coupling alone was determined by repeating the experiments in the absence of phenol.

It was found that the dye had the same extinction at *p*H 5.6 and *p*H 6.5, and that Beer's law was obeyed up to a density of at least 0.7 in the 2.5-cm. cell.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Dye-sensitized Photopolymerization of Acrylamide[1]

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The kinetics of polymerization of acrylamide by visible light using riboflavin as the sensitizer has been studied. The reaction proceeds so rapidly that the course of the polymerization can be followed by adiabatic thermal rise. The rate was found to be proportional to the one-half power of the absorbed light intensity, the square of the initial monomer concentration and the one-half power of the viscosity of the medium. The viscosity dependence of the rate was determined in glycerol–water mixtures. The molecular weights of the polymers were of the order of ten millions; they were independent of the initial monomer concentration but increased with increasing viscosity and decreasing intensity. These results are explained in terms of a kinetic scheme which involves the unimolecular disappearance of part of the initiating free radicals and the diffusion-controlled bimolecular termination of the growing chain radicals.

It has been found that vinyl compounds can be polymerized by visible light in the presence of certain dye-reducing agent combinations.[2,3] Dyes in the presence of mild reducing agents undergo photoreduction to their leuco forms.[4] If this photoreduction is carried out in the complete absence of oxygen no polymerization of vinyl monomer ensues. However, if oxygen is added after photoreduction has taken place, polymerization of the monomer commences. Therefore, the free radicals which initiate polymerization arise from the reaction between the leuco dye and oxygen.

The present paper is concerned with the kinetics of the photopolymerization of acrylamide using riboflavin as the sensitizer. Of all the dyes, riboflavin is unique in that part of the dye itself, namely, the ribose group, acts as its own reducing agent. Under the influence of visible light the polymerization, which is an exothermic reaction, proceeds so rapidly that the course of the polymerization can be followed by adiabatic thermal rise. Some of the experiments described herein were designed to elucidate the role of diffusion-controlled processes in high polymer reactions.

Experimental

Materials.—Acrylamide (m.p. 84.5°) was obtained from American Cyanamid Co. Riboflavin 5′-phosphate sodium was obtained from Hoffman–LaRoche. This form of riboflavin is preferable to the non-esterified form in that it is more water-soluble and seems to be more stable to oxidation in solution. Glycerol was Fisher C.P. grade.

Procedure.—The aqueous solutions containing dye and monomer were placed in test-tubes having a diameter of $^3/_4$ in., the volume of the solution being 11 ml. In some cases glycerol–water mixtures were substituted for pure water.

The solutions were placed 12 in. from a 1000-watt Kodak Master projector using a blue cobalt glass (Corning number 5-58) as a filter. Using a calibrated thermopile, it was found that under these conditions 2.6×10^{16} quanta fell on an area of 1 cm.^{2} per sec. Variations in intensity were made using neutral density filters.

The thermal rise accompanying the polymerization was measured with a copper–constantan thermocouple which was placed at the center of the solution. The thermal e.m.f. was amplified by a Leeds and Northrup stabilized d.c. microvolt amplifier and was continuously recorded on a Leeds and Northrup Speedomax Type G recorder. The thermal rise was used to calculate the per cent. conversion of monomer. The polymerization was allowed to proceed until a certain temperature was reached; the resultant mixture was then quickly dissolved in water, and the polymer was precipitated in a large volume of methanol and was filtered, dried and weighed. Knowing the heat capacity of the original solution and assuming adiabatic conditions for this rapid polymerization, an average of ten experiments showed that 20 kcal. are evolved per mole of monomer converted. Hence, in our experiments a temperature rise of one degree centigrade corresponds to a conversion of 5.5×10^{-4} mole of acrylamide.

The viscosities of the mixtures prior to irradiation were measured in an Ostwald viscometer having a flow time for water of 15 sec. Intrinsic viscosities of the polymer produced were determined in an Ostwald dilution viscometer having a flow time for water of 300 sec. Light scattering measurements at various angles were carried out in an Aminco instrument using Ludox for standardization.[5]

Results

In Fig. 1 are illustrated some typical rate curves. After an initial period of illumination the polymerization commences and accelerates until it reaches a constant rate. At about 20% conversion for the systems illustrated in Fig. 1, the reaction is accelerated due to the Trommsdorff effect. If the light is turned off while the reaction proceeds at a uniform rate, the polymerization continues but at a rapidly diminishing rate. This post-polymerization is particularly prolonged in highly viscous solutions. In all cases the rate of the reaction is taken from the slopes of the linear portions of the curves. The induction period is chosen as the intercept of the time axis with the extrapolation of the linear portion of the rate curve.

