow H_2O + HO_2\cdot \quad (64)$$

$$HO_2\cdot + H_2O_2 \longrightarrow H_2O + O_2 + \cdot OH \quad (65)$$

The chain termination reactions most generally postulated (ref. 39, p. 464) are one or both of the following:

$$2HO_2 \longrightarrow H_2O_2 + O_2 \quad (66)$$

$$OH + HO_2 \longrightarrow H_2O + O_2 \quad (67)$$

Norrish et al. (43) studied the photodecomposition of t-butyl hydroperoxide in solution by the light of wavelength 313 mμ; the quantum yield determined is independent of concentration but increases as the temperature is raised. The main decomposition products are t-butyl alcohol and oxygen. The reaction mechanism is similar to that postulated by Bell et al. (15) for the thermal decomposition.

$$(CH_3)_3COOH + h\nu \longrightarrow (CH_3)_3CO\cdot + \cdot OH \quad (68)$$

$$(CH_3)_3CO\cdot + (CH_3)_3COOH \longrightarrow (CH_3)_3COH + (CH_3)_3COO\cdot \quad (69)$$

$$2(CH_3)_3COO\cdot \longrightarrow 2(CH_3)_3CO\cdot + O_2 \quad (70)$$

A possible reaction yielding t-butyl alcohol and oxygen is the interaction of a t-butyl peroxy and a hydroxy radical.

$$(CH_3)_3COO\cdot + \cdot OH \longrightarrow (CH_3)_3COH + O_2 \quad (71)$$

Photodissociation of alkyl hydroperoxides as studied by Electron

Spin Resonance has been carried out by Piette et al. (44). The identification of the free radical intermediates was inferred from their characteristic hyperfine patterns; in addition, the fission of the O-O bond in hydroperoxides, the formation of alkyl R· and HO_2· radicals and the production of peroxy ROO· and hydrogen radicals were observed.

Luner and Szwarc (45) studied the photosensitized decomposition of acetyl peroxide by aromatic hydrocarbons, e.g., anthracene and naphthacene with a 365 mμ line. The rate of decomposition is proportional to the concentrations of acetyl peroxide and anthracene (at concentrations less than 1.5×10^{-4} M), and the mechanism is similar to that in the thermal decomposition.

References

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III. CHLOROPHYLL - PHOTOSENSITIZED PRODUCTION OF OXYGEN

The present studies were undertaken in the hope of elucidating the mechanism of oxygen production in photosynthesis. Organic peroxides and hydroperoxides which are stable at room temperature were found to readily decompose when chlorophyll is used as the photosensitizer. Throughout, purified chlorophyll a was used and the light excitation was with red light of wavelength 660 mμ (achieved with a 500 watt tungsten lamp and an interference filter). In most cases the intensity of light falling on the sample was about 10^{-4} einsteins per hour per square centimeter. In the majority of studies the changes in absorption spectra were followed while the system was being illuminated with 660 mμ light. In the case of the hydroperoxides, oxygen evolution was measured. Quantitative measurements were carried out at room temperature with benzoyl peroxide and with t-butyl hydroperoxide using benzene as the solvent. Benzoyl peroxide has a half-life of ten hours at 72° C and t-butyl hydroperoxide has a half-life of 10 hours at 172° C. In most cases oxygen was rigorously excluded (by repeated freezing and thawing of the solutions under vacuum). In no case was there any measurable reaction in the absence of red light, nor was there any reaction when the solutions without chlorophyll were illuminated with red light.

On initial exposure to light, solutions with certain peroxides or hydroperoxides exhibit a depression in the red peak (660 mμ) of chlorophyll (with a shift of 2mμ to shorter wavelengths) and an increase in the blue peak (430 mμ). If the illumination is of duration of less than about 10 seconds the sample, when allowed to stand in the dark, will revert to the original spectrum. The rate of dark reversal is first order with a lifetime of 26 seconds. The reversal is not complete, however, and on first illumination 66% is recovered with less recovery if the illumination is repeated or increased in duration. Oxygen inhibits both the production of this unstable intermediate as well as its rate of recovery. The quantum yield of production of the intermediate is independent of light intensity (varied over a ten fold range with neutral density filters).

The spectrum of the intermediate is not unlike that of the fleeting brown intermediate formed in the "phase test" (1). The intermediate is apparently not the same as that reported by Rabinowitch (2) and further studied by Livingston (3) for chlorophyll in oxygen-free methanol.

There the rate of bleaching is proportional to the square root of the intensity and the dark recovery is second order.

On continued illumination of the peroxide-containing solutions the 430 and 660 mμ peaks decrease with the blue peak shifting by 5 mμ to longer wavelengths. On very prolonged illumination (about

30 min. or longer) both peaks are depressed and are shifted to longer wavelengths (by 10 mμ for the blue peak to 2 mμ for the red peak).

Solutions of chlorophyll with t-butyl hydroperoxide in benzene were illuminated in an electron spin resonance cavity. The esr signal is a triplet (line width of 28.7 gauss with hyperfine splitting of 6 gauss) highly suggestive of a nitrogen free radical.

When chlorophyllin a produced by the alkali treatment of chlorophyll (4) is used in place of chlorophyll no signal was obtained. The esr signal might arise from abstraction of a hydrogen atom (at position 10) from the cyclopentanone ring (which is absent in chlorophyllin) and the remaining unpaired electron is then localized at the nitrogen atom by the rearrangement of the double bonds and the structure is thereby stabilized.

The esr signal builds up during continued illumination until a steady state is reached. On removal of light the signal decays rapidly during the first few minutes but is detectable even after 18 hours. This rather stable free radical can be converted back to the original chlorophyll by the addition of reducing agents. The product formed by prolonged illumination, however, is only partially recoverable by reduction (compare Krasnovsky (5)).

The reaction between excited chlorophyll and peroxide involves the long-lived metastable (triplet?) excitation state of chlorophyll since the fluorescence of chlorophyll is not appreciably quenched by peroxide even up to concentrations as high as 10%. The rate of

transformation of chlorophyll is retarded by small amounts of p-phenylenediamine (PPD). Thus 10^{-7}M of PPD is sufficient to reduce the rate by a factor of two. On the basis of diffusional quenching arguments one calculates the lifetime of the excited state to be 3.4×10^{-4}sec. which is ten times longer than that observed from flash spectroscopy of very dilute deoxygenated solutions of chlorophyll in benzene (6). The quantum yield of chlorophyll destruction decreases inversely with the chlorophyll concentration apparently due to self-quenching of the metastable excited state. The fluorescence of chlorophyll is strongly quenched by PPD (Stern-Volmer constant of 333 liters per mole.). Small spectral shifts in absorption spectra are observed indicating complex formation presumably between the amine group of the quencher and the cyclopentanone ring of chlorophyll. DCMU (3-p-chlorophenyl-1,1-dimethylurea)is also a retarder of chlorophyll destruction and is a quencher of fluorescence (Stern Volmer constant 90 liters per mole). The stable free radical DPPH (α,α -diphenyl-β-picryl hydrazyl) is also a retarder of the photo-destruction of chlorophyll and may act in the same way as does oxygen.

The sensitized photo-destruction of t-butylhydroperoxide is accompanied by the evolution of a gas which we identified as oxygen by its coloration of reduced (leuco) dyes. The oxygen evolution was measured in a Warburg manometer. It was found that the rate of oxygen evolution was enhanced by the PPD but that DCMU suppressed

the rate. Under the conditions employed, the quantum yield of oxygen evolution is small (less than 0.02) and it was calculated that each chlorophyll molecule was effective in the production of twenty oxygen molecules. It is of interest that chlorophyllin **a** was ineffectual as a sensitizer for oxygen production, again suggesting the involvement of the cyclopentanone ring in the case of chlorophyll.

Copious amounts of oxygen can be produced by another approach. We found that the chelate, cobalt (III) acetylacetonate is destroyed by light-excited chlorophyll. Cobalt ion is liberated and this ion (like other transition metal ions) catalyses the decomposition of hydroperoxides to liberate oxygen. It would be interesting to repeat these studies with manganese chelates since Mn^{++} is regarded as essential in oxygen evolution in photosynthesis (7).

The present work was supported by the National Aeronautics and Space Agency under grant No. NGR 33-006-017.

SUMMARY.

On brief illumination of chlorophyll in the presence of peroxides a reversible colored species is produced with a life-time of 26 sec. Further illumination gives a stable free radical showing an esr spectrum corresponding to nitrogen with free valences. The product is convertible to chlorophyll with reducing agents.

With t-butylhydroperoxide as the substrate, oxygen is produced. The rate of oxygen production is suppressed by DCMU but is enhanced with p-phenylene diamine. Chlorophyllin is not a sensitizer for oxygen production. Chlorophyll is also a photosensitizer for the

destruction of a cobalt chelate and the released ion catalyses the decomposition of hydroperoxide which is accompanied by the evolution of oxygen.

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DISCUSSION

Duysens: In the photosynthetic systems the photochemical active chlorophyllous pigment has a very small fluorescence yield. If not, it would not be able to trap energy. If it were possible to add a substance increasing the rate of transition from the fluorescent state to the lower photoreaction rate it might be possible to imitate better the high quantum yield at high concentration in the chloroplast.

Vernon: Concerning the specificity for chlorophyll a in comparison to chlorophyllin a for photochemical oxygen evolution, might this not be due to the presence of the free carboxyl

groups in chlorophyllin a? This explanation would obviate a need to involve the cyclopentanone ring of the chlorophyll.

Oster: The chlorophyllin was in ethanol where it is essentially unchanged. Remember too that t-butyl hydroperoxide is likewise unchanged.

Massini: What is the quantum yield of the reaction if you extrapolate to 0-concentration of chlorophyll?

Oster: If one extrapolates the rate to infinitely dilute chlorophyll concentration and chooses the rate where the dependence on peroxide concentration is greatest (the curve actually values a saturation value in rate vs. peroxide concentration), then the quantum yield would be better than one tenth.

Avron: Could you give us some idea as to the concentration of DCMU in the DCMU/chlorophyll ratio required for 50% quenching?

Oster: In our fluorescence quenching experiments the concentration of DCMU necessary to quench 50% of the fluorescence is about 10^{-2}M(10^{-5}M chlorophyll). To retard the rate of oxygen evolution to 50% of its normal value required 10^{-3}M DCMU. These results may have no relevance to DCMU action in plants but merely indicate that DCMU (and, indeed, many other amines) can interact with chlorophyll in the excited state.

Goedheer: 1. Are high quantum yields to be expected at high pigment concentrations in random distribution?

2. Does the reaction work with pheophytins?

Oster: 1. The distrubing factor in all <u>in vitro</u> experiments with pure chlorophyll is that self-quenching becomes important (i.e. photochemical reactions are retarded) except for con-concentrations below 10^{-7} moles per liter. Certainly this does not occur in the plant;otherwise photosynthesis would not exist. To attribute this discord to the ordered structure of the chloroplast is only conjecture. One might also argue on specificity of bonding to substrate or to complex formation with only certain groups of the substrate. In any case, I know of no <u>in vitro</u> experiments with chlorophyll which clarify the situation. My work on the photochemistry of synthetic dyes borne to high polymers in solution may be relevant. 2. I have never tried it.

Arnon: You mentioned that you measured the evolved O_2 by Warburg manometry. How much $^{0}2$ (in micromoles) was actually evolved in a representative experiment?

Oster: Because of our low yields and of the fact that we used non-aqueous solvents and that peroxides are present, we were restricted to the manometric technique for measuring rates of oxygen evolution. The rate depends on several factors (peroxide concentration, pigment concentration and intensity of light). Under typical conditions the order of a micromole of oxygen is produced per minute.

IV. HYDROGEN PEROXIDE AS AN INTERMEDIATE IN PHOTOSYNTHESIS (Nan-Loh Young and G. Oster)

Chlorophyll sensitizes the decomposition of hydroperoxides resulting in the production of oxygen and free radicals (G. Oster and R. Lu). The question now arises whether hydrogen peroxide and/or free radicals are produced in the photosynthetic system of plants. For this study we employed healthy chloroplasts. A convenient procedure which we developed is outlined below.

The preparation of chloroplasts was as follows. Fresh spinach was chilled in a 0° mixture of 0.4 M sucrose, 0.01M NaCl, 0.05M tris-HCl at pH 7.5. The mixture was homogenized in a Braun fruit blender. The juice was passed through glasswool and then centrifuged at 200 g. for two minutes to remove plant debris. The supernatant was washed and centrifuged twice at 1000 g for 10 minutes in the same medium and then stored in the freezer at -32°C. The chloroplasts obtained in this manner were demonstrated to be healthy since oxygen was produced on illumination of the preparation with red light. Oxygen production was recorded with the Clark electrode.

In order to determine whether free radicals are produced in photosynthesis, we employed calcium acrylate. This is a divinyl monomer, the calcium ion is complexed to two acrylic acid molecules via the carboxyl groups. When small amounts of radicals are present (concentrations as low as 10^{-12}M) a visible highly light scattering cross-linked polymeric mass is produced from the monomer.

Calcium acrylate as a powder is obtainable from Monomer-Polymer Corp. (Leominster, Mass.) The monomer solid is dissolved into water with stirring in such a way that no solid is accumulated. If the

undissolved powder accumulates, it will congeal to a hard mass such as is the case with plaster of paris. An alternative procedure is to produce the monomer chemically. Glacial acetic acid is neutralized with an aqueous solution of calcium hydroxide. The system is kept cool with an ice bath during the neutralization. With either procedure, the aqueous calcium acrylate solution is filtered through a coarse sintered glass filter and stored at 4°C in the refrigerator.

Illumination of the chloroplasts suppensions in aqueous calcium acrylate (20% by weight) was carried out using a 500 watt projector (2 x 2 inch slide projector). The light was filtered through a 15 cm. path length solution of 0.025M copper sulphate solution to remove heat. In order to remove shorter wavelengths, a Corning glass filter which has a short wave cut off below 570 millimicrons was employed.

The polymerization reaction was carried out at room temperature. The turbidity due to the presence of polymer was apparent after 90 minutes illumination. Most of the time of illumination is taken up with an induction period. The induction period is vastly reduced if the system had been flushed with nitrogen for about 15 minutes prior to the irradiation. No polymer is formed if the chloroplasts are allowed to stand in the dark in the presence of monomer. In the absence of chloroplasts calcium acrylate is not converted to polymer with prolonged illumination regardless of whether or not the system had been flushed with nitrogen.

In a separate experiment the chloroplasts were heated to 70°C for 15 minutes. The treated chloroplasts were found to be inactive as shown by the fact that on illumination they yielded no oxygen as indicated with the Clark electrode. The inactive chloroplast suspension in calcium acrylate was illuminated. No polymer was produced.

From these experiments we conclude that free radicals are associated with the photosynthetic process. In any case, free radicals are linked with the oxygen-producing step in photosynthesis.

To detect the presence of hydrogen peroxide or other hydroperoxides in photosynthesis offered more difficult problems. Three methods of detection of hydrogen peroxide were employed.

The Russell effect is perhaps the most sensitive test of all. This method employs the silver halide photographic plate. Hydrogen peroxide will produce a latent image in the plate (which has not been exposed to light) and becomes apparent on development (using conventional photographic developers). After many extensive trials we came to the conclusion that the method is unreliable. Complications are introduced by the fact that all the commercially available photographic plates which we employed have interfering substances (anti-oxidants and other preservatives introduced by the manufacturers).

