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# PHOTOPOLYMERIZATION OF VINYL MONOMERS[1]

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## I. INTRODUCTION

By the term *photopolymerization* we mean 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 photocrosslinking of preexisting macromolecules, a subject which is treated elsewhere (*e.g.*, 244, and Chapters 2–4 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.[2] 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. Furthermore, 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 a 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 $10^{-9}$ g. 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 section III below).

Photopolymerization is not only useful for the detection and identification of photochemically produced free radicals; since photopolymerization reactions can be started or stopped at will by the simple expedient of turning on or off the light, a means is provided for studying the nonsteady-state kinetics of polymerization (section 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 photo-

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(2) See recent work of Tazuke (318) for example involving ionic polymerization.

polymerization (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 (section 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 disk electrophoresis (236). Protein or other biological polyelectrolytes are dissolved in an aqueous solution of acrylamide (and a trace of diallyl monomer) containing riboflavin and exposed to visible light (section IV.J). The photopolymerized mass is then subjected to an electric field, and in this manner an electrophoretic 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.

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 Ostromislenski in 1912 (263). He showed that the amount of polymer (poly(vinyl 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, *e.g.*, ref 16, 24, 50, 68, 126, 170; 50 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, *e.g.*, 77, 79).

### 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 section 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 (section 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 $\phi$ and the intensity $I_a$ of absorbed light. Assuming the validity of Beer's law, the rate of radical production is

$$v_R = \phi I_a = \phi I_0(1 - e^{-\epsilon l[S]}) \qquad \text{(Eq 1)}$$

where $I_0$ is the incident light intensity, $l$ the path length in the system, and [S] the concentration of the initiator of extinction coefficient $\epsilon$. For low values of the exponent, Eq 1 becomes the form we shall use throughout, namely

$$v_R = I_0\phi l\epsilon[S] \qquad \text{(Eq 2)}$$

If there are no competitive processes in the photolytic reaction, the quantum yield $\phi$ should equal 2 when 1 quantum absorbed results in two free radicals. More usually, however, $\phi$ is less than this ideal because of competitive processes. Photolytic reactions in solution often have low quantum yields due to recombination of radicals in the "cage" (for reviews, see ref 224, 225). 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 $\phi$. The viscous drag on the radicals opposes their separation in the cage, and hence $\phi$ 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 kcal mole$^{-1}$), and hence the temperature dependence of rates of photopolymerization is determined primarily by the nonphotochemical steps in the reaction. For thermal decomposition of initiators, such as peroxides, the activation energy is high (in the range 30–50 kcal mole$^{-1}$) so that, unlike photochemical production of radicals, the rate of thermal production of radicals is highly temperature dependent.

Once the primary radicals escape from the cage they can attack a monomer molecule M to form RM·, the start of the chain reaction. The rate of the reaction

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

is given by

$$v_i = k_i[R\cdot][M] \qquad \text{(Eq 4)}$$

The rate constant $k_i$ is a measure of the reactivity of R· for the monomer, and its evaluation involves certain complications (sections II.B and II.C). This constant can also be estimated from the comonomer reactivity ratio involving two monomers, one of which is similar to R· and the other similar to M (67). For example, in the system where $\alpha,\alpha'$-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

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

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

$$v_p = k_p[P\cdot][M] \qquad \text{(Eq 6)}$$

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$^{-1}$.

A special feature of the propagation of chain radicals is that the process consists of continuing repetition of an exothermic reaction ($\Delta H$ of from 15 to 20 kcal mole$^{-1}$ 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 a 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.*, $1.93 \times 10^3$ and $1.69 \times 10^3$ l. mole$^{-1}$ sec$^{-1}$ in the case of pure styrene and of half-diluted styrene, respectively) is not great; 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 has predominantly the syndiotactic configuration (59, 127). 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 constants 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 depolymerization. Associated with the chain propagation is a depolymerization process, and the two rates become equal at the ceiling temperature (for a 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

$$v_t = k_t[\mathrm{P}\cdot]^2 \qquad \text{(Eq 7)}$$

This termination could be by combination and/or by disproportionation. Termination by disproportionation has a much higher activation energy. Like most 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 a review, see ref 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 the cross section of the diffusing species. For spherical particles of the 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 simple 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 $10^{11}$ l. mole$^{-1}$ sec$^{-1}$, whereas for chain-radical terminations $k_t$ is of the order of $10^7$ l. 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 (156, 220). 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 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 *via* 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 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-trimethylhexyl methacrylates decrease with increasing bulkiness of the side group (223).

