*Dye-sensitized Photopolymerization of Vinyl Monomers. I. Preliminary Report on the Polymerization of Acrylonitrile by Various Dyes**

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In the past decade it has been found that vinyl monomers can be polymerized by visible light in the presence of certain dyes[1-10]. The following types of the mechanism of dye-sensitized photopolymerization have been proposed; (1) direct energy transfer from the excited dye to monomer[3], (2) direct interaction between an excited molecule of the dye and the vinyl monomer[5,6,10], and (3) the production of free radicals by the self-decomposition of the excited dye or by the reaction of the excited dye with a third substance involved in the system[4,8].

Ueberreiter and Sorge[3], in their study of the sensitized polymerization of styrene by neutral red, attributed the chain initiation to the transference of energy from the excited dye to the monomer. However, Miyama[7] reported later that the polymerization by neutral red was really accompanied by a decomposition of the dye. Koizumi and Watanabe[6,10] investigated the photopolymerization of styrene induced by excited cyanine dyes. They established that direct interaction between the excited dye and the monomer was responsible for the initiation of polymerization. It was shown by Oster et al.[4,8] that vinyl compounds such as acrylonitrile or acrylamide could be polymerized by using the proper combination of a certain dye and an appropriate reducing agent in the presence of oxygen.

From the photochemical point of view, the first two types, in particular the first type, are interesting and important, but there are few reports on the sensitized polymerization belonging to these types. The present investigation was undertaken to select the dyes capable of sensitizing the polymerization of vinyl monomers even in the absence of a third substance and oxygen; it aimed, namely, at selecting such dyes whose excited state might directly take part in the initiation of polymerization, so as to elucidate the mechanism of polymerization sensitized by an excited dye.

Acrylonitrile was used as a vinyl monomer. One of the reasons for this selection is that aqueous solutions of dyes can be conveniently used, as acrylonitrile is able to some extent to dissolve water in itself. Another reason is that the progress of polymerization can be followed by observing the precipitation of its polymer insoluble to the system. Then acridine yellow, when chosen for a more detailed study, was found to be the most effective as a sensitizing agent.

Experimental

Materials.—Commercial acrylonitrile was purified by successive washings with dilute sulfuric acid, an aqueous solution of sodium carbonate, and water. After drying with calcium chloride, it was twice distilled at atmospheric pressure and stored in a dark room.

The dyes used in these experiments were arbitrarily chosen; most of them were made by E. Merck Co. or by G. Grübler Co. The aqueous solutions of dyes were prepared without further purification, the concentrations being about 10^{-2} mol./l.

Experimental Procedure.—In the preliminary experiments, 3 ml. of acrylonitrile and 2 drops of

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1) C. H. Bamford and M. J. S. Dewar, *J. Soc. Dyers Colourists*, **65**, 674 (1949).

2) M. Koizumi, Z. Kuroda and A. Watanabe, *J. Inst. Polytech. Osaka City Univ.*, **2C**, 1 (1951).

3) K. Ueberreiter and G. Sorge, *Z. Elektrochem.*, **57**, 795 (1953).

4) G. Oster, *Photo. Eng.*, **4**, 173 (1953); *Nature*, **173**, 300 (1954).

5) M. Koizumi, A. Watanabe and Z. Kuroda, ibid., **175**, 770 (1955).

6) M. Koizumi and A. Watanabe, This Bulletin, **28**, 136 (1955); A. Watanabe and M. Koizumi, ibid., **28**, 141 (1955).

7) H. Miyama, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 1013, 1016, 1361 (1955); **77**, 691 (1956).

8) G. Oster and Y. Mizutani, *J. Polymer Sci.*, **22**, 173 (1956); M. Taniyama and G. Oster, This Bulletin, **30**, 856 (1957); G. K. Oster, G. Oster and G. Prati, *J. Am. Chem. Soc.*, **79**, 595 (1957).

9) J. J. Moran and H. J. Stonehill, *J. Chem. Soc.*, **1957**, 788.