We then went on to another technique involving the complexation of hydrogen peroxide with titanium sulfate. Micromolar quantities of hydrogen peroxide produce a yellow coloration with titanium

sulfate in 6N sulphuric acid. Our procedure was to irradiate the aqueous chloroplast suspension, centrifuge and test the supernatant. The effects were marginal due to some interfering reaction which was not the result of some natural yellow pigment. To avoid the interference of carotenes, we extracted the supernatent with petroleum ether to remove the carotenes.

The third test which we employed involved the formation of Prussian blue. Low concentrations of hydrogen peroxide will convert a solution of $FeCl_3$ and $K_3Fe(SCN)_6$ into a dark green precipitate. Three drops of the test solution added to an illuminated chloroplast suspension produces the dark green precipitate. Chloroplasts which have not been illuminated do not give a reaction. Still further, chloroplasts which have been inactivated by heating at 70°C fail to give the reaction. Hence, we conclude that associated with photosynthesis is the formation of hydrogen peroxide or an organic hydroperoxide.

V. DYE-SENSITIZED PHOTODECOMPOSITION OF CHELATES (by Mark Goodman and Gerald Oster)

It is known that manganese (as Mn^{++} ion) is necessary for the production of oxygen in photosynthesis. It would be of interest to know if chlorophyll could serve as the sensitizer for the decomposition of manganous complexes. In this study (which is still continuing) we use as a substrate a manganous chelate. As the chelating agent 1-phenyl 1,3-butanedione (also known as benzoyl acetone) was employed. This combines with $MnCl_2 \cdot H_2O$ to give a practically colorless methanol-soluble chelate. Ethylene diamine tetraacetic acid (EDTA) also complexes with the manganese salt but the chelate is not soluble in methanol and hence is incompatible with chlorophyll.

Methylene blue was initially used as a photosensitizer in our experiments. This dye in methanol absorbs maximally at 625 millimicrons. On irradiation with red light of the dye-chelate manganese ion system the dye fades. The rate of fading in linear chelate concentration but saturates for high chelate concentration. There is destruction of the chelate (loss of the weak maximum at 400 millimicrons).

Oxygen inhibits the reaction as shown by the fact that bubbling through nitrogen accelerates the reaction. The faded

dye is leuco-methylene blue and can be regenerated with oxygen. Styrene also accelerates the reaction. The interest in this reaction is that the organic chelating agent serves as an electron donor even when the agent is tied up with manganese. Our previous experience (G.K. Oster and G. Oster, J. Amer. Chem. Soc., 81, 5543 (1959) has been that although chelating agents serve as donors for light excited dyes, they are not effective when tied up as complexes with metal ions. Our results indicate a peculiarity of manganese ion. It is possible that its unique role in photosynthesis may be involved in this way. Our future studies with chlorophyll may help to clarify the problem.

VI. PHOTOCHEMICAL BEHAVIOR OF TETRAZOLIUM SALTS (Futaki and Gerald Oster)

Tetrazolium salts are colorless water-soluble substances which on reduction become insoluble in water (but soluble in benzene) and are highly colored. The colored species is referred to as the formazan. These salts are widely used in biology to test the viability of cells and in our laboratory we have reported on their use in photochemical reactions involving the photoreduction of dyes.

During the course of study of chloroplasts, we noticed that chloroplasts when illuminated do indeed produce reducing species as shown by the reduction of tetrazolium salts. The reaction is not, however, specific to photosynthesis since it occurs also for heat killed chloroplasts as well. In any case, light is required for the reaction.

In running the controls we found that if white light is used the reduction takes place even in the absence of chloroplasts. We have established that blue light will convert the tetrazolium salt to the formazan if an electron donor for light excited species (in this case the organic buffer) is present.

We have undertaken a detailed study of the photochemistry of tetrazolium salts and have found a number of effects not heretofore described in the literature. The results include the following:

A. For 2,3,5-triphenyltetrazolium chloride (TTC) - Near UV converts TTC into a fluorescent (blue and yellow) species and formazan.

The yellow fluorescent species is favored at pH below 4 and the formazan is favored at high pH. Oxygen retards the rate of formation of the formazan. At neutral pH irradiated samples to which luminol is added gives a chemiluminescence presumably due to the presence of some metastable intermediate (a precursor of the formazan). The formazan as a colloidal suspension in water is very sensitive to photooxidation and fades on illumination.

B. p-Nitrotetrazolium blue (NBT) - Itself is insensitive to light but in the presence of electron donors for the light excited NBT blue light can convert it to the formazan. Oxygen has no effect.

Kinetic studies of these photochemical reactions are now in progress.

VII. ZINC OXIDE AS A PHOTOSENSITIZER

(by Anne Zelechow, Michael Mulligan, and Gerald Oster)

The photochemical and photophysical properties of zinc oxide have been recently described in the following papers by Oster and Yamamoto:

1. Environmental factors in the luminescence and photoconductivity of zinc oxide, J. Applied Phys., 37, 823 (1966).
2. Zinc oxide sensitized photochemical reduction and oxidation, J. Phys. Chem., 70, 3033 (1966).
3. Zinc oxide sensitized photopolymerization, J. Polymer Sci., A, 1683 (1966).

Because of the variety of reactions which light-excited zinc oxide can induce we thought it reasonable to attempt to simulate the photosynthesis reaction i.e., the photosensitized production of oxygen from water and the reduction of carbon dioxide. Zinc oxide absorbs strongly below 388 millimicrons.

Preliminary studies were carried out by irradiating aqueous zinc oxide suspensions with ultraviolet light. Carbon dioxide was bubbled through the system prior and during the illumination. Oxygen evolution was measured with a magnetic susceptibility device manufactured by Beckman Instruments. Later we used the Clark electrode for this purpose. We also tested for formaldehyde using the chromotropic acid test (in acidified supernatant).

Our initial results were very encouraging in that oxygen was detected as was formaldehyde. No reaction occured for the unirradiated system. Still further, no oxygen evolution or formaldehyde formation was noted if the system was flushed with nitrogen rather than carbon dioxide.

Zinc sulphides, both doped and undoped, showed the photochemical effect to a lesser extent. Zinc sulphides doped with cadmium have a phosphorescence with a lifetime of about one half hour. The powder was irradiated strongly and then added to water. There was no post effect, however.

The reaction involving zinc oxide as the sensitizer is only poorly reproducible. The effect of many variables were studied including temperature, pH, wavelength of exciting light, and addition of salts. Evidently complicated surface reactions intervene. In no case could it be claimed that the experiments were under proper control. Although we failed to develop this reaction into a problem which could be described in the literature, we feel the qualitative results are interesting and have implications in space biology. Thus, it is conceivable that in an atmosphere of carbon dioxide and water such as has been speculated for Venus, certain minerals could act as photosensitizers to produce oxygen and formaldehyde. If ammonia were also a constituent of this atmosphere the formaldehyde would react with ammonia to form hexamethylenetetramine. This could be the starting point for the synthesis (with heat and water) of many compounds of interest to biochemists.

PHOTOPOLYMERIZATION OF VINYL MONOMERS*

(Intended for Chemical Reviews)

Gerald Oster and Nan-Loh Young

Department of Chemistry
Polytechnic Institute of Brooklyn
Brooklyn, N. Y.

CONTENTS

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I. INTRODUCTION

By the term photopolymerization we mean in this context the initiation by light of a chain polymerization process. In the more general sense photopolymerization implies the increase of molecular weight caused by light and includes the photo-crosslinking of preexisting macromolecules, a subject which is treated elsewhere (e.g.,262, and Chapters 2, 3, 4 of ref. 167) Vinyl polymerization can be initiated by ionic species as well as by free radicals but almost all examples of photopolymerization are of a free radical character. Indeed, photopolymerization provides a simple demonstration of the free radical nature of photochemical processes as will be illustrated in the many examples treated in the present review. Because of the chain nature of the polymerization process, photopolymerization provides a convenient means of detecting very low concentrations of free radicals produced in a photochemical reaction. Quantum yields, reckoned in terms of monomer converted per quantum absorbed, can reach very high values even as great as one million. Added to this feature is the fact that the physical properties of the polymer are drastically different from that of the monomer. Thus, polymerization of a monomer in a medium which is a solvent for the monomer but a precipitant for the polymer allows for the detection by light scattering of incredibly small amounts of polymer. For example, visual observation at an angle close to the transmitted beam for a dilute colloidal suspension can reveal the presence of a single particle of mass of the order of 10^{-9} grams. Such a particle could have been produced by only a few free radicals. The free radical is chemically incorporated into the polymer chain and, since the polymer is readily separable from the system, the identity of the free radical can be ascertained (see Sec. III below).

Not only is photopolymerization useful for the detection and

identification of photochemically-produced free radicals but has many other features. The fact that photopolymerization reactions can be started or stopped at will by the simple expedient of turning on or off the light provides a means of studying the non-steady state kinetics of polymerization (Sec. II C). Photopolymerization also allows for the subtle control of molecular weight and molecular weight distribution by varying the intensity of light.

Photopolymerization can be confined to local regions since the light can be spatially controlled. Thus, images can be produced in this manner and photography based on photopolymerization has been proposed (243). Relief images can be produced by photopolymerization (85) and indeed the detailed three-dimensional structure of the beam of a single flash from a ruby laser was examined in this manner (64). Spatial photopolymerization has significance in the study of lifetimes of growing chain radicals (Sec. II C).

Photochemical production of primary radicals is essentially independent of temperature, unlike thermal free radical initiators. Consequently, photopolymerization can be carried out at very low temperatures. Hence chain transfer processes leading to branched macromolecules will be absent. Photopolymerization at low temperatures yields the low energy stereospecific polymeric species, namely the syndiotactic configuration of the polymer (127). Certain monomers can only be polymerized at low temperature, i.e., they have low ceiling temperatures, and photopolymerization offers this possibility (95).

Because photopolymerization need not be carried out at elevated temperatures it has applications to biochemistry. One important application of the method is in disc electrophoresis (236). Protein or other biological polyelectrolytes are dissolved in an aqueous solution of acrylamide (and a trace of diallyl monomer) containing riboflavin is exposed to visible light (Sec. IV J). The photopolymerized mass is then subjected to an electric

field and in this manner an electropheretic separation of very high resolution is achieved. Such in situ photopolymerization of biological tissue prior to sectioning for electron microscopy could also be useful. Redox polymerization can also be carried out at room temperature but, unlike photopolymerization, cannot be controlled in a subtle manner. By adjustment of the light intensity one could make gels with continuously graded permeation.

The use of photopolymerization has played an important role in the early development of polymer chemistry. One of the first procedures for polymerizing vinyl monomers was to expose the monomer to sunlight. Thus in 1845 Blyth and Hoffmann (57) obtained by this means a clear glass-like product from styrene. Berthelot and Gaudechon (46) were the first to polymerize ethylene to a solid form and they employed ultraviolet light for this purpose. The first demonstration of the chain reaction nature of vinyl polymerization was that by Ostromislensky in 1912 (263). He showed that the amount of polymer (polyvinyl bromide) produced by light was considerably in excess of that for an ordinary photochemical reaction.

II. KINETICS OF PHOTOPOLYMERIZATION

Photopolymerization of vinyl monomers involve the kinetics of linear chain reactions whose features have been extensively studied especially in the past decade (for reviews, see for example, refs. 16, 24, 68, 126, 170, 50 the lastnamed reference contains a review up to 1961). The subject warrants further examination, especially as regards the fate of the primary radicals and the diffusion-controlled termination of the growing chain radicals. Some of the formal kinetics presented in this review are applicable to initiation of polymerization by ionizing radiation, an area where extensive work has been carried out (for reviews see, for example, 79 and 77).

III. A. Elementary Steps

Addition polymerization may be considered to consist of four distinct steps, namely i)the production of the primary radicals, ii)the initiation of the chain radicals, iii)the propagation of the chain radical, and iv)the removal of the radicals, by combination, for example. There may also be chain transfer with various species (e.g., with solvent) in the system.

Primary radicals can be produced by light in a number of ways which will be examined in Sec. IV. For the moment we consider the simplest case, namely the production of primary radicals by direct photolytic decomposition of a substance called the initiator. The initiator absorbs light to raise the molecule to a higher electronic state. The excited species may give off radiation (luminescence) and/or heat. The excited species may react with another substance to give radicals as is the case, for example, of dye - sensitization (Sec. IV J) or it may itself decompose to give radicals. The rate of formation of photolytically-produced primary free radicals R· from the initiator S is the product of the quantum yield ϕ and the intesity I_a of absorbed light. Assuming the validity of Beer's law, the rate of radical production is

$$v_R = \phi I_a = \phi I_o (1 - e^{-\epsilon \ell [S]}) \qquad (1)$$

where I_o is the incident light intensity, ℓ the path length in the system, $[S]$ is the concentration of the initiator of extinction coefficient ϵ . For low values of the exponent eq. 1 becomes the form we shall use throughout, namely

$$v_R = I_o \phi \ell \epsilon [S] \qquad (2)$$

If there are no competitive processes in the photolytic reaction

the quantum yield ϕ should equal two when one quantum absorbed results in two free radicals. More usually, however, ϕ is less than this ideal due to competitive processes. Photolytic reactions in solution often have low quantum yields due to recombination of radicals in the "cage"(for reviews, see refs. 225 and 224). The two radicals have a high probability of escaping from each other if they possess high kinetic energy. Thus it might be expected that the more the energy of the absorbed quantum exceeds the bond energy of the photolyzable linkage the higher will be the value of ϕ. The viscous drag on the radicals opposes their separation in the cage and hence ϕ should decrease when the microscopic (or local) viscosity is increased. This diffusion-controlled process is particularly important for radical recombination since the activation energy is very low. The principal effect of raising the temperature will be to decrease the viscosity and hence to increase the quantum yield. As polymer is formed in a good solvent for the polymer the viscosity of the system will increase. Studies on the diffusion of small molecules in polymer solutions (215) have shown that the microscopic viscosity is practically that of the pure solvent for concentrations of polymer up to about 10%. Above this concentration the microscopic viscosity rises but never approaches that of the macroscopic value. The activation energy of viscosity of liquids is low (in the neighborhood of 1-5 K cal/mole) and hence the temperature dependence of rates of photopolymerization is determined primarily by the non-photochemical steps in the reaction. For thermal decomposition of initiators, such as peroxides, the activation energy is high (in the range 30-50 K cal/mole) so that, unlike photochemical production of radicals, the rate of thermal production of radicals is highly temperature dependent.

Once the primary radicals escape fromthe cage they can attack a monomer molecule M to form RM$\cdot$, the start of the chain reaction. The

rate of the reaction

$$R\cdot + M \xrightarrow{k_i} RM\cdot \qquad (3)$$

is given by

$$v_i = k_i [R\cdot][M] \qquad (4)$$

The rate constant k_i is a measure of the reactivity of R· for the monomer and its evaluation involves certain complications (Secs. IIB and IIC). This constant can also be estimated from the comonomer reactivity ratio involving two monomer one of which is similar to R· and the other similar to M(67) For example, in the system where α,α'-azobisisobutyronitrile is the initiator and vinyl acetate is the monomer, k_i can be estimated from the comonomer reactivity ratio of methylacrylonitrile and vinyl acetate.

The first chain radical RM· reacts with monomer to produce $RM_2\cdot$ which in turn reacts with monomer to produce $RM_3\cdot$, and so on. A typical step in the propagation is

$$RM_n\cdot + M \xrightarrow{k_p} RM_{n+1}\cdot \qquad (5)$$

It is generally assumed that the propagation rate constant, k_p, is the same for all the propagation steps independent of the size of $RM_n\cdot$ (for a justification of this assumption see ref. 326). The rate of the propagation is

$$v_p = k_p [P\cdot][M] \qquad (6)$$

where [P·] is the sum of the concentrations of the growing chain radicals. The propagation reaction is not diffusion-controlled because the activation energy of the propagation steps is about 7 Kcal/mole.