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 carbazole representing increasing stiffness of the chain molecules. The latter two monomers showed a deviation in the Arrhenius plot for $k_t$ below $-10°$. 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, 66, 219), but a missing factor is the effective viscosity. Fluorescence methods might be useful in this regard (253, 254). For example, a study of the quenching of fluorescence by two polymer species, one of which bears a fluorescent 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-sensitized photopolymerization of acrylamide where glycerol was added to the aqueous system (262). 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 a review, see ref 16, Chapter 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

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

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 geminate 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

$$v_{t'''} = k_{t'''}[R\cdot]^2 \qquad \text{(Eq 9)}$$

A chain radical can also be terminated by a so-called inhibitor. The inhibitors 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

$$v_{t''} = k_{t''}[P\cdot][B] \qquad \text{(Eq 10)}$$

Chain transfer which results in termination of a chain radical with initiation of a new chain is a common occurrence 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

$$v_{tr} = k_{tr}[P\cdot][S] \qquad \text{(Eq 11)}$$

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 simultaneous differential equations presents 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.*

$$\frac{[dR\cdot]}{dt} \ll \begin{matrix} v_R \\ v_i + v_{t'} + v_{t'''} \end{matrix} \qquad \text{(Eq 12)}$$

and

$$\frac{d[P\cdot]}{dt} \ll \begin{matrix} v_i \\ v_t + v_{t'} + v_{t''} \end{matrix} \qquad \text{(Eq 13)}$$

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·

$$v_R = \frac{d[R\cdot]}{dt} + [R]\{k_i[M] + k_{t'''}[R\cdot] + k_{t'}[P\cdot]\} \qquad \text{(Eq 14)}$$

and for P·

$$v_i = \frac{d[P\cdot]}{dt} + [P\cdot]\{k_t[P\cdot] + k_{t'}[R\cdot]\} \qquad \text{(Eq 15)}$$

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

$$I_0\phi l_\epsilon[S] = k_i[R\cdot][M] \qquad \text{(Eq 16)}$$

where now $[R\cdot]$ 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

$$[P\cdot] = \left\{\frac{I_0\phi l\epsilon[S]}{k_t}\right\}^{1/2} \qquad \text{(Eq 17)}$$

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

$$-\frac{d[M]}{dt} = v_p + v_i \approx k_p[M][P\cdot] \qquad \text{(Eq 18)}$$

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

$$-\frac{d[M]}{dt} = k_p\left\{\frac{I_0\phi l\epsilon[S]}{k_t}\right\}^{1/2}[M] \qquad \text{(Eq 19)}$$

The concentration of sensitizer is a function of time of irradiation and decreases according to a first-order reaction. If [S] is the initial concentration of sensitizer, then Eq 19 becomes

$$-\frac{d[M]}{dt} = k_p[M]\left\{\frac{I_0\phi l\epsilon[S]}{k_t}\right\}^{1/2} \exp(-{}^1/_2 I_0\phi l\epsilon t) \qquad \text{(Eq 20)}$$

or, on integration

$$[M] = [M]_0 \exp\left\{-\frac{2k_p}{\sqrt{k_t\phi\epsilon l}}\sqrt{\frac{[S]_0}{I_0}} \times [1 - \exp(-{}^1/_2 I_0\phi l\epsilon t)]\right\} \qquad \text{(Eq 21)}$$

where $[M]_0$ is the initial concentration of monomer. The limiting value ($t = \infty$) of the fraction of monomer converted to polymer is, from eq 21

$$\frac{[M]_0 - [M]_\infty}{[M]_0} = 1 - \exp\left\{-\frac{2k_p}{\sqrt{k_t\phi\epsilon l}}\sqrt{\frac{[S]_0}{I_0}}\right\} \qquad \text{(Eq 22)}$$

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 obtain-rate data, the quantum yield of primary radical production can be determined. It should be realized, however, that these three quantities could vary during the course of the polymerization owing to an 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 eq 6, 7, and 17, we obtain for the steady-state value of the average kinetic chain length $\bar{\nu}$

$$\bar{\nu} = \frac{k_p}{\sqrt{k_t}}\frac{[M]}{(I_0\phi\epsilon l[S])^{1/2}} \qquad \text{(Eq 23)}$$

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

$$\bar{\nu} = \frac{k_p}{k_t}\frac{[M]_0}{(I_0\phi\epsilon l[S]_0)^{1/2}} \exp(-{}^1/_2 I_0\epsilon\phi l t) \times \exp\left\{-\frac{2k_p}{\sqrt{kt\phi\epsilon l}}\sqrt{\frac{[S]_0}{I_0}}\,[1 - \exp(-{}^1/_2 I_0\phi l\epsilon t)]\right\} \qquad \text{(Eq 24)}$$