10) A. Watanabe, This Bulletin, **32**, 557 (1959).

an aqueous solution of a dye were put into a glass tube (8 mm. in diameter; 15 cm. in length). The tube was attached to the vacuum system (10^{-4} mmHg), degassed three times by successive evacuations and thawings, and then sealed off. All of these procedures were carried out in a dark room. The concentrations of dyes in the reaction systems thus prepared were of the order of 10^{-4} mol./l. These tubes were placed in a thermostat (40°C) and illuminated for 24 hr. with a 500 W. tungsten lamp 1 m. distant from them. The polymers thus obtained were separated by the use of glass filters, washed with water, and dried to a constant weight. When the concentrations of dyes in the reaction system were allowed to change, more diluted aqueous solutions of dyes were used for the above-mentioned procedure instead of the original stock-solutions.

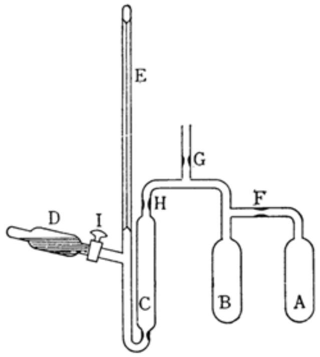

Fig. 1. Dilatometrical apparatus.

A, B : Reservoir for monomer and dye-solution respectively
C : Reaction vessel
D : Reservoir for Hg
E : Capillary tube (30 cm. long)
I : Stopcock

The kinetic experiments were studied dilatometrically, the reaction vessel being suspended in a thermostat (30 or 50°C). Figure 1 shows a schematic representation of the type of dilatometer used in these experiments. This dilatometer was designed to fill its capillary tube with mercury purposely to avoid the precipitation of polymers in it. Definite amounts of the monomer and of the dye solution in *n*-butanol were weighted in storage reservoirs A and B respectively. After a through evacuation as described above, the monomer in A was distilled into B in vacuo and mixed there with the dye solution. Then, the dilatometer was sealed off from reservoir A at F and also from the vacuum system at G. Finally, all of the reactant in reservoir B was allowed to pour into the reaction vessel C by inclining the reservoir. The dilatometer was enclosed at the top of reaction vessel H, turned upside down with caution while keeping the reactant in the reaction vessel, and filled up with mercury through the stopcock I. The meniscus of mercury in the capillary tube being adjusted, the dilatometer was immersed in a thermostat. After thermal equilibrium had been attained, the change in the meniscus was followed by a cathetometer. The light source was a 500 W. tungsten lamp 50 cm. distant from the thermostat.

The rate of polymerization was calculated from the rate of contraction, assuming that a 23.5% contraction at 30°C and a 25.7% contraction at 50°C correspond to a 100% conversion of the monomer[11].

The viscosities of the solutions of acrylonitrile polymers in dimethylformamide were measured at 30°C in an Ostwald viscosimeter. The molecular weights were calculated by using the following equation quoted by Bamford and Jenkins[11]:

$$[\eta]=1.75\times10^{-3}M^{0.66}$$

where the concentration unit was g./100 ml.

Experimental Results and Discussion

The Sensitizing Effects of Various Dyes on the Polymerization of Acrylonitrile. — Table I shows a series of comparative experiments. Of

TABLE I. SENSITIZED PHOTOPOLYMERIZATION OF ACRYLONITRILE BY VARIOUS DYES

Dye group	C. I. No.	Dye	Sensitization*
Nitroso	1	Resorcin green	+
Monoazo	20	Chrysoidine	−
	77	Palatine scarlet A	−
	142	Methyl orange	+
	143	Trapaeolin OO	−
	148	Trapaeolin O	−
	151	Orange II	−
	176	Fast red A	+
Diazo	238	Anthracene brown	+
	252	Crocein scarlet 3B	−
	370	Congo red	−
Pyrazolone	640	Tartrazine	+
Triphenylmethane	657	Malachite green	+
	677	Fuchsine	−
	679	Hoffman's violet	++
	680	Methyl violet	++
	684	Methyl green	+
	705	Soluble blue	−
Xanthene	739	Pyronine G	+++
	766	Uranine	++
	768	Eosine	++
	772	Jodeosine	++
Acridine	785	Acridine yellow	+++
	790	Acryflavine	+++
Indamine	820	Toluylene blue	+
Azine	825	Neutral red	+
	841	Saflanine T	++
Thiazine	922	Methylene blue	+

* In this column, (−) points out no polymerization induced and (+), (++) and (+++) indicate that the polymerization have been well accelerated in that order: namely, (+) shows the conversion less than 1% in 24 hr., (++) less than 10%, and (+++) more than 10%.