A special feature of the propagation of chain radicals is that the process consists of continuing repetition of an exothermic reaction (ΔH of from 15-20 Kcal/mole for vinyl monomers). This coupled with

the rather low activation energy of the individual steps should result in the accumulation of energy at the active site of the chain radical. The "hot radical" thus formed should enter very quickly into the reaction. Alternatively, the energetic radical could lose its excess energy by vibrational deactivation but still be capable of reacting again as a "cold radical" on acquiring its normal activation energy after a relatively long lapse of time. By extension of these ideas it has been proposed (324, 325) that the propagation steps do not proceed in uniform manner but proceed in shorter and longer leaps and the observed k_p is the average over all leaps. The value of k_p should be expected to depend on the ratio of monomer to solvent since the "hot radical" loses its excess energy by collisions with surrounding solvent molecules. The actual range of the observed values of k_p (e.g., 1.93×10^3 and 1.69×10^3 liter $mole^{-1}$ sec^{-1} in the case of pure styrene and of half diluted styrene, respectively) is not great so that this dilution effect does not appear, at the present time, to be significant.

The substituent on a vinyl monomer plays an important role in the stereoregularity of the polymerization when carried out at low temperatures. The energy difference for stereospecific polymers (syndiotactic and isotactic is about 1 Kcal/$mole^{-1}$ and hence for polymerizations at low temperatures the lower energy or syndiotactic form is favored. For example, when photopolymerization of vinyl acetate is carried out at low temperature the polymer is predominently of the syndiotactic configuration (127, 59). At elevated temperatures polymerization results in atactic polymer because the propagation proceeds equally through isotactic and syndiotactic paths. Hence at any temperature the observed k_p is a composite of rate constant for propagation of both possibilities. As a consequence, an Arrhenius plot of k_p over a wide temperature range will not give a straight line. Still

further deviations from the Arrhenius expression arise from dipolymerization. Associated with the chain propagation is a depolymerization process and the two rates become equal at the ceiling temperature (for review, see ref. 95).

When the temperature is lowered to just above the freezing point of the monomer an extremely rapid photopolymerization is observed(293). The effect, referred to as "rapid low temperature polymerization" has been ascribed to domains of monomer in some ordered configuration suitable for almost instantaneous polymerization possibly via a concerted electronic interaction of the constellation of monomers in the domains (4, 161). It might be expected that solvent dilution would interfere with the interaction of the monomers. Such is not the case, however, at least in the photopolymerization of methyl methacrylate near its freezing point when the monomer is diluted with ethyl acetate (218).

The propagation of the chains continue until one or another termination takes place. One type of termination occurs when the growing chain radical reacts with another. The rate of this reaction is

$$v_t = k_t [P\cdot]^2 \qquad (7)$$

This termination could be by combination and/or by disproportionation. Termination by disproportionation has a much higher activation energy. Like most radical-radical reactions the combination of chain radicals has a low activation energy and hence is diffusion-controlled. In the elementary Smoluchowski theory of diffusion-controlled reactions (for review, see 76) the rate constant is given by encounter frequency of the two reacting species, i.e., by the product of the mean diffusion constant and the radius of cross-section of the diffusing species. For spherical particles of hydrodynamic radius

equal to the encounter radius, the rate constant is proportional to the absolute temperature divided by the viscosity of the medium but independent of the size of the particles. A polymeric radical has a very low diffusion constant (10^{-7} cm^2/sec or smaller) and the effective encounter radius of the active site is also very small. As a consequence, the termination rate constant would be expected to be much lower than that calculated by simpler diffusional encounters of the macromolecules (11). Still further, the radical site may well be imbedded in the coiled macromolecule and hence become available for reaction only after the polymer molecule has undergone a number of conformational changes. A further requirement for reaction is that both chain radicals must simultaneously present their radical sites at the same place. All these factors make k_t very small despite the fact that the activation energy is practically zero.

In low viscosity liquids ordinary radical-radical reaction rates are of the order of 10^{11} liter $mole^{-1}$ sec^{-1}, whereas for chain radical terminations k_t is of the order of 10^7 liter $mole^{-1}$ sec^{-1} or lower. Obviously the enormous discrepancy in values for small and for large radicals arises from segmental diffusion as being the rate-determining step for chain radical combination (220, 156). This termination rate constant is generally considered to be independent of molecular weight. This should be approximately the case for molecules of degree of polymerization greater than about six. For high molecular weight species the macromolecules will become entangled, a phenomenon which takes place above a critical concentration that is lower the higher is the molecular weight (215). Hence the polymer molecules can spend an indefinitely long period in this entangled condition of contact. The radical ends of two locked polymer molecules will gradually achieve contact <u>via</u> segmental diffusion.

Segmental diffusion should be related to the energy of rotation about adjacent bonds in the backbone of the polymeric chain. For cyclic monomers the conformation of the polymeric chain is restricted. Thus in the copolymerization of methyl methacrylate and maleic anhydride (221) the rate of termination decreases with increasing anhydride composition, i.e., with the increasing stiffness of the chain. Steric factors may also intervene to reduce termination as would be expected for large side groups. Thus it was found that the values of k_t/k_p in the photopolymerization of methyl, n-butyl, isobutyl and 3, 5, 5-trimethyl hexyl methacrylates decrease with increasing bulkiness of the side group (155).

Segmental diffusion decreases with decreasing temperature. An Arrhenius plot of k_t shows marked deviation from linearity below a certain critical temperature (156). This is attributed to an abrupt cessation of segmental diffusion analogous to the glass transition for solid high polymers. Such studies were carried out by photopolymerization at low temperatures of vinyl bromide, methyl methacrylate and vinyl carbozole representing increasing stiffness of the chain molecules. The latter two monomers showed a deviation in the Arrhenius plot for k_t below $-10^{\circ}C$. The propagation is normal through this transition range in that k_p obeys the Arrhenius expression.

Attempts have been made to construct a theory of segmental diffusion to account for the observed low value of k_t (11, 44, 45, 219) but a missing factor is the effective viscosity. Fluorescence methods might be useful in this regard (251, 252). For example, a study of the quenching of fluorescence by two polymer species one of which bears a fluorescence end group and the other a quenching end group could give direct information about segmental diffusion. Increasing the viscosity of the solvent will decrease k_t. This was demonstrated in the dye-sensitization photopoly-

merization of acrylamide where glycerol was added to the aqueous system (256). Another example is that for the polymerization of methyl acrylate in various esters as solvents having increasing viscosity but being of the same solvent power (222).

Polymers in poor solvents will tend to coil up and the segmental motion will be restricted. Polymerization in poor solvents should show low values of k_t. Homogeneous solution polymerization of styrene in thermodynamically-poor solvents such as 2-butanone shows a lower value of k_t than that for a good solvent such as benzene (133). With extremely poor solvents for the polymer, i.e., precipitating media, the chain radical is removed from the system by occlusion without being terminated (for review, see ref. 16 Chpt. 4). It is conceivable, however, that the primary radicals because of their small size could diffuse into the precipitation particles to terminate the growing chain (200).

Termination of chain radicals could also occur by an encounter between the chain radical and a primary radical in situations other than that given above. This type of termination has a rate given by

$$v_{t'} = k_{t'} [R\cdot][P\cdot] \qquad (8)$$

The rate of encounter of a small molecule with a large molecule is determined primarily by the diffusion constant of the small molecule. This together with the fact that a small molecule can readily diffuse into a macromolecule (215) leads one to expect that $k_{t'}$ should be much greater than k_t. Obviously the segmental diffusion constant of the macromolecule is not of major importance for encounters between a small radical and the radical site of a chain radical. Experiment has shown that for styrene polymerization $k_{t'}$ is nearly two orders of magnitude greater than k_t (22). In emulsion polymerization chain termination takes place exclusively by primary radicals.

Primary radicals themselves may combine even after they have wandered out of the "cage". This is referred to as secondary germinate termination (224,225). Such a reaction could be important in photopolymerization when the v_R is extremely high as with a flash of light) or when the monomer concentration is very low. The rate of this reaction is given by

$$v_{t'''} = k_{t'''}[R\cdot]^2 \tag{9}$$

A chain radical can also be terminated by a so-called inhibitor. The inhibitators could be the photosensitizer for the reaction as is the case with $FeCl_3$, for example. In general for any inhibitor, B , the rate of termination is given by

$$v_{t''} = k_{t''}[P\cdot][B] \tag{10}$$

Chain transfer which results in termination of a chain radical with initiation of a new chain is a common occurance in systems containing molecules with labile groups. Carbon tetrachloride can serve as a photosensitizer as well as being a chain transfer agent. For such substances the rate of chain transfer is given by

$$v_{tr} = k_{tr}[P\cdot][S] \tag{11}$$

The chain transfer reaction has an appreciable activation energy. A detailed review of chain transfer processes is available (145).

B. Steady State

Ten elementary reaction steps in vinyl polymerization have been considered above. Obviously the complete analytical solution of so many time-dependent simultaneously differential equations represents a formidable problem. A simplification is to invoke the steady state hypothesis for

polymerization wherein the net rate of change of concentration of radicals is very much less than both their rate of production and their rates of destruction, i.e.,

$$\frac{d[R\cdot]}{dt} << v_R \quad v_i + v_{t'} + v_{t''} \tag{12}$$

and

$$\frac{d[P\cdot]}{dt} << v_i \quad v_t + v_{t'} + v_{t''} \tag{13}$$

Material balance requires that the rate of production of a species is equal to the sum of the rates of increase and of disappearance of that species. Neglecting inhibition and chain transfer, we obtain for R·

$$v_R = \frac{d[R\cdot]}{dt} + [R] \left\{ k_i[M] + k_{t''}[R\cdot] + k_{t'}[P\cdot] \right\} \tag{14}$$

and for P·

$$v_i = \frac{d[P\cdot]}{dt} + [P\cdot] \left\{ k_t [P\cdot] + k_{t'} [R\cdot] \right\} \quad . \tag{15}$$

In the simplest and most usual case the monomer concentration is more than a million times greater than the radical concentrations in which case, even with due allowance for the rate constants, the first term in the curved brackets in eq. 14 is the dominant term. Applying the steady state condition for the primary radicals, eq. 12, one obtains, using eq. 2,

$$I_o \phi \ell \epsilon [S] = k_i [R\cdot][M] \tag{16}$$

where now [R·] refers to the steady state concentration of primary radicals. If termination of the chain radicals occurs by reaction with other chain radicals (eq. 7) rather than with primary radicals (eq. 8) then the first term in the curved brackets of eq. 15 is the dominant one. Hence in the steady state condition (eq. 13), the steady state concentration of Chain

Radicals becomes

$$[P\cdot] = \left\{ \frac{I_o \phi \ell \epsilon [S]}{k_t} \right\}^{1/2} \tag{17}$$

These results which represent the simplest scheme are not necessarily a realistic description of many actual polymerization reactions.

The rate of consumption of monomer is

$$-\frac{d[\ ]}{dt} = v_p + v_i \approx k_p [M] [P\cdot] \tag{18}$$

where we have assumed that most of the monomer is consumed in the polymerization steps, i.e., we are dealing with high polymers. Combining this with the steady state concentration of chain radicals, eq. 17, then

$$-\frac{d[M]}{dt} = k_p \left\{ \frac{I_o \phi \ell \epsilon [S]}{k_t} \right\}^{\frac{1}{2}} [M] \tag{19}$$

The concentration of sensitizer is a function of time of irradiation and is destroyed according to a first order reaction. If $[S]$ is the initial concentration of sensitizer then eq. 19 becomes

$$-\frac{d[M]}{dt} = k_p [M] \left\{ \frac{I_o \phi \ell \epsilon [S]}{k_t} \right\}^{\frac{1}{2}} \exp\left(-\tfrac{1}{2} I_o \phi \ell \epsilon t\right) \tag{20}$$

or, on intergration,

$$[M] = [M]_o \exp\left\{ -\frac{2k_p}{\sqrt{k_t \phi \epsilon \ell}} \sqrt{\frac{[S]_o}{2_o}} \left[1 - \exp\left(-\tfrac{1}{2} I_o \phi \ell \epsilon t\right)\right] \right\} \tag{21}$$

where $[M]_o$ is the initial concentration of monomer. The limiting value ($t = \infty$) of the fraction of monomer converted to polymer is, from eq. 21,

$$\frac{[M]_o - [M]_\infty}{[M]_o} = 1 - \exp\left\{ -\frac{2k_p}{\sqrt{k_t \phi \epsilon \ell}} \sqrt{\frac{[S]_o}{I_o}} \right\} \tag{22}$$

Thus in this so-called "dead end polymerization" (58, 319) there is a limiting value of conversion of monomer due to depletion of the sensitizer. Dead end polymerization allows one to determine $k_p/\sqrt{k_t \phi}$ so that if two of the constants are known the third can be evaluated. Thus if k_p/ k_t is known from easily obtainable rate data the quantum yield of primary radical production can be determined. It should be realized, however, that these three quantitites could vary during the course of the polymerization due to increase of viscosity of the system as discussed earlier. Hence it is desirable to arrange conditions (low sensitizer concentration and high light intensity) so that the dead end occurs at not too high monomer conversions.

The kinetic chain length, i.e., the ratio of the rate of propagation to the rate of initiation is proportional to molecular weight of the polymer if chain transfer is absent. Combining eqns. 6, 7 and 17, we obtain for the steady state value of the average kinetic chain length $\bar{\nu}$

$$\bar{\nu} = \frac{k_p}{\sqrt{k_t}} \frac{[M]}{(I_o \phi \varepsilon \ell [S])^{\frac{1}{2}}} \tag{23}$$

The kinetic chain length varies with time since [M] and [S] are functions of time. Introducing eq. 21 into eq. 23 and remembering that [S] decreases as a first order reaction then

$$\bar{\nu} = \frac{k_p}{k_t} \frac{[M]_o}{(I_o \phi \varepsilon \ell [S]_o)^{\frac{1}{2}}} \exp(-\tfrac{1}{2} I_o \varepsilon \phi \ell t)$$

$$\exp\left\{-\frac{2k_p}{\sqrt{kt\, \phi \varepsilon \ell}} \sqrt{\frac{[S]_o}{I_o}} [1 - \exp(-\tfrac{1}{2} I_o \phi \ell \varepsilon t]\right\} \tag{24}$$

At any moment during a polymerization there is a distribution of molecular weights and this distribution changes with time. By programming

the monomer concentration or the initiator concentration during the course of the polymerization a distribution of molecular weights is obtained which is fixed throughout the course of the reaction (47,152). In photopolymerization one can simply vary the intensity I_o by some means external to the system and hence avoid the complications associated with continuous addition and mixing of reagents. One could maintain the same average kinetic chain length by varying I_o with time so that $\bar{\nu}$ of eq. 24 remains constant. This is achieved if I_o satisfies the condition

$$t = \frac{2\sqrt{I_o} - \frac{1}{k_p}\sqrt{\frac{k_t}{S_o}}}{\phi \varepsilon \ell I_o^{3/2}} \tag{25}$$

In photopolymerization the overall rate increases with temperature but, unlike with thermal initiation, the molecular also increases with temperature. This is seen from eq. 23 since

$$\frac{d \ln \bar{\nu}}{dt} \sim \frac{E_p - \frac{1}{2} E_t}{R T^2} \tag{26}$$

where E_p and E_t are the activation energies of propagation and termination respectively and hence the term on the left is positive. There is a counter effect, however, if chain transfer agent is present this becomes increasingly important as the temperature is raised. If the photopolymerization is carried out adiabatically the temperature of the system will arise continuously during the course of the reaction due to the heat of the reaction with a consequent increase in molecular weight. By progressively increasing the intensity of the light one should be able to control the molecular weight distribution.