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 $I_0$ 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 $I_0$ with time so that $\bar{\nu}$ of Eq 24 remains constant. This is achieved approximately if $I_0$ satisfies the condition

$$t = \frac{2\sqrt{I_0} - \dfrac{1}{k_p}\sqrt{\dfrac{k_t}{[S]_0}}}{\phi\epsilon l I_0{}^{3/2}} \qquad \text{(Eq 25)}$$

In photopolymerization the over-all rate increases with temperature, but, unlike with thermal initiation, the molecular weight also increases with temperature. This is seen from Eq 23 since

$$\frac{d\ln\bar{\nu}}{dt} \sim \frac{E_p - {}^1/_2 E_t}{RT^2} \qquad \text{(Eq 26)}$$

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 a 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 rise continuously during the course of the reaction because of 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 them becomes

$$\frac{1}{\bar{\nu}} = \frac{\sqrt{k_t}(I_0\phi\epsilon l[S])^{1/2}}{k_p[M]} + \frac{k_{tr}}{k_p}\frac{[S]}{[M]} \qquad \text{(Eq 27)}$$

The chain transfer can in some cases be quite large; for example, with disulfides 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 at small $[S]/[M]$ ratios. 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 monomer; 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 peroxide initiation of styrene at 60° (8). Similarly with azobisisobutyronitrile 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

$$[P\cdot]^3 + \frac{k_i}{k_{t'}}[M][P\cdot]^2 + \frac{v_R}{k_t}[P\cdot] - \frac{v_R}{k_t}\frac{k_i}{k_{t'}}[M] = 0 \quad \text{(Eq 28)}$$

In the case where initiation of the chains is much greater than termination by primary radicals, $[P\cdot] \ll k_i[M]/k_{t'}$, the steady-state concentration of chain radicals becomes (233)

$$[P\cdot] = \sqrt{\frac{v_R}{k_t}}\,\frac{(k_i/k_{t'})[M]}{(k_i/k_{t'})[M] + \sqrt{(v_R/k_t)}} \quad \text{(Eq 29)}$$

or, in terms of the rate of polymerization, $v_p$, using Eq 6 and 2

$$\frac{v_p}{[M]\sqrt{[S]_0}} = \frac{k_p}{\sqrt{k_t}}\left(\frac{v_R}{[S]_0}\right)^{1/2}\left[1 - \frac{k_{t'}v_p}{k_ik_p[M]^2}\right] \quad \text{(Eq 30)}$$

Hence a plot of $v_p/[M][S]_0$ *vs.* $v_p/[M]^2$ gives a straight line from which $k_{t'}/k_ik_p$ can be obtained. Equation 28 can also be written in the form (25, 204)

$$\frac{v_p}{[M]^2}\left\{\frac{1 + \dfrac{v_p{}^2\delta^2}{[M]^2v_R}}{1 - \dfrac{v_p{}^2\delta^2}{[M]^2v_R}}\right\} = k_i\frac{\sqrt{k_t}}{k_{t'}} = \Lambda \quad \text{(Eq 31)}$$

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

$$f = \frac{1}{1 + \dfrac{\Lambda[M]^2}{\delta v_p}} \quad \text{(Eq 32)}$$

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 $\Lambda$ 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 $\Lambda$ for methyl methacrylate and of styrene initiated by azobisisobutyronitrile at 60° is 0.5 for $[M] = 0.0844$ *M* (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 furnish information regarding the extend 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 are the same, *i.e.*, $k_t = k_{t'} = k_{t''}$, then from Eq 14 and 15, using the steady-state argument (158), one obtains

$$\frac{1}{v_p} = \frac{k_t}{k_pk_i[M]^2} + \frac{\sqrt{k_t}}{k_p[M]v_R} \quad \text{(Eq 33)}$$

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 nonsteady state (section II.C).

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.

$$2\left\{\frac{k_t[S]_0}{\phi\epsilon l I_0}\right\}^{1/2}\exp(-{}^1/_2\epsilon\phi l I_0 t) \geqslant 1 \qquad \text{(Eq 34)}$$

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

$$[S]_{0(\min)} = \frac{\phi\epsilon l I_0}{4kt} \qquad \text{(Eq 35)}$$

Furthermore, 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

$$\left\{\frac{[S]_0}{[S]_{0(\min)}}\right\}^{1/2}\exp(-{}^1/_2\epsilon\phi l I_0 t) \gg 1 \qquad \text{(Eq 36)}$$

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

$$t \ll \left\{\frac{\ln\, [S]_0/[S]_{0(\min)}}{\phi\epsilon l I_0}\right\} \qquad \text{(Eq 37)}$$

Since $I_0^{-1}$ 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) leaks to essentially the same result derived above.