The monomer concentration (21–64%) was varied keeping all other factors constant. It was found that the rate of monomer consumption was proportional to the second power of the initial monomer concentration. The induction period was not sensibly dependent on the initial monomer concentrations under the conditions described in Fig. 1.

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(1) Presented before the 130th National Meeting of the American Chemical Society, Atlantic City, September 20, 1956.

(2) G. Oster, *Nature*, **173**, 300 (1954).

(3) For other methods of sensitized photopolymerization see G. M. Burnett and H. W. Melville, *Proc. Roy. Soc.* (*London*), **A189**, 481 (1947); M. G. Evans, M. Santuppa and N. Uri, *J. Polymer Sci.*, **7**, 243 (1951).

(4) G. Oster, *Photo. Engr.*, **4**, 173 (1953).

(5) G. Oster, *Anal. Chem.*, **25**, 1165 (1953).

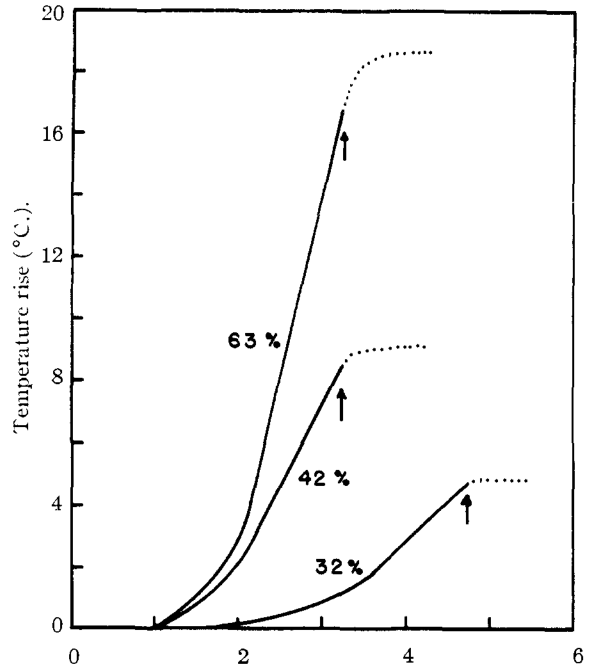

Fig. 1.—Thermal rise as a function of time of irradiation with blue light (4.3 × 10^{-8} einstein absorbed per cm.^{3} per sec.). Percentages on curves give initial monomer concentrations. Concentration of riboflavin 0.01%. Arrows indicate when light is turned off.

The intensity was varied over a 50-fold range keeping the dye and monomer concentration fixed (0.01 and 42%, respectively). The induction period varied roughly inversely as the first power of the intensity, and the rate of polymerization increased proportional to the one-half power of the absorbed intensity (Fig. 2) The same behavior was observed when the absorbed intensity was varied by changing the dye concentration. Beer's law is obeyed for riboflavin over the concentration range considered in this paper and hence the relative intensity of light absorbed is readily calculated.

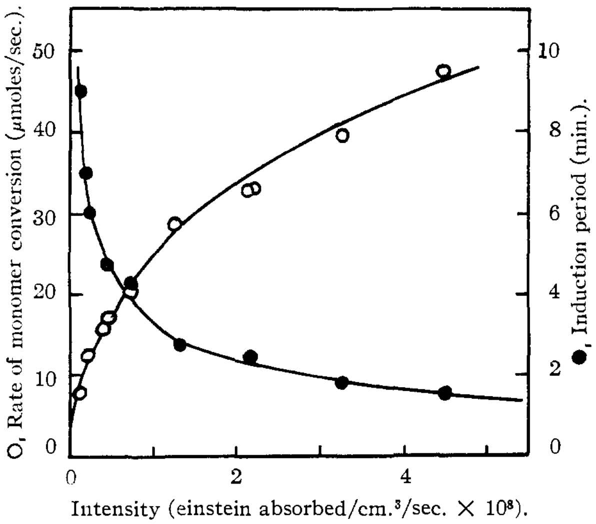

Fig. 2.—Rate and induction period as a function of intensity (monomer concentration 42%; riboflavin concentration 0.01%).

The viscosities of the initial dye–monomer mixtures were varied by substituting part of the water by glycerol (concentrations up to 90% by weight of glycerol). The induction period was sensibly independent of the viscosity of the mixture but the rate of polymerization was proportional to the square root of the viscosity of the medium (Fig. 3).