If the sensitizer is also a chain transfer agent, as can sometimes be the case, increasing the temperature enhances chain transfer and hence

works oppositely to the molecular weight rise discussed above. The reciprocal of the average kinetic chain length then becomes

$$\frac{1}{\bar{\nu}} = \frac{\sqrt{k_t}\,(I_o\,\phi\,\varepsilon\,\ell\,[S])^{\frac{1}{2}}}{k_p\,[M]} + \frac{k_{tr}}{k_p}\,\frac{[S]}{[M]} \qquad (27)$$

The chain transfer can in some cases be quite large; for example, with disulphides the chain transfer constant, k_{tr}/k_p, has a value of as high as 50 . In such cases the second term in eq. 27 would be dominant and the molecular weight of the polymer would be drastically reduced with increasing ratio of sensitizer to monomer concentrations. The chain transfer constant also depends on the nature of the monomer; for example, with carbon tetrachloride it is a few thousand times greater for vinyl acetate than for methyl methacrylate. The activation energy for chain transfer is usually greater than for propagation. Sometimes a possible sensitizer does not yield a high molecular weight polymer in a photochemical reaction because it is a strong chain transfer agent. Chain transfer is minimized by carrying out the photopolymerization at low temperatures and where $[S]/[M]$ is small. Likewise, a possible photochemical free radical reaction could be overlooked by an improper choice of monomer.

The simplest scheme described above does not include an important possibility, namely termination by primary radicals whose rate is given by eq. 8 . Primary radical termination would be favored if the concentration of monomer is low or if the primary radicals react only slowly with the nomer; both factors make the value of v_i lower. Likewise, if there is a high rate of production of primary radicals (e.g., high light intensity and/or high sensitizer concentration) the primary radicals could terminate the chain. It has been shown by tracer techniques that the fraction of

primary radicals entering into chain termination could be as high as 0.231 for benzoyl perioxide initiation of styrene at 60°C(8). Similarly with azo-bisebutyrenitrile as the initiator it was shown in the kinetics of the polymerization of styrene, that some termination by primary radicals takes place (22).

In place of the simplest scheme we will now include termination by primary radicals. Neglecting the reaction of a primary radical with another primary radical, eq. 14 together with eq. 15 becomes for the steady state

$$[P\cdot]^3 + \frac{k_i}{k_t'}[M][P\cdot]^2 + \frac{v_R}{k_t}[P\cdot] - \frac{v_R}{k_t}\frac{k_i}{k_t'}[M] = 0 \qquad (28)$$

In the case where initiation of the chains is much greater than termination by primary radicals, $[P\cdot] << k_i[M]/k_t'$, the steady state concentration of chain radicals becomes (233).

$$[P\cdot] = \sqrt{\frac{v_R}{k_t}} \quad \frac{\frac{k_i}{k_t'}[M]}{\frac{k_i}{k_t'}[M] + \sqrt{\frac{v_R}{k_t}}} \qquad (29)$$

or, in terms of the rate of polymerization, v_p, using eqs. 6 and 2

$$\frac{v_p}{[M]\sqrt{[S]_o}} = \frac{k_p}{\sqrt{k_t}}\left(\frac{v_R}{S_o}\right)^{\frac{1}{2}}\left[1 - \frac{k_t'}{k_i k_p}\frac{v_p}{[M]^2}\right] \qquad (30)$$

Hence a plot of $v_p/[M][S]_o$ versus $v_p/[M]^2$ gives a straight line from which $k_t'/k_i k_p$ can be obtained. Eq. 28 can also be written in the form (25, 204).

$$\frac{v_p}{[M]^2}\left\{\frac{1 + \frac{v_p^2 \delta^2}{[M]^2 v_R}}{1 - \frac{v_p^2 \delta^2}{[M]^2 v_R}}\right\} = k_i\frac{\sqrt{k_t}}{k_t'} = \qquad (31)$$

where $\alpha = k_t^{\frac{1}{2}} k_p^{-1}$. The fraction f , of primary radicals which participate in the termination step is then given by

$$f = \frac{1}{1 + \frac{\Lambda [M]^2}{\alpha v_p}} \tag{32}$$

Thus for high intensity, i.e., high v_R, f approaches 0.5 . Primary radical combination, eq. 9, is indicated if f is greater than 0.5. The parameter Λ determines the extent of the perturbation on the simple scheme due to primary radical termination.

Thus if there is no primary radical termination $k_t' = 0$ whereupon $\Lambda = \infty$ so $f = 0$. The value of Λ for methyl methacrylate and of styrene initiated by azobisbutyrlnitrile at 60°C is 0.5 for [M] = 0.0844 moles liter^{-1} (25, 204). Extensions of these arguments have been made to include the combination of primary radicals, eq. 9 (10).

Primary radical termination gives molecular weights which are lower than those expected from the simplest scheme. Molecular weight data together with rate data furnishes information regarding the extent of primary radical termination (144, 146). A more general scheme includes both chain transfer as well as primary radical termination (190, 229).

One possible method of determining the relative values of k_t and k_t' is to carry out the polymerization at various temperatures. Since k_t depends on segmental diffusion more than does k_t' , f should decrease with increasing temperature and this temperature dependence gives some value for the segmental conformational energy barrier. The effect of viscosity may be more complex, however, since both types of termination are diffusion-controlled. Experimentally it was found (112) that addition of polystyrene to a polymerizing system of styrene changed the exponent of the

dependence of the rate on the sensitizer concentration from 0.5 to 0.3 . This suggests that increased viscosity enhanced the primary radical termination by lowering the segmental diffusion in the chain radicals.

If one makes the crude assumption that the rate constants for every mode of radical-radical termination is the same, i.e., $k_t = k_t' = k_t''$ then from eqs. 14 and 15 using the steady state argument (158) one obtains

$$\frac{1}{v_p} = \frac{k_t}{k_p\, k_i [M]^2} + \frac{\sqrt{k_t}}{k_p [M]\quad v_R} \tag{33}$$

Hence from the rate of polymerization as a function of v_R, eq. 2 , one obtains $k_i/\sqrt{k_t}$ as well as $k_p/\sqrt{k_t}$. To obtain the individual rate constants, however, one must carry out a study of the polymerization in the non-steady state (Sec. IIC).

The steady state assumption is valid only for restricted conditions. Since the chain radicals are generated by the primary radicals then it is necessary that $v_R \geq d[P\cdot]/dt$. Differentiating $[P\cdot]$ of eq. 17 with respect to time and, remembering that S decays with time according to a first order reaction, the following condition must be satisfied

$$2 \left\{ \frac{k_t [S]_o}{\phi \varepsilon \ell I_o} \right\}^{\frac{1}{2}} \exp\left(-\tfrac{1}{2}\, \varepsilon\, \phi\, \ell\, I_o t\right) \geq I \tag{34}$$

From this equation it is seen that the initial concentration of the sensitizer must exceed a certain minimum value namely

$$[S]_{o(\min)} = \frac{\phi \varepsilon \ell I_o}{4\, kt} \tag{35}$$

Still further for the steady state to apply, the rate of chain radical production must be considerably greater than the rate of initiation of the chains, eq. 13, whence

$$\left\{ \frac{[S]_o}{[S]_{o(min.)}} \right\}^{\frac{1}{2}} \exp\left(-\tfrac{1}{2}\, \varepsilon\, \phi\, \ell\, I_o t \right) >> 1 \qquad (36)$$

Therefore the steady state is achieved only if the time of measurement is short enough to satisfy the equation

$$t << \left\{ \frac{\ln\ [S]_o / [S]_{o(min)}}{\phi\, \varepsilon\, \ell\, I_o} \right\} \qquad (37)$$

Since I_o^{-1} is the dominant factor, we see that lowering the intensity increases the time over which the steady state assumption is valid. A more formal mathematical presentation (130) leads to essentially the same result derived above.

C. Non-Steady State

Elementary treatments of non-steady state polymerization (16, 24, 50, 68, 126, 170) assume that the primary radicals are in the steady state even at the commencement of the polymerization. This assumption was implied in the derivation of eqs. 34-37 above. There are conditions in photopolymerization where omission of the non-steady state for primary radicals could be serious. First, however, we will neglect this condition, in which case we can take $v_R = v_i$

If termination is between chain radicals then from eg. 15

$$\frac{d\ p}{dt} = v_R - k_t\ [p.]^2 \qquad (38)$$

This differential equation is readily solvable to give P. in terms of v_p, eg. 6, namely

$$\frac{v_p}{(v_p)_s} = \tanh\ t/\tau \qquad (39)$$

where the subscript s denotes the steady state value and τ is the lifetime is the average value of the time for creation and anihilation of the growing

chain radicals. Hence τ is the ratio of the concentration of radicals to the rates of termination of the radicals. From eqs. 6 and 7, the lifetime is

$$\tau = \frac{k_p}{k_t} \frac{[M]}{v_p} \tag{40}$$

In the early stages of polymerization, namely for t/τ small, eq. 39, the pre-effect, can be expressed as a power series in t/τ, the leading term being linear in this ratio. If at a moment t during the steady state polymerization the light is turned off, then the concentration of chain radicals $[P\cdot]$, and hence v_p, decays hyperbolically with time according to eq. 38 ($v_R = 0$), so for the post-effect

$$\frac{(v_p)_s}{v_p} - 1 = \frac{t-t}{\tau} \tag{41}$$

Hence from either the pre-effect or the post-effect the lifetime, τ, can be determined. Combining eq. 40 and the steady state expression, eq. 33 one can obtain values for k_t k, and k_i individually. For lifetimes of the order of milliseconds the rotating sector technique has proven very useful (69). In this repetitive light interruption technique one avoids the generally more difficult procedure of measuring changes in rate of polymerization in short intervals of time. The method is not valid, however, if the chain termination is exclusively of first order. With mixed order termination the sector technique is valid (71).

Now consider the case where the primary radicals are likewise in the non-steady state. The results are quite complex but solvable (67) if termination via the primary radicals are considered negligible. Then v_i, eq. 4, is time-dependent and $[R\cdot]$ is the solution of the differential equation, eq. 14, where we neglect reactions of eqs. 8 and 9, or

$$\frac{d[R\cdot]}{dt} = v_R - k_i[R\cdot][M] \tag{42}$$

whence, using eq. 2,

$$[R\cdot] = \frac{\phi \epsilon \ell I_o[S]_o}{k_i[M]} \left\{1 - \exp(- k_i[M]\, t)\right\} \tag{43}$$

Hence eq. 38 is replaced by the equation

$$\frac{d[P\cdot]}{dt} = \frac{\phi \epsilon \ell I_o[S]_o}{k_i[M]} \left\{1 - k_t[P\cdot]^2 - \exp(- k_i[M]t)\right\} \tag{44}$$

This is a soluble differential equation of the Riccatti type whose solution is

$$[P\cdot] = \left\{\frac{\epsilon \ell I_o[S]_o}{k_t}\right\}^{\frac{1}{2}} U(t)\, F(q, U) \tag{45}$$

where the function F(q, U) involves Bessel functions of the q and -q order and their derivatives and q and U are defined respectively as

$$q = 4 \left\{\frac{k_t \epsilon \ell I_o[S]_o}{k_i[M]}\right\}^{\frac{1}{2}} \quad \text{and} \quad U(t) = \exp\left(-\frac{k_i}{2}[M]t\right) \tag{46}$$

The significance of q is that q/2 is the ratio of the verage lifetime of the primary radicals in the steady state to τ, the average lifetime of the chain radicals in the steady state. Hence q indicates the extent to which the system deviates from the convential non-steady state case. In ref. 67 is a plot of $v_p/(v_p)_s$ as a function of t/τ. As q becomes larger more time is required to reach the steady state condition for the chain radicals. Considerable errors are obtained for neglect of the non-steady state for primary radicals especially if $k_i[M]$ is small and/or $I_o[S]_o$ is large.

Closely related to the rotating sector method is the spatial intermittancy method. If two widely separated beams of light fall on the system

the rate of polymerization would be determined by the effects of the sum of the two beams. When the beams are brought closer together, however, radicals diffusing out of one beam may terminate with the radicals diffusing out of the other beam, hence resulting in less overall rate of reaction. Thus if the rate of the reaction is studied as a function of beam separation, using a striped pattern, for example, some information can be obtained regarding radical lifetimes. This is complicated, however, in that the diffusion rate of the radicals is involved. For the case of gases, on the other hand, where collisional frequencies can be calculated, this offers no serious problem. Even for the relatively simple case of the photochemical decomposition of iodine molecules in the solution the calculated diffusion constant of the radicals, the termination rate being known, is somewhat higher than expected (181,288). Spatial photopolymerization has been carried out for methyl methacrylate using variable amounts of sensitizer to achieve various molecular weight polymer (106). The lifetime of the chain radicals in these systems were known from independent measurements and hence the diffusion coefficients for the chain radicals could be calculated. From Brownian theory the mean square displacement of a molecule during a certain time is equal to twice the product of the diffusion constant and the time. If every encounter between chain radicals leads to a termination then one calculates the diffusion constant for the radicals for the time equal to τ. Such an argument is not applicable, however, for termination of polymer radicals as discussed earlier and large deviations will occur due to the importance of segmental diffusion. In high viscosity medium it has been our experience that spatial photopolymerization yields very sharp polymer images. This is apparently due to two compensating factors; increase of viscosity increases the lifetime but also suppresses diffusion. If the polymerizing system contains some divinyl compound, the resultant crosslinked chains

will not, of course, wander beyond the illuminated regions.

Photopolymerization is readily adaptable to flow methods. If a solution of monomer containing sensitizer is allowed to flow in a tube and at one point intense light is applied, the polymerization will proceed beyond the irradiated region just as in spatial polymerization for which eq. 41 applies. During the time of flow the chain radicals will grow. If now the growth is arrested by allowing the stream to flow into a solution containing a high concentration of inhibitor the amount of polymer obtained will depend on the time interval between the moments of ligh initiation and termination by inhibitor. Thus the shorter the pathlength with a given rate of flow the smaller is the amount of polymer produced. Obviously, if the flow rate is slow the amount of polymer produced is independent of the time for the monomer solution to pass between the light-struck region and the chain quenching solution. Hence a plot of amount of polymer produced as a function of time between initiation and quenching will at first increase linearly with time, then slope off and finally reach a plateau. The time to reach the leveling-off value gives the lifetime, τ, of the growing chain radical (134,176). In the early stages of photopolymerization the distribution of chain radicals will change and eventually, after time τ, reach a constant distribution (333).

The flow method can be used to synthesize block copolymers whose composition can be controlled (149, 150). The polymerization of one vinyl monomer is photoinitiated at one point in the flowing system and allowed to flow into a second monomer solution. The growing chain radicals then initiate polymerization of the second monomer to give a block copolymer. It is necessary, of course, that the time of flow be within the period of the lifetime of the light-produced chain radicals. If the flow is extremely rapid the copolymer will have a low concentration of the first monomer relative to the

second. With slow rates of flow, on the other hand, homopolymer of the first monomer will be obtained as well as some copolymer. Thus by controlled rates of flow one can vary the composition of the copolymer.