### C. NONSTEADY STATE

Elementary treatments of nonsteady-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 Eq 34–37 above. There are conditions in photopolymerization where omission of the nonsteady 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 Eq 15

$$\frac{d[P]}{dt} = v_R - k_t[P\cdot]^2 \qquad \text{(Eq 38)}$$

This differential equation is readily solvable to give $P\cdot$ in terms of $v_p$ (Eq 6), namely

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

where the superscript s denotes the steady-state value, and $\tau$, the lifetime, is the average value of the time for creation and annihilation of the growing chain radicals. Hence $\tau$ is the ratio of the concentration of radicals to the rates of termination of the radicals. From Eq 6 and 7, the lifetime is

$$\tau = \frac{k_p}{k_t}\frac{[M]}{v_p} \qquad \text{(Eq 40)}$$

In the early stages of polymerization, namely for $t/\tau$ small (Eq 39), the pre-effect can be expressed as a power series in $t/\tau$, the leading term being linear in this ratio. If at a moment $t_0$ during the steady-state polymerization the light is turned off, then the concentration of chain radicals [P.], and hence $v_p$, decays hyperbolically with time according to Eq 38 ($v_R = 0$), so for the post-effect

$$\frac{(v_p)_s}{v_p} - 1 = \frac{t - t_0}{\tau} \qquad \text{(Eq 41)}$$

Hence from either the pre-effect or the post-effect, the lifetime, $\tau$, can be determined. Combining Eq 40 and the steady-state expression (Eq 33), one can obtain values for $k_t$, $k_p$, 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 nonsteady state. The results are quite complex but solvable (67) if terminations *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 Eq 8 and 9, or

$$\frac{d[R\cdot]}{dt} = v_R - k_i[R\cdot][M] \qquad \text{(Eq 42)}$$

whence, using Eq 2

$$[R\cdot] = \frac{\phi\epsilon l I_0[S]_0}{k_i[M]}\{1 - \exp(-k_i[M]t)\} \qquad \text{(Eq 43)}$$

Hence Eq 38 is replaced by the equation

$$\frac{d[P\cdot]}{dt} = \frac{\phi\epsilon l I_0[S]_0}{k_i[M]} \times \{1 - k_t[P\cdot]^2 - \exp(-k_i[M]t)\} \qquad \text{(Eq 44)}$$

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

$$[P\cdot] = \left\{\frac{\epsilon l I_0[S]_0}{k_t}\right\}^{1/2} U(t)F(q, U) \qquad \text{(Eq 45)}$$

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

$$q = 4\frac{k_t \epsilon l I_0 [\mathrm{S}]_0^{1/2}}{k_i[\mathrm{M}]}$$

$$U(t) = \exp\left(-\frac{k_i}{2}[\mathrm{M}]t\right) \qquad \text{(Eq 46)}$$

The significance of $q$ is that $q/2$ is the ratio of the average lifetime of the chain radicals in the steady state to $\tau$, the average lifetime of the chain radicals in the steady state. Hence $q$ indicates the extent to which the system deviates from the conventional nonsteady-state case. In ref 67 is a plot of $v_p/(v_p)_s$ as a function of $t/\tau$. 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 nonsteady state for primary radicals especially if $k_i[\mathrm{M}]$ is small and/or $I_0[\mathrm{S}]_0$ 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 over-all 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 lifetimes 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, one calculates the diffusion constant for the radicals for the time equal to $\tau$. 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 a 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 cross-linked 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 light initiation and termination by inhibitor. Thus the shorter the path length 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, $\tau$, of the growing chain radical (134, 176). In the early stages of photopolymerization the distribution of chain radicals will change and eventually, after time $\tau$, 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 a 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 soap micelles is kept constant during the course of polymerization (339) might be helpful in the photopolymerization of emulsions to obtain sharp molecular weight distributions.

## III. SURVEY OF EXPERIMENTAL METHODS

Photopolymerization is particularly adaptable to automatic techniques. Thus actinic light can be interrupted at will, and its intensity can be varied in a programmed manner. Furthermore the polymerization itself can be followed continuously and recorded electrically. This means, that the data can be analyzed immediately *via* on-line computers. The intention of the present section is to point out the existence of certain types of equipment, which have recently become commercially 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 m$\mu$ 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 Chapter 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 continuously operating lamp by introducing an electrooptical 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 stroboscopic 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 spectra 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 commercially available 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 m$\mu$, 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 (256). In some cases the quantum yield of photochemical reaction is known for a substance which is also a sensitizer for photopolymerization; hence such a substance serves as a convenient actinometer even if 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 $\mu$ decreases as polymerization proceeds (12). 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 vinylpyrrolidone has an absorption peak at about 250 m$\mu$ which decreases on polymerization of the monomer (250).

