Dye-sensitized Photopolymerization of Vinyl Monomers. II. Photobleaching of Acridine Yellow in Some Vinyl Monomers[*]

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In the first paper of this series[1], it was reported that, among the various dyes tested, acridine yellow was the most effective in sensitizing the polymerization of acrylonitrile and that, from the kinetic study of that polymerization using this dye, the initiation of polymerization seemed to be attributable to the direct interaction of the excited molecule of the dye with the monomer. However, no knowledge of the behavior of the dye in the course of polymerization could be obtained, since it was impossible to measure the absorption spectra of the dye in the reaction system because of the precipitation of polymers thereby produced.

Now, in order to account in more detail for the mechanism of such a sensitization by acridine yellow, we have undertaken to examine the bleaching of the dye in some vinyl monomers (vinyl acetate, styrene, α-methylstyrene and methyl methacrylate) besides acrylonitrile, and to discuss the mechanism of sensitization.

Experimental

Materials.—Acrylonitrile was purified by the same method as that employed in the first paper[1]. Vinyl acetate was obtained from the Katayama Kagaku Co. and was distilled three times at atmospheric pressure. It was shown by dilatometrical measurement that, whenever vinyl acetate and a solution of the dye were put together into a reservoir and were degassed in vacuo, the monomer was appreciably polymerized even in the dark, perhaps owing to impurities such as aldehyde. This was overcome by further distillation of the monomer in vacuo. Therefore, not only vinyl acetate but also all of the other monomers were enclosed in reaction vessels by the procedure of distillation in vacuo as described below. Styrene was prepared from β-phenylethyl alcohol by dehydration, heating it with caustic potash. The crude styrene thus obtained was washed with aqueous solutions of caustic soda and sodium bisulfite, dried with calcium chloride, and distilled twice under reduced pressure. α-Methylstyrene was obtained from the Tokyo Kasei Co. and was purified in the same way as styrene. Methyl methacrylate was made by the Fujikura Kagaku Co. It was shaken with an aqueous caustic soda solution to remove the inhibitor, washed with water, dried with potassium carbonate anhydride, and then twice distilled under reduced pressure.

Acridine yellow was added to the reaction systems as a *n*-butanol solution with the exception of the case of acrylonitrile. Azobisisobutylonitrile was twice recrystallized from ethanol. Hydroquinone was used without further purification.

Apparatus.—The thermostat was doubly constructed; the inner bath was regulated within ±0.002° at 30°C, and the outer bath, within ±0.02° at a slightly lower temperature than 30°C. The cell holder supporting a reaction vessel in the inner bath was the same as that usually used in a spectrophotometer. The light source (a 75V,750W. tungsten projection lamp) in the outer bath was convered with a metallic housing with a window and was supplied by a. c. source controlled at 60 V. by means of a voltage regulator or by means of a slide rheostat and a resistance box. In order to prevent overheating caused by the light source, cold water was forced to flow into the metallic housing during the experiment by a gear pump controlled by a relay connected with a toluene-Hg regulator.

In all of the experiments, a Mazuda color glass filter V-B3$_B$ was inserted between the reaction vessel and the light source. It had its maximum transmission near the maximum (about

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[*] Presented at the 11th Annual Meeting (April, 1958) and at the 12th Annual Meeting (April, 1959) of the Chemical Society of Japan.

[1] F. Takemura, This Bulletin, 35, 1073 (1962).

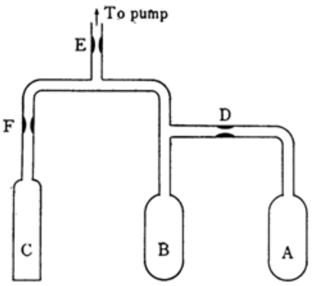

Fig. 1. The glass apparatus for sampling.
A, B; Reservoir
C; Reaction vessel

460 mμ) of the absorption band of acridine yellow. The intensity of light was, if necessary, changed with a blackened metallic net, whose shielding efficiency was 30.5%.

The reaction vessel was the same glass cell, 1 cm. in thickness, used as a absorption cell for a spectrophotometer except that it was provided with an arm, as is shown in Fig. 1.

Experimental Procedure.—In the glass apparatus shown in Fig. 1, definite amounts of monomer and dye-solution were weighted in storage reservoirs A and B respectively. After complete degassing by successive evacuation and thawing, the monomer in A was distilled into B in vacuo and mixed with the dye-solution. Then, having been sealed off from reservoir A at D and from the vacuum system at E, the reaction vessel was filled with the reaction mixture by inclining it and was sealed off at F. The quantity of the reaction mixture was sufficient to fill it up above the edge of the window of a cell holder, and if necessary, it was obtained from the initial quantities of monomer and dye-solution substracted the residual quantity in reservoir B.

Generally the reaction systems in photobleaching experiments were prepared from 1 ml. of an acridine yellow solution in *n*-butanol and 3 ml. of vinyl monomers. The initial concentrations of the dye in the reaction systems were about 2×10^{-5} mol./l. In changing the monomer concentration,the monomer was replaced with appropriate amounts of a suitable solvent, e. g., ethyl acetate instead of vinyl acetate, or benzene or ethylbenzene instead of styrene, α-methylstyrene and methyl methacrylate. By way of exception, acrylonitrile was diluted with dimethylformamide, which was a good solvent for the polymer of acrylonitrile. Otherwise polyacrylonitrile would be precipitated in the course of the reaction. The dye was, of course, added as a solution in dimethylformamide in this case.