In emulsion polymerization each propagating chain grows in its own separate soap micelle until it is terminated by a primary radical. The rate constant for propagation, k_p, is determined from the rate of polymerization and from the number of micelles and the monomer concentration in the micelle (for review, see ref. 60). Emulsion polymerization can be photochemically initiated wherein the rate of production of primary radicals can be controlled. By using repetitive bursts of light to periodically generate primary radicals one can produce polymer with a very sharp distribution of sizes (56). The method yields a narrow Poisson distribution of molecular weights. The interval between light bursts determines the time of growth of the chain radicals. Thus in the ideal case the termination of one set of chain radicals and the initiation of a new set occurs in the same burst of light. It has been demonstrated that highly monodispersed polystyrene can be produced in this manner (56). Considerable deviation from such ideal kinetics might take place, however, since the chain radicals growing in the micelles could survive the next burst of primary radicals giving rise to multiples of the idealized molecular weight. Still further, a slow polymerization in the phase external to the micelle could take place with burst of high concentrations of primary radicals to yield some low molecular weight polymer (280,292). Recent techniques wherein the size of the soup micelles is kept constant during the course of polymerization (339) might be helpful in the photopolymerization of emulsions to obtain sharp molecular weight distributions.

IV. SURVEY OF EXPERIMENTAL METHODS

Photopolymerization is particularly well adaptable to automatic techniques. Thus the actinic light can be interrupted at will and its intensity

can be varied in a programmed manner. Furthermore the polymerization itself can be followed continously and recorded electrically. This means, that the data can be analyzed immediately via on-line computors. The intention of the present section is to point out the existence of certain types of equipment which have recently become commerically available and to outline some newer approaches for following polymerization continuously and automatically.

A number of very high intensity continuously operating light sources are now available. Such lamps include the mercury and mercury-xenon high pressure point arc sources (140, 237). The xenon lamp provides a practically continous spectral output from about 300 millimicrons through the visible region. Superposed on this emission are the well known mercury spectral lines. In addition to the manufacturers data there is a useful survey of the characteristics of a variety of commercially available light sources (165 and Chpt. 7 of ref. 72).

Interruption of light can be achieved with a rotating sector but it does not give a square pulse (69). Square pulses can be achieved from a continously operating lamp by introducing an electro-optical shutter of the Kerr-cell type or of the Poeckels crystal type. One manner of producing periodically interrupted light is to use one of the newer high intensity roboscopic systems (121)

If required, the light can be rendered monochromatic with an interference filter, for example, and these are now available for the ultraviolet region as well as the visible region. A much higher degree of spectral purity is obtainable with lasers. Lasers have an additional important feature in that the light beam has practically no divergence and hence is particularly useful for spatial photopolymerization. In addition to the red light ruby flash and the continuously operated helium neon lasers, there are now

available commercially lasers such as the Argon laser which produce light in the near ultraviolet as well as in the visible range. The intensity of the light can be determined with a calibrated thermopile or by chemical actinometry. For light of wavelength below about 500 millimicrons the Parker-Hatchard ferrioxalate system (pp. 783-786 of ref. 72) is particularly useful and for longer wavelengths a dye-photoreduction system can be used (258). In some cases the quantum yield of photochemical reaction is known for a substance which is also a sensitizer for photopolyization, hence such a substance serves as a convenient actinometer even polychromatic light is used and when the geometry of the system is ill-defined.

A number of methods are available to follow the course of polymerization. Either the disappearance of monomer or the appearance of polymer is followed. The disappearance of monomer is monitored by observing a loss in some property of the monomer. Thus infrared absorption of the vinyl group at about 6.2 microns decreases as polymerization proceeds. The infrared spectrometer is set at this wavelength and the increased transmittance is observed with time. It may be desirable to circulate the fluid into the infrared cell from the vessel containing the polymerizing system (151). Vinyl monomers also show characteristic ultraviolet absorption spectra which differ from the polymeric species. Thus vinyl pyrrolidone has an absorption peak at about 250 millimicrons which decreases on polymerization of the monomer (249).

Many vinyl monomers exhibit characteristic polarographic activity (347). Methyl methacrylate, for example, is readily reduced at the electrode to methyl isobutyrate (172). Since different monomers show different activities (different reactions at different applied voltages), the polarographic method has the useful feature

of being able to allow the simultaneous determination of the concentrations of more than one monomer in a copolymerizing system (54, 55). In this method the usual procedure is to separate the polymer from the reaction system prior to the polarographic analysis. Some monomers do not exhibit polarographic activity at a convenient magnitude of applied voltage. In such cases the monomer can be chemically converted into a derivative of manageable polarographic characteristics (55). Since the diffusion rates of polymer and of monomer differ so widely, it might be possible to carry out the polarographic analysis in situ.

One general technique for following polymerization of vinyl monomers involves the density change which takes place when a monomer is converted to a polymer. The conversion of monomer to polymer is accompanied by a contraction of the solution since the monomer has a larger molal volume than the corresponding monomeric unit in the polymer chain. This arises from loss on polymerization of the bulky pi electron cloud perpendicular to the vinyl double bond. The contraction in going from pure monomer to pure polymer can be more than 30 per cent. The change in volume is greater for ethylene than for styrene, i.e., greater the smaller the residue on the vinyl group. The contraction during polymerization is often followed in a dilatometer which consists of a vessel to which is attached a capillary tube open at one end. The visual observation (with a cathetometer) of the height of the fluid in the capillary tube can be replaced by automatic procedures. Thus the height could be measured continuously by recording the electrical conductivity of a conducting fluid in contact with the solution in the capillary (88). Alternatively, one could follow continuously the changes in electrical capacitance as the surface of the fluid in the capillary tube moves between charged plates.

Very small fractional changes in volume of the liquid in a dilatometer are accompanied by large changes in level of the solution in the capillary tube. In a typical dilatometer (total volume about 50 ml.) a contraction of 0.1 per cent corresponding to a conversion of pure monomer of about 1 per cent produces a change in capillary height which is readily observable by the naked eye. The dilatometric method is limited, however, to isothermal conditions. A rise in temperature of only $0.01^{\circ}C$ will cause an expansion of the liquid sufficient to offset a 1 per cent conversion of monomer. Since vinyl polymerization is always accompanied by an evolution of heat (see below), it is usually not feasible to use a dilatometer for reactions which take place over a period of less than about 10 minutes. To be used for shorter times, a dilatrometer designed for good heat transfer (large surface to volume ratio) would be required (37).

Minute changes in density (as small as one part in 10^7) can be measured in a density gradient column. Normally one would have to withdraw a drop of the reactive solution from time to time to measure its density in the gradient. It is possible, however, to carry out a photopolymerization directly in the density gradient column (259). A droplet of an aqueous solution of acrylamide containing riboflavin which is a sensitizer for blue light was suspended in a non-aqueous density gradient. On illumination the droplet settles downward. Polymerization phenomena such as induction, non-steady state processes, steady state rate, and post effects are readily observable by observing the descent of the drop in the column. Heat exchange of the reaction mixture with the gradient fluid is rapid because of the small size of the droplet. The distance from the top of the gradient is linear in density, if the column is properly prepared (259), and hence the distance, in turn, is directly proportional to the extent of polymerization.

The change in density in a polymerizing system is also manifiested by a change in velocity of sound propagation. This is followed by monitoring the time of propagation of sound through the reaction system. The velocity of an ultrasonic pulse is much faster in polymer than in the monomer and, for large enough molecules, is in some cases, independent of molecular weight(342, 302).

The polarizability of a vinyl monomer is greater than the monomer unit in the corresponding polymer. The index of refraction decreases, however, when a monomer is converted to a polymer because the volume contraction more than compensates for the change in polarizability. Thus the refractive index increase is greatest for those monomers which show the greatest density change. The refractive index increases on going from the pure monomer to the polymer is in the neighborhood of 3 per cent. Refractive index changes can be measured to one part in 10^7 (29) but here again the method requires good thermostatic conditions. Automatic methods such as photoelectric fringe counting could be employed.

The conversion of monomer is accompanied by a considerable evolution of heat. The heat evolved per mole is approximately 15-20 Kcal $mole^{-1}$: more specifically 16.4, 13.0, and 21.3 Kcal $mole^{-1}$ for styrene, methyl methacrylate, and vinyl acetate, respectively. Thus a conversion of 1 per cent of pure monomer in a volume, say, of 10 ml. would, under adiabatic conditions, see a rise in temperature of $1^{\circ}C$. Thus observing the heat rise provides a means of following a polymerization reaction as long as the reaction is sufficiently rapid so that adiabatic conditions are preserved and the thermal rise is not too great as to appreciable influence the reaction. The method is particularly suitable for small conversions and the temperature rise can easily be followed continuously and automatically with the use of thermocouples (40, 41)or,better still, with thermistors (210).

The method is also useful for studying non-steady state conditions in photopolymerization (38).

Instead of following the disappearance of monomer one can follow the appearance of polymer. Two methods which are immediately suggestive are viscometry and light scattering. Both these methods are complicated by the fact the magnitude of the effects depend on polymer concentration, molecular weight, size, shape distribution, and extent of interaction with the solvent in an involved way. The problem is simplified somewhat if the polymerization is carried out to low conversion since for low conversions the size and size distribution is more or less unchanged in the course of the reaction. Furthermore, if the conversion is small one is effectively dealing with dilute polymer solutions and hence the interparticle effects are minimal.

The scattering of light can, of course be followed photoelectrically. The turbidity of a dilute polymer solution is determined by the weight average molecular weight. For chain polymerization the turbidity should increase with time and for sufficiently low rates becomes linear with time (238). The light scattering method has been used to study the non-steady state as well as the steady state in photopolymerization (33 , 34 , 35).

The viscosity method has been used effectively for post-effects (19, P 32 of ref. 16) using a flow viscometer. This type of viscometer is limited to low rates of polymerization and is not amenable to continous or automatic recording. Perhaps a torque method involving a continuously rotating cylinder and incorporating the newer solid state strain gauges could be developed for use in following polymerization reactions. For high conversions (greater than about 10 per cent) one can measure changes in the local or microscopic viscosity by means of the electrical conductivity of

the system (13 , 65 , 334). Electrical conductivity of non-aqueous solutions presumably arises from the fortuitous presence of ions and decreases with increasing local viscosity. Local viscosity can also be determined by fluorescence methods. Certain dyes, notably auramine O , is not appreciably fluorescent in low viscosity media but fluoresces strongly in high viscosity media (250, 251). The fluorescence intensity is determined by the ratio of the local viscosity to the absolute temperature, i.e., proportional to a diffusional relaxation time. The method is useful for following the extent of polymerization for high conversions as long as the excitation of fluorescence does not interfere with the photopolymerization. In addition to auramine O a few other dyes whose absorption extend into the red region of the visible spectrum can be chosen (252). A closely related phenomenon is the depolarization of fluorescence. As polymerization proceeds at high conversion the polarization of emission from a dissolved fluorescent dye increases with increasing local viscosity (169, for review see ref. 251).

A third approach to following the course of polymerization is to determine the concentration of radicals in the system at every moment. Such information would aid considerably in understanding the nature of the reaction as explained in Sec. II. Electron spin resonance measurement is immediately suggestive but in photopolymerization the concentration of free radicals is usually below that of the ultimate sensitivity of the ordinary e s r apparatus, namely 10^{-5} molar. For cases where radical concentrations are large, i.e., where the chain radicals are very long lived as occurs in glasses (173) or in extremely viscous media (166), one can follow by e s r the changes in concentration of the chain radicals. In low temperature photopolymerization radical concentrations as high as 10^{-4} molar can be built up and e s r measurements have been made

to follow the reaction (173). Both the lifetime and the steady state concentration of radicals were obtained and hence k_t was evaluated.

The e s r method when it can apply has the feature that the resonance spectrum helps in the identification of the radical species. Using a flow method it was possible to identify both the primary and the chain radicals and their individual concentration changes with time (125). A more positive identification of the initiating species requires an end group analysis of the isolated polymer. One method involves the use of tagged initiating substances (for review, see ref. 49). Another technique, namely activation analysis (induction of radioactivity by thermal neutrons), although expensive, is extremely sensitive. It is particularly well adapted for the detection of metallic atoms (184) such as might occur in electron-transfer photopolymerization (Sec. IV I). Useful end-group techniques have been recently developed which involve the interaction of dye molecules with polymer end groups. Such methods have been developed to detect hydroxyl, amino, and halogen end groups (267) each of which could appear in certain photopolymerization reactions

V. PHOTOCHEMICAL INITIATING SYSTEMS

Free radicals capable of initiating polymerization of vinyl monomers can be produced photochemically from a wide variety of substances. Not all free radicals initiate polymerization. Such stable radicals as diphenyl picryl hydrazyl and triphenylmethyl although not chain initiating are, however, efficient chain terminators. Commercially-available vinyl monomers often contain hydroquinone which in its semiquinone form act as inhibitors. Iodine atoms produced photochemically from molecular iodine are not particularly good initiators of polymerization. In order for a radical to initiate the polymerization of a vinyl monomer, it must satisfy certain

energetic criteria. The chain radical formed must be sufficiently stable relative to the primary radical and hence the problem involves the bond energies and resonance stabilization of the species in question (228).

The examples of photoinitiator polymerization considered in the present review are confined exclusively to condensed phase systems. Superficially one might consider gaseous polymerizing systems as being simpler to interpret especially since a large body of information regarding the mechanism of gas state photochemistry has been accummulated (e.g., ref 307). In photopolymerization, however, the reaction very quickly develops into a case of heterogeneous catalysis with all its theoretical and practical complications. In certain industrial problems, however, such as those involving the formation of polymeric thin coatings, gas state photopolymerization might be advantageous. Vapors of metal atoms, notably mercury and cadmium, are efficient sensitizers when illuminated with lamps containing these atoms under resonance emission conditions. The sensitization reactions are complicated, however, as seen by the fact that in the presence of organic compounds metallic hydrides and metallo-organic compounds appear as products. With vinyl monomers polymerization also occurs (for review, see ref 108)

A. Direct Photolysis of Monomers

In some cases photolytic decomposition of the monomer itself can lead to free radicals. This requires, of course, that the absorption spectrum of the monomer lies within the spectral range of the exciting radiation. The isolated vinyl bond has an absorption maximum in the vacuum ultraviolet region and only in the case where the monomer residue is conjugated with the vinyl group or where it contains groups such as carbonyl or bromine will it absorb appreciably above 300 millimicrons. When the monomer acts as

the sensitizer, i.e., [S] = [M], then for the simple scheme the rate should be proportional to the three-halves power of the monomer as seen from eq. 19. Many examples of photopolymerization of supposedly pure monomers using light sources such as sunlight or mercury lamps with Pyrex glass envelopes must be due to the presence of fortuitous traces of a sensitizer. Oxygen can react with vinyl monomers to produce carbonyl compounds or, as is certainly the case with styrene, to produce peroxides. A standard procedure for the elimination of trace amounts of impurities is to partially polymerize the monomer and then vacuum distill the remaining monomer into the reaction vessel.

It is well known that some monomers, notably styrene are polymerized simply by heating. The mechanism of the initiation is obscure. Prolonged irradiation with light sources with no provision for the removal of infrared radiation can lead to polymerization of vinyl monomers by mechanisms of a non-photochemical nature. High intensity bursts of light can produce local heating effects. It is not known at the present time what fraction of the effects of a ruby laser red flash are of thermal origin. Quantum doubling which takes place with high intensity coherent radiation could be responsible for the apparent ultraviolet radiation effects associated with the laser flash. Pure styrene and some of its derivatives have been polymerized at low temperatures by repetitive ruby laser flashes (269) but polymerization due to local heating effects cannot be discounted. Quantum doubling increases as the square of the intensity and this might provide a criterion for the phenomenon.

Although an understanding of photochemical radical formation of vinyl monomers in general has not been classified, it is clear, however, how photopolymerization can take place with monomers which have residues

which are known to be photochemically active. As an example one may cite the case of vinyl ketone which displays the photochemical behavior typical of carbonyl compounds (see Sec. IV 2). Another example is vinyl bromide which behaves photochemically like other bromine compounds (see Sec. IV 6).