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%. 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% corresponding to a conversion of pure monomer of about 1% 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° will cause an expansion of the liquid sufficient to offset a 1% 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 min. To be used for shorter times, a dilatometer 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 (257). A droplet of an aqueous solution of acrylamide containing riboflavin which is a sensitizer for blue light was suspended in a nonaqueous density gradient. On illumination the droplet settles downward. Polymerization phenomena such as induction, nonsteady-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 (257), and hence the distance, in turn, is directly proportional to the extent of polymerization.

The change in density in a polymerizing system is also manifested 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 (302, 342).

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 increase on going from the pure monomer to the polymer is in the neighborhood of 5%. 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 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% of pure monomer in a volume, say, of 10 ml, would, under adiabatic conditions, see a rise in temperature of 1°. 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 appreciably 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 nonsteady-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 are 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 nonsteady state as well as the steady state in photopolymerization (33–35).

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 continuous 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%), 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 nonaqueous 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, are not appreciably fluorescent in low-viscosity media but fluoresce strongly in high-viscosity media (252, 253). 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 (254). 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 253).

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 section 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 esr apparatus, namely $10^{-5}$ *M*. For cases where radical concentrations are large, *i.e.*, where the chain radicals are very long lived as in glasses (173) or in extremely viscous media (166), one can follow by esr the changes in concentration of the chain radicals. In low-temperature photopolymerization, radical concentrations as high as $10^{-4}$ *M* can be built up and esr 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 esr method, when it can apply, has the feature that the resonance spectrum helps to identify 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 a 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 (section 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.

## IV. 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 diphenylpicrylhydrazyl and triphenylmethyl although not chain initiating are, however, efficient chain terminators. Commercially available vinyl monomers often contain hydroquinone which in its semiquinone form acts as an inhibitor. 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 accumulated (*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. (See, for example a recent reference by Wright (339a).) 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 a 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 lie 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 m$\mu$. 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, peroxides. A standard procedure for the elimination of trace amounts of impurities is to partially polymerize the monomer and then vacuum distil 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 can lead to polymerization of vinyl monomers by mechanisms of a nonphotochemical 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 clarified, it is clear 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 a vinyl ketone which displays the photochemical behavior typical of carbonyl compounds (see section IV.B). Another example is vinyl bromide which behaves photochemically like other bromine compounds (see section IV.F).

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 (*e.g.*, ref 226, 272, 296, 306, and Chapter 5 of ref 72). The aliphatic aldehydes and ketones have a weak absorption in the ultraviolet region beginning at about 330 m$\mu$ and a maximum at about 270 m$\mu$. 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. With acetone, for example, methyl and acetyl 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 acrylonitrile 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 because of ring closure of the cyclohexanone monomer diradical but more likely because of 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 transmit radiation in the 300-m$\mu$ 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 carbonyl groups have been used as sensitizers. Biacetyl, for example, absorbs in the near-ultraviolet region and the blue regions (up to 467 m$\mu$) 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 m$\mu$) as the source (132). Polymers obtained with biacetyl are initially deeply yellow but become 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 m$\mu$ 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 m$\mu$ (see, for example, ref 80). This sensitizer was also used in the photopolymerization of methyl methacrylate at the temperature range from $-35$ to 0° for the study of the relation between temperature and stereospecificity in free-radical polymerization (159). The carbonyl group in benzoin is the active group since its oxime is not a sensitizer. Aromatic carbonyls with an hydroxyl group *ortho* to the carbonyl are likewise inactive as photoinitiators, presumably because of 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 14 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 over-all 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, bromal, and acrolein dibromide are good sensitizers when using near-ultraviolet radiation. The relative conversion rates of methyl methacrylate using 17% of the sensitizers, azobisisobutyronitrile, benzoin methyl ether, and bromoacetophenone, and bromoisobutyrophenone were found under the conditions employed to be 1.00, 1.43, 2.22, 2.33, respectively (319). Extensive studies of photopolymerization have been carried out with 9-bromoacetophenone (266, 312). This sensitizer has a molar extinction coefficient of 46 at 365 m$\mu$, and the studies gave values for the monomer transfer constant, $k_t/k_p^2$, and over-all activation energy for the reaction for vinyl acetate (266). The polymer obtained and the poly(vinyl alcohol) produced on saponification have an absorption maximum at 245 m$\mu$, suggesting the presence of an acetophenone residue on the polymer molecule. Bromine atoms (1.33 per 1000 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 m$\mu$ for the photografting of vinyl monomers to polyethylene (255). The sensitizer is converted to benzhydrol by hydrogen abstraction 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 significant that in the absence of monomer benzophenone is a sensitizer for the crosslinking of polyethylene whereas benzoin is not.