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[11] C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc.* **A216**, 515 (1953).

course, no polymerization was induced by any dye in the dark at 40°C. From Table I, it will be seen that the overall efficiency varies over a very wide range. Of all the dyes tested, acridine dyes are the most effective, followed by xanthene dyes. It was shown by Oster⁽⁴⁾ that acrylonitrile in an aqueous solution could be polymerized by eosin and erythrosin (jodeosin) only in the simultaneous presence of a mild reducing agent and of oxygen. However, in the present preliminary experiments, both eosin and erythrosin were shown to be able to induce to some degree the polymerization, even in the absence of a reducing agent and of oxygen.

The concentrations of dyes used in these preliminary experiments were not necessarily the same for all dyes, though they were of the order of 10^{-4} mol./l. Thereupon, the dependence of the rate of polymerization on the concentration of these effective dyes was roughly examined; the results are shown in Fig. 2. For acridine yellow and acryflavine, there appears to be an optimum concentration, probably indicating that they play the role of retarder for polymerization as well as that of sensitizer.

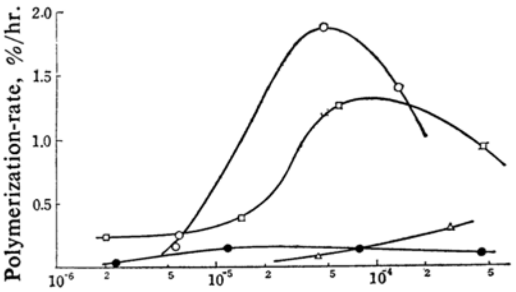

Fig. 2. Dependence of the rate of photopolymerization of acrylonitrile on dye-concentration.
○ Acridine yellow ● Iodeosin
□ Acryflavine △ Pyronine

In view of the fact that acridine yellow is the most effective, this dye was chosen for a more detailed study in these preliminary investigations.

Acridine Yellow-Sensitized Polymerization of Acrylonitrile.—The course of a typical run is shown in Fig. 3, where it will be seen that there is a gradual increase in the rate of contraction and, thus, in the rate of polymerization also, until a steady state is reached. This would appear to mean that the initial stage of polymerization is complicated by the necessity of generating some intermediate product before real sensitization can occur, or by an induction period resulting from the presence of a trace of an inhibitor such as oxygen.

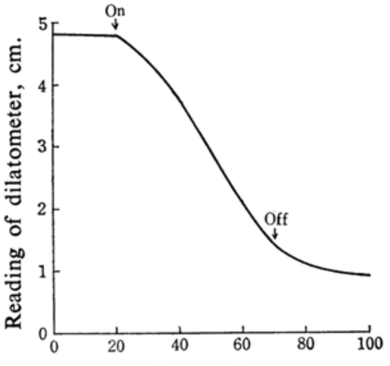

Fig. 3. Course of acridine yellow-sensitized polymerization of acrylonitrile.

When the light was switched off, the reaction did not cease immediately but exhibited a long decay period. This may be caused by the after-effect owing to the presence of trapped radicals in the precipitated polymers. Bamford and Jenkins⁽¹¹⁾ made a kinetic study of the polymerization of acrylonitrile and found that the reaction showed kinetic features which were different from those of homogeneous vinyl polymerization, e.g., (a) an initial increase in rate with time in the thermal catalyzed- and photo-polymerization, and (b) a photochemical after-effect. The observations in the present study are similar to those made by Bamford and Jenkins.

When the steady rates of polymerization are plotted against the concentration of acridine yellow (Fig. 4), the rate is shown to be proportional to the concentration in the range studied at both temperatures (30 and 50°C). This seems to be different from the usual

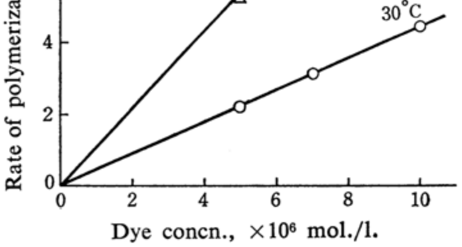

Fig. 4. Dependence of polymerization-rate on dye concentration.