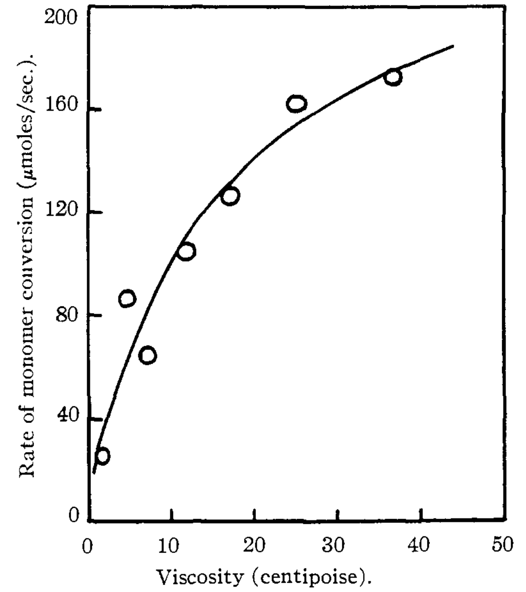

Fig. 3.—Rate as a function of the viscosity of the medium (monomer concentration 30%; riboflavin concentration 0.01%; 4.3 × 10^{-8} einstein absorbed per cm.^{3} per sec.).

Some qualitative experiments were performed with aqueous dye–monomer mixtures. The photopolymerization did not take place at all in the total absence of oxygen achieved by flushing the solution with carefully purified nitrogen for one hour prior to the irradiation. In other experiments mixtures of nitrogen and oxygen in varying proportions were bubbled through the solutions and it was found that the greatest over-all rate of polymerization was achieved with about 1% oxygen in the gaseous mixture. Since our quantitative experiments were carried out under atmospheric conditions, they obviously were not under optimal conditions.

In some experiments the illumination was arrested shortly before the onset of polymerization and the system was then allowed to stand in the dark. On irradiating this pre-illuminated solution, no induction period was observed but the photopolymerization commenced almost immediately. If the same experiment is performed but air is bubbled through the pre-illuminated solution while it is standing in the dark, the system exhibits another induction period when irradiated for the second time. With the addition of allyl thiourea (concentration 10^{-2}%) the induction period is markedly decreased.

The intrinsic viscosities (in 0.1 *N* KCl) of the polymer samples were extraordinarily high, with values varying between 11 and 30 deciliters per g.

The highest values were obtained either when the polymerization was carried out in glycerol mixtures or when very low light intensities were employed. Variation of the initial monomer concentration had no effect on the intrinsic viscosities of the resulting polymers. Solutions containing very small amounts of dye (less than 0.001%) when polymerized were so viscous that they were unmanageable and their intrinsic viscosities certainly exceeded 30 deciliters per g. The intrinsic viscosity $[\eta]$ of polyacrylamide as a function of molecular weight, M, has been given[6] as $[\eta] = 3.73 \times 10^{-4} M^{0.66}$. Hence we calculate that the molecular weights of the samples, whose intrinsic viscosities could be measured, range from 5.1 millions to 22.8 millions.

Light scattering measurements were carried out on the polymer samples starting with a 1% polymer solution (in 0.1 N KCl) which had been subjected to centrifugation to remove dust particles. The dissymmetry at 45 and 135 degrees when extrapolated to infinite dilution gave a value of about 3.0 for all the samples. The scattering envelope is that expected for a tightly coiled molecule. The extrapolated values of the reciprocal specific turbidity corrected for dissymmetry showed that the weight average molecular weights of all the samples exceeded five millions.

Discussion

The mechanism for the production of the initiating free radicals in dye-sensitized photopolymerization is imperfectly understood at the present time. The light-excited dye undergoes reduction in the presence of a hydrogen donor. This reduced form of the dye is oxidized by oxygen to some intermediate form which participates in the formation of substances needed in the initiation of polymerization. This is borne out by the fact that visible light in the total absence of oxygen reduced the dye to a colorless form but no polymerization takes place. Polymerization occurs either when oxygen is present during the irradiation or is introduced after the photoreduction has taken place. For certain sensitizers there is spectral evidence to show that vinyl compounds participate in the formation of the initiating free radical.[7]

The polymerization of acrylamide, as is observed with other monomers, is inhibited by oxygen. Since oxygen is necessary in photopolymerization for the formation of initiating radicals, there should be some optimal concentration of oxygen where the reaction proceeds but with a negligibly small induction period, as was found to be the case. Excess oxygen which inhibits polymerization is consumed during the induction period by some compound which is formed in the light. Higher intensities increase the rate of formation of this oxygen-consuming compound and hence shorten the induction period. Riboflavin sensitizes the autoöxidation of allyl thiourea which is accompanied by the consumption of oxygen and hence the induction period is decreased by the addition of allyl thiourea.