### C. PEROXIDES

The chemistry of peroxide compounds has been reviewed in a number of monographs and reviews (*e.g.*, ref 105, 119, 141, 142, 178, 186, 201, 320). Peroxides contain two adjacent oxygen atoms with overlapping lone-pair orbitals. The average bond energy of the linkage is abut 34 kcal mole$^{-1}$. On excitation with the mercury arc spectral lines of 313 and 254 m$\mu$, an excess energy of 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 photosensitizers is that they show appreciable absorption only below 320 m$\mu$. 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-m$\mu$ radiation yields *via* induced decomposition *t*-butyl alcohol and oxygen as the main decomposition products (192). Dialkyl peroxides are less susceptible to induced decomposition. Benzoyl peroxide on thermal decomposition yields *via* the benzoyloxy radical carbon dioxide and a phenyl radical. Radical scavengers such as diphenylpicrylhydrazyl suppress completely the formation of carbon dioxide. In the photolysis of benzoyl peroxide in styrene as the scavenger, 30% of the decomposed peroxide appears as carbon dioxide and phenyl radicals as the primary photochemical products. This result suggests that benzoyloxy 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 benzoyloxy 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-*t*-butyl peroxide at wavelengths shorter than 300 m$\mu$, the primary products of photodecomposition are oxygen and the *t*- butyl radical (128). Cleavage at the oxygen–oxygen bond yields *t*-butoxy 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 photopolymerization. This compound begins to absorb light at 400 m$\mu$ 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° is 0.3 and 0.5 for radiation of wavelength 313 and 254 m$\mu$, respectively (31, 94), and increases with shorter wavelengths. Acrylonitrile, which absorbs only below 230 m$\mu$, is photoinitiated by hydrogen peroxide when ultraviolet radiation above 290 m$\mu$ is used (93). Hydrogen peroxide was used as the sensitizer to determine kinetic rate constants of acrylamide (103) and methacrylamide (101) using the rotating sector. For radiation of 313 m$\mu$, the quantum yield for initiation was found to be 0.87 at 25°. The polymerization rate 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 the esr spectrum showed that the chain radical produced is $-CH{=}\dot{C}CHOH$ which was produced by hydroxyl radical abstraction of the methylenic hydrogen atom from the monomer. Kinetic data indicate that the hydroxyl radicals migrate readily and react with the monomer.

In what is probably the first use of photopolymerization for the manufacture of fibers 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 volatility of the initiator. (234). Thus di-*t*-butyl peroxide can be distilled from the system when desired. This sensitizer can be decomposed by radiation of wavelength below about 350 m$\mu$ but is thermally more stable than, 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 initiation 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 m$\mu$ and its first maximum is at 275 m$\mu$ (with log $\epsilon$ 3.42). Nevertheless, it will decompose when exposed to a high-intensity radiation of 365 m$\mu$. 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 about 2% conversion. These results are attributed to induced decomposition of the peroxide and complexation to styrene. Benzoyl peroxide was used as the photoinitiator for the room-temperature polymerization of styrene at high pressures (up to 3000 atm). 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 m$\mu$, although not appreciably absorbed by the peroxide, can be used by a sensitizer whose excitation energy is transferred to the peroxide. Examples of sensitizers for the near-ultraviolet region are anthracene and naphthalene which on excitation with 365-m$\mu$ light will cause the decomposition of acetyl peroxide in isooctane (183). Fluorenone is a sensitizer in the blue region for the colorless compound, fluorenone hydroperoxide (328). The sensitizer forms a complex *via* hydrogen bonding with the hydroperoxide. This system is a good photoinitiator for the polymerization and for blue light is 100 times more effective than is fluorenone alone.

Chlorophyll is also a sensitizer for the decomposition of peroxides (251). Chlorophyll in organic solvents has absorption maxima at about 430 and 660 m$\mu$. Solutions of chlorophyll and organic peroxides show on 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 time is less than *ca.* 10 sec. Oxygen inhibits both the light production of this unstable intermediate and its recovery rate 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. However, 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 might involve energy transfer.

### D. ORGANIC SULFUR COMPOUNDS

Aliphatic disulfides absorb maximally in the neighborhood of 254 mμ 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 α to the S–S linkage. The disulfide bond is also cleaved by ultraviolet light to yield free radicals. Some aryl disulfides absorb 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° (265, 322, 323). Tetraalkylthiuram 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 weight polymer. This sensitizer is also a poor thermal initiator.

Several S-aryldithiocarbamate derivatives 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 *para*-substituted carbamate derivative. The chain-transfer constant at room temperature for benzodithiocarbamate is 5.5 so that its concentration should be very low in order to obtain reasonably high molecular weight polymer.