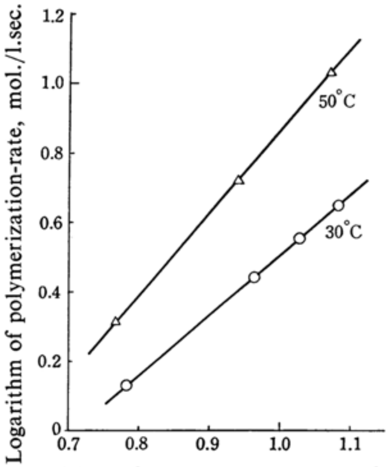

Fig. 5. Dependence of polymerization-rate on acrylonitrile concentration.

cases, in which the rate depends upon the square root of the concentration of the sensitizer, and seems to be characteristic for the polymerization of acrylonitrile in a heterogeneous system, in which Thomas and Pellon[12] have shown a 0.82 power dependence of the rate on the concentration of an initiator (azobisisobutylonitrile).

In Fig. 5 the logarithm of the rate is plotted against the logarithm of the monomer concentration, which was changed by the use of *n*-butanol as a solvent. The experimental points determine a line whose slope is about 1.7 and 2.4 at 30 and 50°C respectively. It is difficult at present to interpret these results satisfactorily, but Nakatsuka[13] has also found a discrepancy in the dependence of the rate on the monomer concentration between at 30°C and at 60°C, i. e., one power and two power dependence at the two temperatures respectively. This discrepancy may be attributed to the heterogeneous condition of the polymerization of acrylonitrile. In view of such a higher power dependence of the rate on the monomer concentration, it seems probable that the monomer plays a part in the initiation process, together with an excited molecule of the dye, and that the interaction between them give rise to the bleaching of the dye.

The dependence of the molecular weight of the polymer thus obtained on the dye and the monomer concentration were also investigated. They are shown in Tables II and III, together with kinetic data. It is worth noticing that the molecular weight of polymer is nearly independent of the dye concentration at 30°C, although the rate is dependent on it. From Table III it is found that the molecular weight decreases with the decrease in the monomer concentration. This may be caused by chain transfer to the solvent and will be discussed below in detail.

TABLE II. THE EFFECT OF ACRIDINE YELLOW CONCENTRATION ON THE RATE OF POLYMERIZATION OF ACRYLONITRILE AND ON THE MOLECULAR WEIGHT OF ITS POLYMER

Temp. °C	Concn. of dye $\times 10^{-6}$ mol./l.	Concn. of monomer mol./l.	Rate $\times 10^{-5}$ mol./l.sec.	$\overline{M}$ $\times 10^4$
30	10	12.1	4.46	12.6
	7	12.1	3.12	11.0
	5	12.1	2.22	11.7
50	10	11.7	10.8	9.40
	7	11.7	7.93	—
	5	11.7	5.25	—

TABLE III. THE EFFECT OF MONOMER CONCENTRATION ON THE RATE OF POLYMERIZATION OF ACRYLONITRILE AND ON THE MOLECULAR WEIGHT OF ITS POLYMER

Temp. °C	Concn. of monomer mol./l.	Concn. of solvent mol./l.	Rate $\times 10^{-5}$ mol./l.sec.	$\overline{M}$ $\times 10^4$
30	12.1	2.19	4.46	12.6
	10.6	3.28	3.62	—
	9.15	4.38	2.78	5.85
	6.05	6.56	1.35	2.87
50	11.7	2.1	10.8	9.40
	8.7	4.2	5.3	2.92
	5.8	6.4	2.1	1.60

The overall activation energy can be roughly estimated from the rates at two temperatures. It is about 8.6 kcal./mol., the value being conceivable for the photochemical reaction.

In short, these results are not concordant with a simple familiar theory on homogeneous free radical polymerizations with respect to the following points: (1) one power dependence of the rate on the sensitizer concentration, (2) a higher power dependence of the rate on the monomer concentration, and (3) the molecular weight of the polymer independent of the sensitizer concentration.

Development of a Kinetic Scheme. — In developing a kinetic scheme to account for these observations, it is assumed that: the polymers obtained in this system, being highly insoluble in the monomer, precipitate as soon as they are formed, so that the propagating free radical chains become occluded in polymer aggregates during polymerization, resulting in a unimolecular termination. As mentioned above, the initiation process seems likely to be an interaction between the excited dye and the

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[12] W. H. Thomas and J. J. Pellon, *J. Polymer Sci.*, **13**, 329 (1954).