Dye-sensitized photopolymerization can proceed at rates far exceeding that of any other controllable free radical initiated polymerization. For example, with 42% monomer and 0.01% dye the quantum yield for conversion of monomer using an intensity of 1.35×10^{-9} einstein/sec./cc. absorbed blue light is 4.9×10^{3}. Still higher quantum yields are achieved using lower light intensities. The extraordinarily high rate of this reaction is probably not due to any unusually high value for the rate constants of the chain propagation steps. The rate of initiation cannot be particularly great since the molecular weights of the polyacrylamide samples obtained are extremely large. It therefore appears that the high rate of polymerization is caused by a very low rate of termination between the growing polymer radicals. Apparently, the free radical polymer ends are not easily accessible. The light scattering data show that these very large molecules are compact (possibly due to hydrogen bonding between the polymer chain members) and this would favor the shielding of the radical chain ends of the growing polymer.

Since the chain radicals are very large, termination of bimolecular encounters between the chain ends should be diffusion-controlled. This effect is particularly enhanced if the chain ends are hidden somewhere in the very large polymer molecules. Since diffusion constants decrease with increasing viscosity of the medium, the rate of termination should be decreased by the addition of glycerol to the solution. The slow termination is manifested by the prolonged post-polymerization of these systems which is particularly pronounced when the viscosity is high.

The rate of monomer conversion was taken from the linear part of the curves since this portion is associated with the steady-state polymerization. The toe in the early stages of the reaction is the non-steady portion of the polymerization.[8]

A kinetic scheme which is compatible with our experimental observations can now be proposed. This scheme involves two features which are not contained in typical catalyst-initiated vinyl polymerizations. Firstly, we assume that the monomer itself participates in the formation of the initiating free radicals. Secondly, we assume that some of the initiating radicals produced are rendered inactive by a unimolecular process. The elimination of radicals from the polymerization reaction could arise by entrapment of the radicals in the polymer or by a spontaneous conversion to a non-initiating free radical. The first assumption is represented symbolically by step 1. This process actually involves several steps whose net effect is the absorption of light and the consumption of monomer to produce an initiating free radical.[7,9] The scheme is then given by

(1) $\mathrm{M} + \mathrm{D} \xrightarrow{h\nu} \mathrm{R}\cdot$ (formation of initiating radicals by light)

(2) $\mathrm{R}\cdot + \mathrm{M} \longrightarrow \mathrm{RM}\cdot$ (initiation of the chain)

(3) $\mathrm{RM}\cdot + \mathrm{M} \longrightarrow \mathrm{RM}_2\cdot$ (propagation steps, each with the same rate constant)

$\vdots \quad \vdots \quad \vdots$

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[6] "Polyacrylamide," New Product Bulletin, American Cyanamid Co., New York, N. Y., 1955.

[7] G. K. Oster, to be published.

[8] See M. Magat, *J. Polymer Sci.*, **16**, 491 (1955), for quantitative treatment.

[9] G. Oster and A. H. Adelman, This Journal, **78**, 913 (1956).

$RM_n\cdot + M \longrightarrow RM_{n\cdot + 1}$

(4) $RM_n\cdot + RM_n\cdot \longrightarrow P$ (formation of "dead" polymer by bimolecular termination)

(5) $R\cdot \longrightarrow S$ (removal of initiating radicals from the reaction)

Applying the steady-state hypothesis with respect to the concentrations of the initiating radicals R· and of the growing chain radicals $RM_n\cdot$, and neglecting the monomer consumption in the initiation step 2 compared with that of the propagation steps 3, we obtain for the rate of consumption of monomer

$$-\frac{d(M)}{dt} = k_3(M)\left[\frac{k_2}{k_4} \times \frac{k_1 I (M)^2}{k_2(M) + k_5}\right]^{1/2}$$

where I is the intensity of light absorbed. If it is further assumed that the velocity of initiation (step 2) is negligible compared with the rate constant for the elimination of radicals (step 5) then agreement with experiment is obtained. The rate of monomer consumption is proportional to the second power of the monomer concentration, as is observed, and to the square root of the light intensity, as is observed. Incidentally, it follows from this latter fact that the quantum yield is inversely proportional to the square root of the intensity. For a diffusion-controlled termination of growing radicals k_4 should be inversely proportional to the viscosity of the medium. Hence the rate of monomer consumption should be directly proportional to the square root of the viscosity, as is observed.

The number average degree of polymerization $\overline{DP}$ which is the rate of propagation divided by the rate of initiation of growing radicals, becomes for our scheme, using the approximations mentioned above

$$\overline{DP} = k_3\left(\frac{k_5}{k_1 k_2 k_4}\right)^{1/2} \frac{1}{I^{1/2}}$$

This is in agreement with our qualitative observations, namely, that the molecular weight is greater the greater the viscosity of the medium and the smaller the light intensity but is independent of monomer concentration.

It should be noted that both the rate *and* the molecular weight are increased by the simple expedient of increasing the viscosity of the medium.

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