Tetramethylthiuram monosulfide is an excellent sensitizer for photopolymerization (124). This sensitizer is particularly attractive in that it has an absorption maximum at 400 mμ, 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-naphthyl 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 arylthio radical and desyl radical, the relative ease of breaking the C–S bond being related to the resonance stabilization of the arylthio radical.

Sulfur compounds have also found use in photografting and in the photochemical production of block copolymers. Polystyrene prepared by tetraethylthiouram disulfide used as a thermal initiator has as an end group, the diethyldithiocarbamate 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 tetraethylthiouram disulfide to yield a polymer containing diethyldithiocarbamate groups. The new polymer, when irradiated in the presence of methyl methacrylate, yields a graft copolymer. Sodium diethyldithiocarbamate will react with polyvinyl chloride to yield a polymer containing as much as 30 mole % of diethyldithiocarbamate groups (230). This polymer is cross-linked by ultraviolet light and, in the presence of methyl methacrylate, can be photografted. The photoactive dithiocarbamate 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 NC(=S)SR dithiocarbamate group is readily cross-linked by ultraviolet light 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 the 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 (240). This result may be relevant to the action of ultraviolet light on proteins, as in the case of ovalbumin which showed accelerated heat denaturation when it had previously received a short dose of ultraviolet light. Perhaps the conformational changes associated with denaturation are expedited by preliminary cleavage of the disulfide 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 mμ. 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 (249). When ovalbumin 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 $sp^3$ hybrid which leads for the $Q \rightarrow N$ transition to a near-ultraviolet band for the isolated bond with a maximum at 350 mμ. Whereas arylazo compounds are stable in light, alkylazo compounds are readily dissociated by light to give free radicals. Photodecompositions of the simplest alkylazo compounds, *e.g.*, azomethane and azothane, 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 in 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 derivative of azomethane, namely, hexafluoroazomethane, 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 tetrafluoroethene, 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 kinetic rate studies of the polymerization of styrene (206, 207). If nitrile is one of the α substituents on an alkylazo compound, the material is a highly efficient photoinitiator, presumably because of the formation of the resonance-stabilized cyanoalkyl radicals.

Among the azonitriles, the most commonly used photoinitiator is α,α′-azobisisobutyronitrile. Its photodecomposition can be followed spectroscopically with the disappearance of the absorption at 345 mμ. This compound has been used in nonstationary state studies of the photopolymerization of vinyl acetate (194, 205, 208), styrene (195, 208), vinyl chloride (70), and methyl methacrylate (208). There are some side reactions associated with photoinitiation using azobisisobutyronitrile. 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 azobisisobutyronitrile standing for long periods of time in the presence of oxygen exhibit complications because of the formation of tetramethylsuccinodinitrile and acetone cyanohydrin, both of which are photosensitive (53). The photodecomposition of azobisisobutyronitrile 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 mμ ($\epsilon_{max}$ 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-mμ region, the ketenimine 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-cyclohexanecarbonitrile. This compound has a broad absorption band with a maximum at 260 mμ ($\epsilon_{max}$ 16) and follows Beer's law up to a concentration of 0.01 *M* (40, 205). As a photoinitiator α-azobis-1-cyclohexanecarbonitrile seems to be more efficient than azobisisobutyronitrile, judging from the quantum yield for monomer conversion (182). The advantage of this initiator is that it does not have a dark rate due to thermal decomposition at 25° (182). It has been used as a photoinitiator for kinetic studies of vinyl acetate (36, 209) 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. 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 and 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, azobisisobutyronitrile treated with sulfuric acid gives the azoisobutyramide, a water-soluble photoinitiator (56).

Diazonium salts are readily decomposed by light (for review, see ref 346, Chapter 7) but do not necessarily produce free radicals. On the other hand, the thermal reaction between diazonium salts and phenol produced by the light reaction is a free-radical reaction as evidenced by the fact that polymerization of a water-soluble monomer ensues on heating (260).

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 mμ (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 1:1 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 $Cl_2$, $Br_2$, and $I_2$ are at 284, 420, and 520 mμ, respectively, with increasing absorption coefficient as the atomic number increases. Most of the radiant energy absorbed by halogen molecules leads to 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-mμ 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 chloroform or carbon tetrachloride, have been used as photoinitiators for styrene and 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 bromotrichloromethane can be decomposed by radiation of 365-mμ wavelength (196). Bromoform is a photoinitiator of polymerization for radiation of 330-mμ wavelength, but for dibromomethane radiation shorter than 310 mμ 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 50:1 mixture of carbon tetrachloride and styrene yields on irradiation essentially polymer. On the other hand, even a much lower concentration of bromotrichloromethane gives halogenated styrene as the principle photoproduct (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).