[13] K. Nakatsuka, *Chem. High Polymers* (*Kobunshi Kagaku*), **14**, 613 (1957).

monomer, which leads also to bleaching of the dye. Therefore, the reaction scheme will be as follows:

Absorption	$D \xrightarrow{h\nu} D^*$	I
Deactivation	$D^* \rightarrow D +$ heat or light	
Initiation	$D^* + M \rightarrow R\cdot$	k_i
Propagation	$R\cdot + M \rightarrow R\cdot$	k_p
Transfer to monomer	$R\cdot + M \rightarrow P + R\cdot$	k_{trM}
Transfer to solvent	$R\cdot + S \rightarrow P + S\cdot$	k_{trS}
Reinitiation	$S\cdot + M \rightarrow R\cdot$	k'_{tr}
Termination	$R\cdot \rightarrow P$	k_t

where D, D*, M, S, R·, S· and P indicate dye, excited dye, monomer, solvent, propagating free radical, solvent radical and stable polymer involving an occluded radical respectively. Furthermore, I is the light intensity absorbed, and k_i, k_p, k_{trM}, k_{trS}, k'_{tr} and k_t are the rate constants of initiation, propagation, transfer to monomer, transfer to solvent, reinitiation of solvent radical and termination respectively.

Assuming that most of the excited molecules of the dye are deactivated with the release of energy and also that these concentrations are proportional to the light intensity absorbed or approximately to the dye concentration at the constant light intensity, the following reaction rate, R_p, may be given by the steady-state treatment:

$$R_p = \frac{-d[M]}{dt} = \frac{kk_ik_p}{k_t} I[D][M]^2 \qquad (1)$$

where k is a constant, corresponding to the quantum efficiency for the initiation. The average degree of polymerization of polymer, $\overline{P}$, may be expressed by

$$\overline{P} = \frac{k_p[M]}{k_t + k_{trS}[S]} \qquad (2)$$

if the chain transfer to the monomer is disregarded. In regard to the variation in dye concentration, the experiments support Eq. 1, although the dependence of the rate on the monomer concentration is not necessarily coincident with the experimental results. This may be due to the complications of the heterogeneous system. The experimental finding that the molecular weight of the polymer is independent of the dye concentration at the constant monomer concentration appears to satisfy Eq. 2.

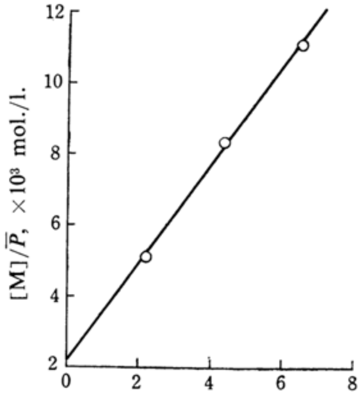

Fig. 6. Plots of $[M]/\overline{P}$ against butanol concentration according to Eq. 3.

As shown above, the molecular weight of the polymer varied with the concentration of the monomer. Supposing that the proposed kinetic scheme is true, the degree of polymerization must be given by Eq. 2, rewriting it, the following equation is obtained:

$$\frac{[M]}{\overline{P}} = \frac{k_t}{k_p} + \frac{k_{trS}}{k_p}[S] \qquad (3)$$

Eq. 3 shows that $[M]/\overline{P}$ will vary in a linear relation with the solvent concentration. The data at 30°C fell reasonably close to a straight line, as shown in Fig. 6, though those at 50°C did not do so well. The slope of the line gives a value of k_{trS}/k_p of 13.7×10^{-4}, while the intercept gives a value of k_t/k_p of 22×10^{-4} mol./l.

As described above, the conclusion that the initiation process is the interaction between excited dye and monomer has been obtained only from the kinetic study of the polymerization. However, it will be desirable to confirm it from a absorption-spectrometric investigation of the dye in the reaction system. Such a kind of investigation was abandoned in the present system, due to the disturbance of the insoluble polymers, but it will be taken up in future studies, so as to elucidate the mechanisms of sensitization in detail.

Summary

Among various dyes, the dyes suitable for the sensitization of the polymerization of acrylonitrile have been determined. Acridine and xanthene dyes have been found to be the most effective.

Using acridine yellow, one of the most effective, the dye-sensitized photopolymerization has been investigated in detail; it has been shown that the reaction has several features characteristic of heterogeneous polymerization, e. g., its order is higher than one-and-a-half on monomer concentration.

Assuming the initiation process to be a direct interaction between excited dye and

monomer, and assuming the unimolecular termination by occlusion of the propagating radicals, the kinetic data has been interpreted.

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