Whether or not the triplet excited state, when it exists, plays a role in photochemical reactions is an outstanding problem in photochemistry. It has been suggested that the initiation process in the photopolymerization of pure styrene (217) and of pure methyl methacrylate (168) involves the triplet excited state.

B. Organic Carbonyls

The photochemistry of organic carbonyl compounds has been extensively studied and several reviews on the subject have appeared (for example, refs. 226, 272 , 296, 306 and Chapter 5 of ref. 72). The aliphatic aldehydes and lactones have a weak absorption in the ultraviolet region beginning at about 330 millimicrons and a maximum at about 270 millimicrons. The energy absorbed by the carbonyl group can be transferred to the neighboring carbon-carbon bond and causes cleavage to produce radicals which can initiate polymerization of vinyl monomers. For acetone, for example, methyl and methyl carbonyl radicals are produced and the latter decomposes thermally to produce another methyl radical and carbon monoxide. The radicals also react with acetone, to give a variety of other stable products and radicals (226). Acetone has been used as a photoinitiator in the gas phase polymerization of vinyl chloride, styrene, butadiene, and acrylonitride at room temperature (177) and for ethylene and acetylene at elevated temperatures (317). Cyclohexanone was used both as a solvent and photoinitiator in the polymerization of vinyl chloride (330). The quantum

efficiency for this system is low possibly due to ring closure of the cyclohexanone-monomer diradical but more likely due to the excessive concentration of sensitizer employed (note eq. 23).

Because of their absorption spectra, aliphatic carbonyl compounds are somewhat limited in their use as photoinitiators. These compounds must be dissolved in solvents which transient radiation in the 300 millimicron region and the vessels must be of quartz or vycor. The most serious objection, however, is that the absorption spectrum overlaps with the absorption spectrum of most vinyl monomers and poses difficult photometric problems. As a consequence, aliphatic compounds containing two or more vicinal carcarbonyl groups have been used as sensitizers. Biacetyl, for example, absorbs in the near ultraviolet region and the blue regions (up to 467 millimicrons) of the spectrum. This compound has been used as a sensitizer for the kinetic study of photopolymerization of methyl methacrylate using the blue line of mercury (436 millimicrons) as the source (132). Polymer obtained with biacetyl are initially deeply yellow but became colorless after prolonged irradiation (187).

When a carbonyl group is conjugated to an aromatic ring the absorption peak associated with the carbonyl group is shifted to longer wavelengths (e.g., maximum at 340 millimicrons in the case of benzophenone). Benzophenone and benzanthrone are effective photoinitiators even when the system employs ordinary glass vessels (275). Benzoin has been extensively used as a photoinitiator in polymerizations using as the light source the high pressure mercury lamp which is particularly rich in radiation at 365 millimicrons (see, for example, ref. 80). This sensitizer was also used in the photopolymerization of methyl methacrylate at the temperature range from -35° to 0°C for the study of the relation between

temperature and stereospecifity in free radical polymerization (159). The carbonyl group in benzoin in the active group since its oxime is not a sensitizer. Aromatic carbonyls with an hydroxyl group ortho to the carbonyl are like-wise photochemically inactive, presumably due to internal hydrogen bonding.

Benzoin as a sensitizer for the polymerization of methyl methacrylate shows an unexpected behavior. Using carbon-14 tagged benzoin methyl ether, it was found that fourteen benzoin molecules are incorporated into each polymer molecule (211). Nevertheless, the rate of polymerization is proportional to the square root of the concentration of benzoin and the overall quantum yield is 1250 monomers per absorbed quantum which is somewhat surprising in view of the analytical result.

It has been shown that alpha-halogen derivatives of carbonyl compounds are more effective photoinitiators than are their parent compounds (187). Chloroacetone, bromol, and acrolein dibromide are good sensitizers when using near ultraviolet radiation. The relative conversion rate of methyl methacrylate using 17% of the sensitizers, azobutyrolenitrile, benzoin methyl ether, and bromoacetophenone, and bromoisobutyrophenone were found under the conditions employed to be 1.00, 1.43, 2.22, 2.33, respectively (318). Extensive studies of photopolymerization have been carried out with ω-bromoacetophenone (266,312). This sensitizer has a molar extraction coefficient of 46 at 365 millimicrons and the studies gave values for the monomer transfer constant, k_t/k_p^2 and overall activation energy for the reaction for vinyl acetate (266). The polymer obtained and the polyvinyl alcohol produced on saponification has an absorption maximum at 245 millimicrons suggesting the presence of an acetophenone residue on the polymer molecule. Bromine atoms (1.33 per

1,000 monomer units) are also present in the polymer and block copolymers were produced by irradiating a solution of the polymer which also contained another vinyl monomer.

Benzophenone is an effective sensitizer with radiation of 254 millimicrons for the photo-grafting of vinyl monomers to polyethylene (254). The sensitizer is converted to benzhydrol by hydrogen abstration from polyethylene and the polymer then serves as a radical site for the initiation of vinyl monomers. Benzoin, on the other hand, is a poor sensitizer for grafting and yields only the homopolymer of the polymerized vinyl monomer. It is of significance that in the absence of monomer benzophenone is a sensitizer for the cross-linking of polyethylene whereas benzoin is not.

C. Peroxides

The chemistry of peroxide compounds has been reviewed in a number of monographs and reviews (see, for example, refs. 105, 119, 141, 142, 178, 186, 201, and 320). Peroxide contains two adjacent oxygen atoms with overlapping lone-pair orbitals. The average bond energy of the linkage is about 34 Kcal. mole^{-1}. On excitation with the mercury arc spectral lines of 313 and 254 millimicrons an excess energy as much as 56 and 78 Kcal. mole^{-1}, respectively, is carried away by the primary radicals. One drawback in the use of peroxides as photsensitizers is that they show appreciable absorption only below 320 millimicrons. When photopolymerization is carried out with peroxide sensitizers the problem is complicated by the thermal initiation effect associated with peroxides. The interpretation of the mechanism of initiation is rendered more difficult by induced decomposition which would invalidate eq. 2 . Hydroperoxides and diaryl peroxides are particularly susceptible to induced decomposition. To account for induced decomposition at high concentrations of peroxide

a term involving an order greater than unity in concentration of sensitizer must be added to eq. 2 .

Photolysis of t-butyl hydroperoxide in carbon tetrachloride using 313 millimicron radiation yields via induced decomposition t-butyl alcohol and oxygen as the main decomposition products (192). Diakyl peroxides are less susceptible to induced decomposition. Benzoyl peroxide on thermal decomposition yields via the benzoyloxyl radical carbon dioxide and a phenyl radical. Radical scavengers such as diphenyl picrylhydrazl suppress completely the formation of carbon dioxide. In the photolysis of benzoyl peroxide in styrene, the scavenger, 30% of the decomposed peroxide appears as carbon dioxide and phenyl radicals as the primary photochemical products. This result suggests benzoyloxyl radicals were generated in an unstable electronically excited state or that an electronically excited benzoyl peroxide molecule might dissociate into aryl radicals directly. Whether or not the polymerization is initiated by benzoyloxyl or by phenyl radicals can be decided by tracer studies (26, 51).

For sufficiently short wavelength radiation the peroxide can be decomposed at the carbon-oxygen linkage. Thus for di-tertiarybutyl peroxide at wavelengths shorter than 300 millimicrons the primary products of photodecomposition are oxygen and that tertiary butyl radical (128). Cleavage at the oxygen-oxygen bond yields tertiary butoxyl radicals which would further decompose into a ketone and an allyl radical (9 , for review on alkoxy radicals, see ref. 135). Complications in the photodecomposition of alkyl peroxides, as well as of aryl peroxides, is minimized if the reaction is carried out at low temperatures.

Hydrogen peroxide has been employed as a sensitizer in the photopolymerization. This compound begins to absorb light at 400 milli-

microns and shows a structureless spectrum rising steadily but does not exhibit a maximum even down into the vacuum ultraviolet region. The quantum yield for photolysis of hydrogen peroxide at 25°C is 0.3 and 0.5 for radiation of wavelength 313 and 254 millimicrons, respectively (31 , 94) and increases with shorter wavelengths. Acrylonitrile which, by the way, absorbs only below 230 millimicrons, is photoinitiated by hydrogen peroxide when ultraviolet radiation above 290 millimicrons is used (93). Hydrogen peroxide was used as the sensitizer for the determination of kinetic rate constants of acrylamide (103) and methacrylamide (101) with employment of the rotating sector. For radiation of 313 millimicrons the quantum yield for initiation was found to be 0.87 at 25°C. The rate of polymerization over a wide variety of conditions was found to be proportional to the square root of the absorbed intensity and the first power of the monomer concentration in accord with eq. 19 . In these studies, chain transfer to the monomer and to the sensitizer was minimized by using low concentrations of hydrogen peroxide and high intensities of light.

Hydrogen peroxide was used as the photoinitiator at liquid nitrogen temperatures for the polymerization of propargyl alcohol ($CH \equiv CCH_2OH$) (314), vinyl acetate, and methyl methacrylate (173). At such low temperatures the steady state radical concentration produced in the solid mixtures is sufficiently high to be followed by electron spin resonance. In the case of propargyl alcohol e s r spectra showed that the chain radical produced is $-CH = C - \dot{C}HOH$ which was produced hy hydroxylradical abstraction of the methylenic hydrogen atom from the monomer. Kinetic data indicates that the hydroxyl radicals migrate readily and react with the monomer.

In what is probably the first use of photopolymerization for the

manufacture of fibres hydrogen peroxide was the sensitizer for the polymerization of acrylonitrile in concentrated zinc chloride, a solvent for the polymer (341). The system showed good homogeneity in both rate of polymerization and molecular weight of the polymer along the light path. The polymer was spun into fibers as it was being produced.

The dialkyl peroxide, di-t-butyl peroxide has been used as a photoinitiator for studies of the kinetics of polymerization of acrylonitrile in dimethylformamide. The studies were carried out in a vacuum viscometer which takes advantage of the fact that the initiator is volatile (234). Thus di-t-butyl peroxide can be distilled off from the system when desired. This sensitizer can be decomposed by radiation of wavelength below about 350 millimicrons but is thermally more stable than is, for example, benzoyl peroxide.

Cyclic peroxides, for example, ergosterol peroxide, have been used as photoinitiators for the Polymerization of styrene (32). The relationship between the number average molecular weight and the rate of polymerization is normal indicating that initiating occurs via a monoradical produced from the cyclic peroxide.

Benzoyl peroxide, the most widely used thermal initiator is not a particularly good sensitizer in photopolymerization. It absorbs only weakly above 300 millimicrons and its first maximum is at 275 millimicrons (with $\log \epsilon = 3.42$). Nevertheless it will decompose when exposed to a high intensity of radiation of 365 millimicrons. This sensitizer causes complications in the kinetic studies of the polymerization of styrene (198). The rate is not proportional to the sensitizer concentration at low peroxide concentrations; the rate being higher than the expected value. Furthermore, the rate shows a rather sudden decrease with time at out 2% conversion. These results are attributed to induced decomposition of the

peroxide and complexation to styrene. Benzoyl peroxide was used as the photoiniator for the room temperature polymerization of styrene at high pressures (up to 3, 000 atmospheres). The pressure had no effect on the rate of initiation but the propagation constant increased exponentially with pressure (214).

The bond energy of the oxygen-oxygen linkage in peroxides is less than that of the energy of visible light quanta. Radiation longer than 300 millimicrons although not appreciably absorbed by the peroxide can be utilized by a sensitizer whose excitation energy is transfered to the peroxide. Examples of sensitizers for the near ultraviolet region are anthracene and napthalene which on excitation with 365 millimicrons will cause the decomposition of acetyl peroxide in isooctane (183). Fluorenone is a sensitizer in the blue region for the colorless compound, fluorenonehydioperoxide (328). The sensitizer forms a complex via hydrogen bonding with the hydroperoxide. This system is a good photoinitiator for the polymerization and for blue is one hundred times more effective than is fluorenone alone.

Chlorophyll is also a sensitizer for the decomposition of peroxides (257). Chlorophyll in organic solvents has absorption maxima at about 430 and 660 millimicrons. Solutions of chlorophyll and organic peroxides show an initial exposure to red light a depression in the long wavelength maximum and an increase in the short wavelength maximum which reverts to the original spectrum if the exposure is of less than about ten seconds duration. Oxygen inhibits both the light production of this unstable intermediate as well as its rate of its recovery in the dark. Chlorophyll a sensitizes the decomposition of t-butyl hydroperoxide as well as benzoyl peroxide. In the former case molecular oxygen is produced. The

peroxide - chlorophyll system can be used in the photopolymerization of styrene with red light. It is of interest that chlorophyllin, that is chlorophyll with the cyclopentanone ring broken, is ineffectual as a sensitizer for the decomposition of the peroxide and hence the system is not a sensitizer for photopolymerization. The mechanism of sensitization of peroxide decomposition is not known but conceivably it might involve energy transfer.

D. Organic Sulfur Compounds

Aliphatic disulphides absorb maximally in the neighborhood of 254 millmicrons with molar extinction coefficients from about 200 to 600 (282). Loss of the maximum at high pH is associated with alkali cleavage via the hydrogen alpha to the S-S linkage. The disulphide bond is a is also cleared by ultraviolet light to yield free radicals. Some aryl disulphides absorbed in the near ultraviolet region and hence are particularly useful as sensitizers for polymerization. Examples of sensitizers for the photopolymerization of vinyl monomers include diphenyl , dibenzoyl and dibenzothiazol disulfides (265). Unlike their corresponding peroxides these compounds do not initiate thermal polymerization at least up to 120°C (265, 322, 323). Tetraalkyl thiuram disulfide is a sensitizer for vinyl acetate and styrene but, surprisingly, not for acrylonitrile and vinyl chloride. Conceivably this could be due to chain transfer to the sensitizer or to its photoproduct, a mercaptan, to give very low molecular polymer. This sensitizer is also a poor thermal initiator.

Several derivatives of S-acryldithiocarbamate have been studied as photoinitiators for methyl methacrylate (231). The order of effectiveness was found to be $CH_3O > CH_3 > Cl$ where the group refers to the

parasubstituted carbamate derivative. The chain transfer constant at room temperature for benzodithio carbamate is 5.5 so that its concentration should be very low in order to obtain resonably high molecular weight polymer.

Tetramethyl thiuram monosulfide is an excellent sensitizer for photopolymerization (124). This sensitizer, is particularly attractive in that it has an absorption maximum at 400 millimicrons and its absorption extends considerably into the visible region. Desyl aryl sulfides where the aryl group is phenyl, o-tolyl, p-tolyl, p-anisyl, and β-napthol have been used for the photopolymerization of tetraethylene glycol dimethacrylate (271). The initial rates of polymerization are proportional to the one-half power of the sensitizer concentration. The initiating process is believed to involve the ultraviolet photolysis of the sensitizer to give this aryl radical and desyl radical, the relative case of breaking the C-S bond being related to the resonance stabilization of the aryl thio radical.