Hypohalites absorb generally in the near-ultraviolet regions to produce alkoxy radicals (5), but their use as photoinitiators for polymerization has not been explored Other halogated 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 a review, see ref 308). Manganese carbonyl, $Mn_2(CO)_{10}$, and rhenium carbonyl, $Re_2(CO)_{10}$, 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-mμ wavelength for manganese carbonyl and with 365-mμ wavelength for rhenium carbonyl. The radical $CCl_3$ was confirmed by tracer studies to be the initiating species. If in place of carbon tetrachloride the polymer polyvinyl trichloroacetate is used, a gel is obtained indicating that the initiating species is a polymer radical. The polymerization rate 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 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 1 hr, 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 tetrachloride to give the $CCl_3\cdot$ radical which initiates the polymerization. The difference in high dark rate for rhenium carbonyl as compared to 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 (*cf.* ref 317a). 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 are present. This reaction, which has been known for many years (30), involves a synergistic effect and has been correlated with the photoconductivity and luminescence of zinc oxide (258). 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 (259). Zinc oxide is a photosensitizer for both oxidations and reductions when the exciting radiation is less than 380 mμ 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 mμ. In the temperature range 200–400°, 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 but becomes brown when its activity is spent. The purple color is restored by exposure to ultraviolet radiation (245).

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 sensitizes the photopolymerization reaction (180, 212). Appropriate combinations of the components can provide a system which polymerizes on exposure to light of wavelengths between 250 and 700 mμ.

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 a 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 pass 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 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 out 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 cations, but now the hydration shell is replaced by anions or ligands. The long-wavelength limit of the electron-transfer spectrum and whether the metal ion is oxidized or reduced depend 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 (1–3).

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 mμ $Fe^{+3}\,OH^-$ 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 complexes with $V^{+3}$ as manifested in a blue shift of 60 mμ 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) ($4d^{10}$), $Ag^+$(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 on introducing $v_{t''}$ of Eq 10 into the simple scheme, the rate equation becomes

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

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

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

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 $10^{-3}$ *M* (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 $10^{-4}$ *M* (96, 97).

For anions the long-wavelength 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 $10^{-4}$ *M*. Kinetic studies of the photopolymerization of aqueous solutions of acrylonitrile have been carried out with $I^-$ as the sensitizer with exciting radiation of 254-mμ wavelength (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 methyl methacrylate since chlorine and sulfate end groups were detected. The experiments involved prolonged exposure to 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 a 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 photoinitiator (118, 338). 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 +3 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, expecially if oxygen is absent (143, 303).

The uranyl ion $UO_2^{+2}$ is a photoinitiator for radiation up to about 500 mμ and has been used for nonaqueous (336, 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 is a secondary dark reaction (189). More recent work indicates that the primary process involves the photoexcitation 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 semiconducting properties (299, 300).

The literature on the use of ferrous and ferric complexes as sensitizers in photopolymerization is extensive (for example, see ref 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 undergo photoreduction to give ferrous ion and the initiating radical ions $C_2O_4\cdot^-$ and $Hcitr\cdot^-$, respectively (313). 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 also accompanied by an increase in the efficiency of photoreduction. Thus with blue light, ferric chloride complex $Fe^{+3}Cl$ is photoreduced 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 mμ, ferrous ion produced in the photoreduction of ferric complexes can, in turn, be photooxidized 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 chloropentaamminecobalt(III) chloride, $[CoCl(NH_3)_5]Cl_2$, and aquopentaamminecobalt(III) nitrate, $[CoH_2O(NH_3)_5](NO_3)_3$, 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 7 (109) suggesting hydrolysis of the coordination complex (see ref 28, p 115). If the system contains a photosensitizer such as riboflavin, termination is enhanced by increasing the concentration of the coordination complex. 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 suppressed 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 vinyl photopolymerization 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, 247). Many other dyes, notably those of the fluorescein, the acridine (actually the 3,6-diaminoacridines), and the thiazine families 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 photoautoxidation (241, 248). 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 ethylenediaminetetraacetic acid and other secondary and tertiary amines serves as electron donors for light-excited dyes (258).

Very high quantum yields of monomer conversion were achieved with acrylamide using riboflavin as the photosensitizer (262). Introduction of glycerol into the system suppresses termination because of the diffusional process discussed in section II.A. 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 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 competitively with light-excited dye in the metastable excited state (248). 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 (111). 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 a chain terminator. Another way of destroying dimers of the dye is to add anionic 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 calcium 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 by varying the light intensity, for example) (261). This inverse relation is attributed to chain termination by stable dye photoperoxides produced during the induction period. Photopolymerization of acrylamide with a few per cent of a diallyl monomer produces by dye sensitization a practically grainless three-dimensional image which is nonscattering 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 (246).

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