Sulfur compounds have also found use in photografting and in the photochemical production of block copolymers. Polystyrene prepared by tetraethyl thiuram disulphide used as a thermal initiator has as an end group the diethyldithio carbamate group (264). The polymer is now light sensitive and serves as the photosensitizer for the polymerization of methyl methacrylate to yield the block copolymer. One can start with ordinary polystyrene and reflux it with tetraethyl thiouram disulfide to yield a polymer containing diethyldithiocarbamate groups. The new polymer when irradiated in the presence of methyl methacrylate yield a graft copolymer. Sodium diethyldithio carbamate will react with polyvinyl chloride to yield a polymer containing as much as 30 mole per cent of diethyl dithio carbamate groups (230). This polymer is crosslinked by ultraviolet light and, in the presence of methyl methacrylate, can be photografted. The photoactive dithio carbamate

can be introduced into polyethylenimine by heating the polymer with alkali and carbon disulfide and treating the resulting water soluble polymer with either benzyl chloride, ethyl chloroacetate or butyl bromide (232). The water insoluble modified polyethylenimine containing the photoactive NCSR dithiocarbamate group is readily crosslinked by ultraviolet light
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and, in the presence of styrene or methyl methacrylate, is photografted.

Sulfur compounds have long been employed for the vulcanization of rubber. Vulcanization can also be carried out photochemically when dibenzodithiazoyl disulfide and hydrogen sulfide are present (114). The vulcanizing effect was assumed to involve benzothiazoyl disulfide radicals.

The photochemical cleavage of the disulfide bond may be important in biology. Certainly this provides a way in which disulfide linkage between polypeptide chains in proteins may be systematically cleaved. Ultraviolet light can effect the interconversion of cystine and cysteine (291). Thioctic acid, a five membered ring with a disulfide linkage will polymerize on exposure to ultraviolet light (27). Glutathione, a mercaptan containing tripeptide, will in the oxidized form sensitize the polymerization of water-soluble monomers using ultraviolet light (248). This result may be relevant to the action of ultraviolet on proteins such as is the case for ovalbumin which shows accelerated heat denaturation when it had previously received a short dose of ultraviolet light. Perhaps the conformational changes as associated with denaturation are expedited by preliminary cleavage of the disulphide bonds responsible for the tertiary structure. Proteins such as ovalbumin and serum albumin will sensitize the polymerization of acrylonitrile and of acrylamide when irradiation with ultraviolet light of wavelength greater than 280 millimicrons. Horse myoglobin does not contain disulfide linkages and does not sensitize the polymerization. The

sensitizing action of serum albumin has been attributed to energy transfer from the excited phenyl group of the phenylalanine residue of the protein to an adjacent peptide bond with resultant cleavage of the bond and production of radicals (279). This suggestion does not appear to be tenable since the dipeptide, phenylalanylglycine, is not a sensitizer for photopolymerization (248). When ovalbumine is heat denatured prior to irradiation in the presence of monomer, the induction period of polymerization is considerably less than that when using the native protein (248). Presumably, the photochemically-produced sulfur radicals are more readily accessible in the case of the denatured protein than for the native form.

E. Azo Compounds

The azo group has two lone pair electrons in an approximate s p^3 hybrid which leads for the Q → N transition to a near ultraviolet band for the isolated bond with a maximum at 350 millimicrons. Whereas aryl azo compounds are stable in light, alkyl azo compounds are readily dissociated by light, to give free radicals. Photodecomposition of the simplest alkyl azo compounds, e. g., azomethane and azoethane have been extensively studied (14,75, 113, 147, 281, 307, 337). The photolysis probably involves either a synchronous cleavage of both C-N bonds in the excited state or the formation of the short lived intermediate $RN_2\cdot$ radical (see ref. 72, p. 462). Despite the interest of azomethane as a source of free radicals, this compound has not been used as a photosensitizer for photopolymerization.

It would be of interest to employ the perfluoro derivation of azomethane, namely hexafluoro-azomethane as a photoinitiator. This compound can be photolyzed to give $F_3C\cdot$ radicals (92, 273, 274) which should, in the presence of excess vinyl monomer, initiate polymerization. If the monomer were tetrafluoroethane, the resulting fluorocarbon polymer

would be free of foreign end groups. The next compound in the alkyl homologous series, namely 2, 2' -azobispropane has been employed as a photoinitiator in the kinetic rate studies of the polymerization of styrene (206, 207). If nitrile is one of the alpha substituents on an alkyl azo compound, the material is a highly efficient photoinitiator presumably due to the formation of the resonance stabilized cyanoalkyl radicals.

Among the nitronitriles, the most commonly used photoinitiator is a' -a - azobisisobutyronitrile. Its photodecomposition can be followed spectroscopically with the disappearance of the absorption at 345 millimicrons. This compound has been used in the non-stationary state studies of the photopolymerization of vinylacetate (194, 205, 208), styrene (195, 208), vinyl chloride (70), and methyl methacrylate (208). There are some side reactions associated with photoinitiation using azobisisobutyro nitrile. In the presence of oxygen the cyanoisopropyl radicals can react with oxygen in a very complicated manner (316, 331, 345). A peroxy radical could be formed which in turn combines with a cyanoisopropyl radical or can abstract hydrogen from the medium to give unstable peroxide or hydroperoxide, respectively. Solutions of azobisisobutyrlnitrile standing for long periods of time in the presence of oxygen exhibit complications because of the formation of tetramethyl-succino dinitrile and acetone cyanohydrin. both of which are photosensitive (53). The photodecomposition of azobisisobutyrlnitrile is further complicated by the formation of dimethyl-N-(2-cyano-2-propyl)-ketenimine (52, 137, 139, 305, 315). This latter compound absorbs maximally at 291 millimicrons (ϵ_{max} = 150) and is an efficient thermal initiator and presumably a photoinitiator as well. Hence if the temperature is moderately high and the light source contains radiation in the 300 millimicron region, the ketene-imine serves as an initiator and its concentration would pass through a maximum as a function of time so that the photoinitiation is partly

a consecutive process.

Also of interest as an initiator is α-azobis-1-cyclohexane carbonitrile. This compound has a broad absorption band with a maximum at 260 millimicrons (ϵ_{max} = 16) and follows Beer's law up to a concentration of 0.01 moles/liter (40, 205). As a photoinitiator α-azobis-1-cyclohexane carbonitrile seems to be more efficient than azobisisobutyronitrile, judging from the quantum yield for monomer conversion (182). The advantage of this former initiator is that it does not have a dark rate due to thermal decomposition at 25°C (182). It has been used as a photoinitiator for the kinetic studies of vinyl acetate (209, 36) and in the flow system for the synthesis by photopolymerization of block copolymers (148, 150).

Azonitriles as photosensitizers have the obvious advantage over peroxides in that they absorb radiation of longer wavelengths. Still further, they exhibit low chain transfer (174) and low induced decomposition (48) as well as having a rate of photodecomposition insensitive to the nature of the solvent (except, of course, when complexation occurs)(7, 86, 179).

There are azo photoinitiators which are water-soluble. Esters, guanyl, and amidine groups, for example, can be introduced into azo compounds to render them soluble in water (56, 115, 137, 138, 182, 344). Thus, azobisisobutyrolnitrile treated with sulfuric gives the azoisobutyramide a water-soluble photoinitiator (56).

Diazonium salts are readily decomposed by light (for review see ref. 346, Chapt. 7).but do not necessarily produce free radicals. On the other hand, the thermal reaction between diazonium salts and the phenol produced by the light reaction is a free radical reaction as evidenced by the fact that polymerization of a water-soluble monomer ensues (253).

Azoxy compounds should also serve as photoinitiators. It is known that the azoxy group is converted by light to the hydroazo group (91).

The azoxy compound, m, m'-azoxystyrene has been shown to be an effective photoinitiator for the polymerization of acrylonitrile using light of wavelength 435 millimicrons (61).

F. Halogen-Containing Compounds

Halogenated organic compounds are generally light sensitive (188). Their photochemical addition reactions to olefinic compounds have been extensively studied and are known to involve free radicals. The photochemically produced halogen radicals will initiate polymerization efficiently if one to one addition to the double bond of the vinyl monomer is suppressed.

Halogen molecules themselves show considerable absorption somewhere in the near ultraviolet and visible regions. The absorption maxima of F_2, Cl_2, Br_2 and I_2 are at 284, 420, and 520 millimicrons, respectively, with increasing absorption coefficient as the atomic number increases. Most of the radiant energy absorbed by halogen molecules result in the production of halogen atoms.

Chlorine has been used as a photoinitiator for the polymerization of acrylonitrile in concentrated zinc chloride and dimethylformamide, which are solvents for the polymer, to achieve high molecular weight polymer. The resultant transparent concentrated polymer solution is suitable for spinning fibers by the wet method (277). Iodine sensitizes the production by visible light of a peroxide in methyl methacrylate when oxygen is present, the resultant peroxide then serves as an initiator of polymerization (131). Bromine atoms can be introduced into the polymer chain end via chain transfer or by using a halogenated compound as a photoinitiator . Subsequent photolysis of the polymer in the presence of a second monomer results in a block copolymer (62, 116, 117, 203).

Brominated polystyrene is light sensitive and can be used as the backbone chain for photografting (175). Photosensitive polymers of this type can also be made by polymerizing a monomer in the presence of a small amount of a halogen-containing monomer such as α-chloroacrylonitrile (202).

Halogen-containing monomers can be photopolymerized directly with radiation of relatively long wavelengths even in the absence of sensitizers. Unlike ethylene, vinyl fluoride (213) and vinyl chloride (162) can be photopolymerized by 254 millimicrons radiation. In halogen-substituted vinyl monomers interaction between the lone-pair orbitals of the halogen and the ethylene π-orbital results in a red shift of the $\pi \rightarrow \pi^*$ absorption.

Alkanes containing multiple halogen atoms such as is the case for chloroform or carbon tetrachloride have been used as photoinitiators for styrene and for vinyl acetate (23, 129). Such compounds show greater light absorption than the corresponding alkanes containing a single halogen atom and there is a red shift with increasing halogenation. Thus bromotrichloro methane can be decomposed by radiation of wavelength 365 millimicrons (196). Bromoform is a photoinitiator of polymerization for radiation of wavelength 330 millimicrons but for dibromomethane radiation shorter than 310 millimicrons is required (203). Halogenated alkanes differ over a wide range in their ability under ultraviolet light to form addition products with vinyl monomers in preference to initiating polymerization. Thus a 50 to 1 mixture of carbon tetrachloride and styrene yields on irradiation essentially all polymer. On the other hand, even a much lower concentration of bromotrichloro methane gives halogenated styrene as the principle photo-product (160). Chain transfer for polymer radicals to halogenated alkanes can often be very great;

only telomer or low molecular weight polymer is produced (43, 278).

Hypohalides absorb generally in the near ultraviolet regions to produce alkoxy radicals (5), but their use as photoinitiators for polymerization have not been explored. Other halogenated photoinitiators namely α-halogenated carbonyls, silver chloride, and metal halogen salts are treated elsewhere in this Review.

G. Metal Carbonyls

Metal carbonyls are generally light sensitive and undergo photochemically-induced substitution by n- and π-electron donors (for review, see ref. 308). Manganese carbonyl, $Mn_2(CO)_{10}$, and rhenium carbonyl, $Re_2(CO)$ are effective photosensitizers for the polymerization of methyl methacrylate (17, 18). A small amount of carbon tetrachloride is required for this reaction. The reaction was carried out with 436 millimicrons for manganese carbonyl and with 365 millimicrons for rhenium carbonyl. The radical $CCl_3^{\bullet}$ was confirmed by tracer studies to be the initiating species. If in place of carbon tetrachloride the polymer polyvinyltrichloroacetate is used a gel is obtained indicating that the initiating species is a polymer radical. The rate of polymerization increases with increasing carbon tetrachloride concentration up to some limit beyond which it becomes independent of its concentration. The rate of photopolymerization is proportional to the square root of the carbonyl concentration and the intensity. The rhenium carbonyl system, unlike the case for manganese carbonyl system, showed a high dark reaction, after light is removed, which persisted for several hours. When a mixture of rhenium carbonyl and methyl methacrylate is irradiated and allowed to stand in the dark for as much as one hour, subsequent addition of carbon tetrachloride results in the production of a considerable amount of polymer (21). This suggests that a rather stable intermediate is formed during the

irradiation which can react with carbon tetrachloride to produce the initiating species. It has been proposed that for metal carbonyls the photochemical reaction results in the production of $M(CO)_4$ where M is the metal and that this intermediate abstracts chlorine from carbon trachloride to give the radical $C Cl_3 \cdot$ which initiates the polymerization The difference in high dark rate for rhenium carbonyl as compared to that for manganese has been ascribed to the relative reactivities of $M(CO)_6$ which is also produced in the photochemical reaction.

The reactions described above were carried out with radiation at the long wavelength absorption regions of the metal carbonyls. At shorter wavelength regions of the near ultraviolet all the carbonyl groups may be split off and the appearance of carbon monoxide does not require the presence of carbon tetrachloride (309, 311). When the photochemical reaction is carried out with propylene oxide as the solvent and subsequently heated to an optimum temperature, a good yield of high molecular weight polypropylene oxide is obtained. This is a general method for polymerizing monoepoxy monomers. It appears here that the initiating species are not free radicals. Not all metal carbonyls are photosensitizers. Indeed, some such as $Fe(CO)_5$ and $Mo(CO)_4(CH_3CN)_2$ are inhibitors for both the photochemical and thermal polymerization of ethyl acrylate (310).

H. Inorganic Solids

On illumination of powdered zinc oxide with near ultraviolet light, hydrogen peroxide is produced if oxygen and water is present. This reaction, which has been known for many years (30), involves a synergistic effect with O_2 and H_2O and has been correlated with the photoconductivity and luminescence of zinc oxide (260). Such studies as well as electron spin resonance studies (171) indicate that oxygen

traps the conducting electrons at the surface of the zinc oxide particles. The chemisorbed oxygen may appear as O_2^- or, at higher temperatures as O^-, which could react with water to produce hydrogen peroxide (45, 340). In the absence of oxygen zinc oxide is a sensitizer for photoreduction (261). Zinc oxide is a photosensitizer for both oxidations and reductions when the exciting radiation is less than 380 millimicrons where the absorption edge of the solid occurs.

Zinc oxide is a photosensitizer for the polymerization of vinyl monomers (171, 191). The reaction requires water as well as oxygen (340) and the rate is proportional to the water content of the system in the region of low concentrations of water. End group analysis shows that hydroxyl radicals are the initiating species and copolymerization studies confirm the free radical nature of the process (340).

Lead tetraethyl, as a suspension, is a sensitizer for photochemical reactions. The absorption spectrum extends up to 450 millimicrons. In the temperature range 200° - 400°C, lead tetraethyl will thermally initiate the polymerization of vinyl monomers and, by applying pressure to the system, the effective temperature range can be lowered. At room temperature lead tetraethyl is a sensitizer for the photopolymerization of, for example, acrylonitrile (193).

Mixed catalysts of lead tetraethyl and titanium tetrachloride are photoinitiators of polymerization (193). The polymer produced does not possess the high crystallinity which is obtainable with the Ziegler type catalysts. The Ziegler catalyst (titanium chloride and aluminum alkyl halide) is purple-colored but becomes brown when its activity is spent. The purple color is restored by exposure to ultraviolet radiation (244).

Solid mercurous bromide is a photoinitiator for the polymerization of tetrafluoroethylene gas (6). Mercuric bromide is likewise a photoinitiator but is less effective. The polymer (Teflon) is attached

either to the solid photoinitiator surface or to the glass surface of the vessel.

Silver halides serve as photoinitiators for the polymerization of vinyl monomers (107, 180, 212). In a silver halide emulsion (in polyvinyl-alcohol) containing acrylamide the rate of photopolymerization is first order with respect to monomer concentration and rises with the square root of both the silver halide concentration and the specific surface of the solid grains (107). Addition of cyanine dyes and other well-known silver halide photographic sensitizers likewise sensitize the photopolymerization reaction (180, 212). Appropriate combinations of the components can provide a system which polymerizes on exposure to light of wavelengths betweeen 250 and 700 millimicrons.

Silver halide which had been exposed to light will, during the course of development to silver, initiate the polymerization of vinyl monomers (242). This arises from the free radical intermediates produced on oxidation of the developer. If development is carried out and monomer is subsequently added, however, polymerization will not occur.

I. Inorganic Ions

The process of electron transfer in systems of inorganic ions and complexes may produce free radicals or metal ions in their unstable valence states which can initiate polymerization of vinyl monomers. This process can take place spontaneously in " redox" initiating systems (for review, see ref. 15) or can be provoked by externally supplied energy. The required energy can be that of light quanta absorbed by the ions or complexes to produce the electron transfer spectra (276). The light absorbing species can be a simple cation or anion in the hydration shell or ionic complexes.

For simple anions the primary process involves the transfer

of an electron to the water molecules in the hydration layer. From this intermediate state the electron can either return to its initial state or passes over to a final state resulting in a chemical reaction wherein hydrogen atoms are produced (123, 276). A back reaction, the so-called secondary back reaction, can also take place. The hydrogen atoms produced could combine to give off molecular hydrogen. In the presence of vinyl monomer, however, the hydrogen atoms can initiate polymerization. The presence of monomer serves not only to scavenge the hydrogen atoms but also increases their yield by suppressing the secondary back reaction (197). The role of hydrogen atoms as the initiating species could be proven by carrying the photopolymerization in deuterium oxide and subsequently looking for the 2200 cm^{-1} C-D band in the infrared spectrum of the polymer obtained.

For cations the process is essentially the same as for anions except that the light-excited cation can either oxidize or reduce water molecules, depending on the ionization potential and the wavelength of the radiation. Hydroxyl radicals are produced on oxidation and hydrogen atoms are produced on reduction, both of which can serve as initiating species.

With complexes the cations are in contact with one or more anions or ligands. The process associated with light excitation is the same as with with cations but now the hydration shell is replaced by anions or ligands. The long wave length limit of the electron transfer spectrum and whether the metal ion is oxidized or reduced depends on its ionization potential and the electron affinity of the anions or ligands. The coordination complexes of transition metals show two distinct absorption bands. One band occurs chiefly in the visible region associated with d-d transitions. The other band, which is in the ultraviolet region, has a much greater

extinction coefficient and is the charge transfer spectrum (235, 276). It might be expected that absorption in the region of the charge transfer spectrum leads to redox reactions while absorption in the d-d leads to substitution reactions. The experimental results, however, turn out to be more complicated than anticipated (1, 2, 3).

For metal ions in solution it is frequently not clear which species is absorbing the light and the different species will behave differently as regards their photochemistry. Thus for radiation of wavelength 313 millimicrons $Fe^{+3}OH^{-}$ will yield hydroxyl radicals but $Fe(H_2O)_6^{+6}$ will not (102, 122). A further complication in photopolymerization is introduced by the complexation of vinyl monomers (P. 350 of ref. 28). Acrylonitrile, for example, forms strong complexs with V^{+3} and is manifested as a blue shift of 60 millimicrons in the electron transfer spectrum (96). The metal ions or their complexes can also act as chain terminators by oxidizing or reducing the chain radicals, depending on the relative oxidation potential of the ion and the polymeric radical (73, 74, 87, 89, 90, 96, 100, 270). Metal ions having fully filled d-shells, such as Ce^{5} aq $(4d^{10})$, $Ag^{+1}aq(4d^{10})$, $Hg^{+2}aq(4d^{10})$ and $Hg^{+2}aq(5d^{10})$, exhibit invariably low oxidizing termination rate constants (90)

In the polymerizing system where the photoinitiator also functions as a terminator, and if the initiator concentration is low, then an introducing V_t'' of eq. 10 into the simple scheme, the rate equation becomes

$$-\frac{d[M]}{dt} = \frac{k_p[M]}{2k_t}\left\{-k_{t''}[S] + [(k_{t''})^2[S]^2 + 4k_t V_R]^{1/2}\right\} \quad (47)$$

The rate of polymerization increases as [S] increases. If the initiator concentration is high then $v_{t''} >> v_t$ in which case the rate equation becomes

$$-\frac{d[M]}{dt} = \frac{k_p[M]}{k_{t''}[S]} v_R \qquad (48)$$

At high values of [S], v_R cannot be described by eq. 2 but approaches a constant value because of the large absorption of the light. As a consequence, the rate becomes inversely proportional to the initiator concentration. In other words, the rate of polymerization as a function of initiator concentration passes through a maximum. This has been observed for $FeCl_3$ as the initiator in the photopolymerization of acrylonitrile in dimethylformamide and the maximum rate occurs at a concentration of the metal ion of 10^{-3} molar (39, 42). Many other ions, for example, Cr^{+2}, Eu^{+2}, Ti^{+3}, U^{+3}, Mo^{+3}, and Sn^{+2}, are sensitizers for the photopolymerization of acrylonitrile but only at concentrations below 10^{-4} molar (96, 97).

For anions the long wave length limit of the electron transfer spectrum shifts toward the red the lower its electron affinity. It has been found that I^-, SH^-, SO_3^{-2}, and $HCOO^-$ serve as photoinitiators of polymerization when the appropriate radiation is employed (97). These anions are effective sensitizers over a wide range of concentration but N_3^- is effective only at concentrations below 10^{-4} molar. Kinetic studies of the photopolymerization of the aqueous solutions of acrylonitrile has been carried out with I^- as the sensitizer with exciting radiation of wavelength 254 millimicrons (99). Methyl methacrylate can be photopolymerized with oxalates as sensitizers to obtain a high molecular weight species having a carboxylic end group (268). It has been claimed that hydrochloric acid and sulfuric acid are sensitizers for the photopolymerization of methylmethacrylate since, chlorine and sulfate end groups were detected. The experiments involved prolonged irradiation with

ultraviolet radiation (283), however, and the unsensitized monomer could also be polymerized under such conditions (185) and such polymerization could involve chain transfer.

A number of cations such as V^{+3} V^{+4} V^{+2}, and Fe^{+2} are effective photoinitiators for acrylonitrile even when used over a wide range of concentrations (96, 97).

Cerous ion has been used as the sensitizer in the kinetic study of the photopolymerization of acrylonitrile and of methacrylic acid at various pH values (157). The rate increases with lowering pH and this is attributed to the influence of the hydronium ion on the rate of the secondary back reaction. A complication associated with cerous ion is that the ceric ion produced in the photochemical reaction is both a thermal (287) as well as a photo (118, 338) initiator. Polymer produced by the photochemical reaction contains no cerium atoms but polymer thermally initiated with ceric ion contains the metal as end groups (118). Other lanthanides in the plus three valence state also serve as sensitizers for photopolymerization (155, 297).

Soluble silver salts are photoinitiators for polymerization of acrylonitrile using near ultraviolet radiation (290). It has been suggested that the initiation involves the photoreduction of Ag^{+}(289). Silver ions are known to complex with acrylonitrile and in fact, concentrated silver salts in acrylonitrile will cause polymerization to occur spontaneously and with explosive violence, especially if oxygen is absent (143, 303).

The uranyl ion UO_2^{+2} is a photoinitiator for radiation up to about 500 millimicrons and has been used for non-aqueous (335, 336) as well as aqueous systems (74, 227, 329, 332). The primary photoinitiating process has been attributed to be electron transfer from the monomer to the excited free uranyl ion in a secondary dark reaction (189). More

recent work indicates that the primary process involves the photo-excitation of a pre-existing photosensitive cluster of the uranyl ion and monomer in equilibrium with energy transfer to the monomer (332). Uranyl ion also terminates acrylonitrile chain radicals and, furthermore, can act as a thermal initiator (74). Another element in the actinide series, namely thorium ion, is also a photoinitiator (298). It is of interest that lactones whose polymerization generally requires an ionic catalyst are, however, photoinitiated by uranyl ions (285, 286). The monomer complexes with uranyl ions and the polymerization is inhibited by typical radical scavengers such as benzoquinone.

Tin tetrachloride is a photoinitiator for styrene, the sensitizer being reduced to tin dichloride (343). Concentrated tin tetrachloride is an effective photoinitiator for acrylonitrile. The polymer is highly crystalline and exhibits semi-conducting properties (299, 300).

The literature on the use of ferrous and ferric complexes as sensitizers in photopolymerization is extensive (for example, see refs. 74, 102, 120, 136, 197, 284, 329). Ferric thiocyanide is a sensitizer for the photopolymerization of acrylonitrile using blue light and the polymer obtained has thiocyanide as the end group (120). The ferric oxalate complex $FeC_2O_4^+$ as well as the citrate $FeHCitr^+$ are known to under photoreduction to give ferrous ion and the initiating radical ions $C_2O_4^-$. and H $Citr^-$, respectively (313). It should be pointed out that ferric oxalate also serves as a standard actinometer (P. 783 of ref. 72).

Ferric hydroxide complex, Fe^{+3} OH^-, is reduced by near ultraviolet and by blue light to give ferrous ions and hydroxyl radicals, the latter serving as primary radicals for polymerization (98, 102, 104, 199, 329). With different anions of a ferric complex, the long wavelength limit of the absorption spectrum is shifted toward the

red as the electronegativity of the anion is lowered. This is also accompanied by an increase in the efficiency of photoreduction. Thus with blue light ferric chloride complex, $Fe^{+3}Cl^{-}$, is phoreduced with a quantum yield nearly three times that for ferric hydroxide complex, $Fe^{+3}OH^{-}$. Recent results (284) show that, hydroxyl groups are found as end groups using ferric chloride and ferric bromide as photosensitizers indicating that these substances are present as $Fe^{+3}OH^{-}$ in solution. Alternatively, halogen atoms which may be produced in the photolysis react with water. With short ultraviolet radiation, such as 254 millimicrons, ferrous ion produced in the photoreduction of ferric complexes can, in turn, be photo-oxidized to give ferric ions and hydrogen atoms. If a photostationary state is established there will be a continuous production of both hydrogen atoms and hydroxyl radicals.

Some coordination compounds are photoinitiators. Thus, chloropentaamine cobalt (III), $[CoCl(NH_3)_5]\ Cl_2$, and aquopentaamine cobalt (III), $[CoH_2O(NH_3)_5]\ (NO_3)_3$, will sensitize the polymerization of acrylamide. The former shows a rate of polymerization proportional to the first power of the monomer concentration while the latter shows a second order dependence (109). The second order dependence is attributed to the participation of the monomer in the formation of the initiating radicals. The rate of polymerization is pH dependent with an optimum between pH 5 and pH 7 (109) suggesting hydrolysis of the coordination complex (see ref. 28, p. 115). If the system contains a photosensitizer such as riboflavin the termination is enhanced by increasing the concentration of the coordination complex. This termination could take place by electron transfer.

Ordinarily the photochemistry of complex ions and coordination compounds is carried out by irradiation and subsequent analysis of the

equilibrium products. Such results are often difficult to interpret because of the back reactions. Using such substances as photoinitiators, however, the back reactions are supressed because of the rapid removal of primary radicals into the polymerization process.

J. Dye-Sensitization

It is possible to extend the spectral range of photopolymerization into the visible region by the use of dyes. There have been earlier reports in the literature of photopolymerization of vinyl monomers apparently sensitized by dyes. Such studies (e. g., 20, 163, 164, 327) involved prolonged irradiation over several hours often with intense light sources and hence it is difficult to evaluate such work. On the other hand, using riboflavin as a sensitizer under similar conditions a large conversion of monomer takes place in a duration of irradiation of the order of milliseconds (240). It is this rapid type of dye and sensitized photopolymerization which is more amenable to interpretation and constitutes the bulk of the more recent work.

Riboflavin is unique among the sensitizing dyes in that it contains a built-in reducing agent, the ribose group. This dye in aqueous solution without monomer undergoes reversible photoreduction (153, 154, 246). Many other dyes, notably those of the fluorescein, acridine (actually the 3, 6 amino acridines) and the thiazine familes are sensitizers for photopolymerization if an electron donor for the light excited dye is present. Such dyes undergo photoreduction in the presence of electron donors and if oxygen is present also serve as sensitizers for photo-autoxidation (241, 247). The electron donor may be a very mild reducing agent, such as ascorbic acid which does not, of course, reduce the dye in the dark (236). Even substances like ethylenediamine tetraacetic acid and other secondary and tertiary amines serve as electron donors for light-excited

dyes (258).

Very high quantum yields of monomer conversion was achieved with acrylamide using riboflavin as the photosensitizer (256). Introduction of glycerol into the system suppresses termination because of the diffusional process discussed in Sec. IIA. Post polymerization and pre-effects are readily observed with this system. It is difficult, however, to separate the pre-effect from inhibition by oxygen. A trace amount of oxygen seems necessary for the reaction since a single flash of the helium-flushed system does not produce polymerization until after the system is opened to air (240). Oxygen reacts competively with light-excited dye in the metastable excited state (247). As a consequence, it is difficult at the present time to generalize whether or not oxygen is required for dye-sensitized photopolymerization (c. f., 78, 83, 110, 321)

One suggested mechanism for free radical production is that the photoreduced dye is autoxidized by oxygen to give peroxy radicals (240). Another proposal is that photoreduced dye reacts with oxygen to give hydrogen peroxide which reacts with the reducing agent to produce radicals (11). There is some spectral evidence that dye is incorporated into the polymer (304) but many dyes are good transfer agents (216). Such studies may not elucidate the mechanism of dye-sensitization but they do provide convenient methods for the production of graft and block copolymers (304).

Methylene blue forms dimers in solution whose absorption maximum is at shorter wavelength than that for the monomer. The dimer is not photoreducible (63). As a consequence, the introduction of ethylene glycol or possibly other organic solvents which break up the dimer enhances the rate of photopolymerization (81). Furthermore, the dimer seems to be chain termination. Another way of destroying dimers of the

dye is to add anion dyes to the cationic methylene blue (82). In some cases, dye-sensitized photopolymerization of acrylamide was carried out without the addition of a reducing agent (294, 321) but subsequent analysis has shown that the electron donor is nitrilotripropionamide, a trace impurity in acrylamide (110). Such pitfalls should be taken into account when considering detailed theories of dye-sensitized photopolymerization (e.g., ref 295).

Dye-sensitization has been applied to the solid state photopolymerization of acrylamide (84). The free radical nature of the reaction was observed by electron spin resonance spectra and the extent of the reaction was followed by dissolving the irradiated crystals and isolating the polymer.

By using the appropriate dye, sensitization of photopolymerization can be achieved for any portion of the visible spectrum. This has obvious applicability to photography and image formation based on dye-sensitized photopolymerization is well developed (243). One system which is particularly convenient is that using calcuium acrylate. This monomer has two vinyl groups, the two carboxyl groups being complexed to calcium, and hence produces on polymerization a tight three-dimensional polymer network with high light scattering power. With triethanolamine as the electron donor and a photoreducible dye such as methylene blue, the system will polymerize to give an image with a photographic speed about that of silver bromide enlarging paper. The calcium acrylate system is shown in the presence of oxygen to exhibit an induction period which is inversely proportional to the rate of polymerization (rate varied to varying the light intensity, for example) (255). This inverse relation is attributed to chain termination by stable dye photoperoxides produced during the induction period. Photopolymerization of acrylamide with a few percent

of a diallyl monomer produces by dye sensitization a practically grainless three-dimensional image which is non-scattering and which on development (merely washing out unreacted monomer) gives a raised image whose height is roughly proportional to the square root of the intensity of the light. In this way one can convert an image of variable transmission into an image of variable optical path length. In other words, intensity modulation is converted into optical phase modulation. This converse of the imagery which one obtains in the Zernicke phase microscope, for example, has obvious applicability to the production of holograms (245).

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