In a run of irradiation, the vessel was taken out of the thermostat at some minutes' intervals, and the absorption spectra were measured with a Hitachi spectrophotometer (model EPU-2).

Results and Discussion

Preliminary Tests of the Photobleaching in Various Solvents.—The bleaching of the dye was preliminarily investigated in such solvents as dimethylformamide, methanol, *n*-butanol, benzene and ethylbenzene. In these experiments one of these solvents (except dimethylformamide) was taken up instead of the monomer in the recipe of the reaction mixture described above. (As the bleaching of the dye in the solution of acrylonitrile in dimethylformamide needed to be compared with that in dimethylformamide alone, the dye was added as a solution in dimethylformamide in this case.)

In all solvents examined, the bleaching of the dye was very slight even in the light, not to mention in the dark, and may be considered negligible as compared with the photobleaching in the presence of monomers. Therefore, the appreciable photobleaching in the presence of monomers described below is undoubtedly due to the interaction of some excited molecules of the dye with the monomers.

No bleaching was observed when a solution of the dye in benzene was heated in the presence of azobisisobutylonitrile at 60°C for 80 min. From this finding, it appears that the dye is not attacked by radicals from azobisisobutylonitrile nor, presumably, by polymer radicals.

Photobleaching in the System of Acrylonitrile.—No shift of the absorption maximum of the dye in this reaction system was observed during irradiation, and the main absorption band in the visible region declined monotonously with irradiation. The relation of the optical density at the absorption maximum (465 mμ) to the irradiation time is simple, with no induction period (Fig. 2).

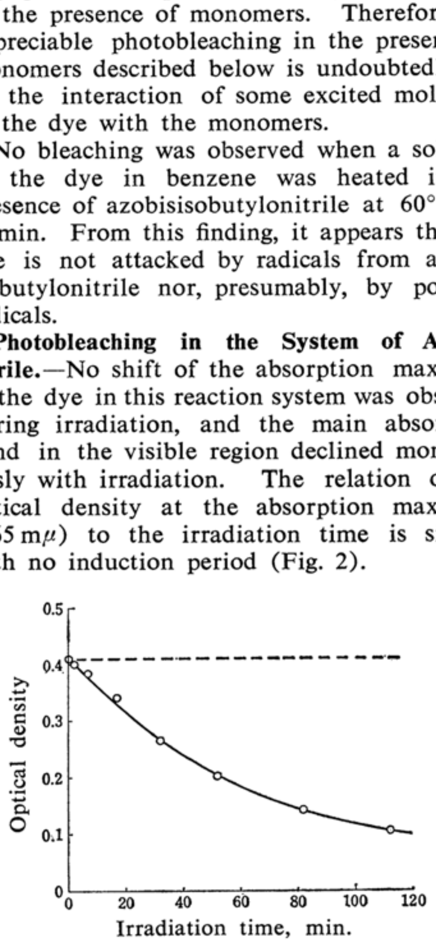

Fig. 2. The variations of optical densities at 460 mμ of the dye in acrylonitrile with irradiation time.
Dotted line; in the presence of KI or in the dark

After the irradiation, the reaction mixture was poured into a large amount of methanol, and the polymer was precipitated. Therefore, the bleaching seems to be accompanied by the polymerization of acrylonitrile.

In the presence of potassium iodide, which was added as a quencher of fluorescence, it was shown that neither photobleaching nor polymerization occurs. This fact suggests that the singlet-excited dye molecule would otherwise lead to the photobleaching and the polymerization.

Rate Formula of the Bleaching.—According to Imamura[2], such a simple photobleaching curve can be expressed by Eq. 1 under the assumption that the rate of photobleaching depends on and is proportional to only the light absorbed:

$$-\frac{dc}{dt}=k'I_0(1-e^{-\alpha cd}) \tag{1}$$

where c is the concentration of the dye; d, the thickness of the solution, α, the average molar absorption coefficient; I_0, the total light intensity, and k', the overall rate constant.

By integration, Eq. 1 may be transformed into

$$\ln(1-e^{-\alpha c_0 d})-\ln(1-e^{-\alpha cd}) + \alpha d(c_0-c)=\alpha dk'I_0t \tag{2}$$

where c_0 is the initial concentration of the dye.

For the sake of convenience in dealing with the data, Eq. 2 was rewritten in terms of optical density as follows:

$$\log(1-10^{-D_0})-\log(1-10^{-D}) + D_0-D=\varepsilon dk'I_0t \tag{3}$$

where D and D_0 are the optical densities at time $t=t$ and $t=0$, and ε is the average molar extinction coefficient.

Since ε, d, k' and I_0 are constant in each run, the product, $\varepsilon dk'I_0$, is expressed in k and the left side of Eq. 3 is expressed in terms of S for convenience. Therefore, Eq. 3 shows that S would be proportional to t. As is shown in Fig. 3, it seems that these results are consistent with Eq. 3. From the slope of the straight line, the apparent overall rate constant k was found to be 0.0074 min^{-1} in this experimental condition.

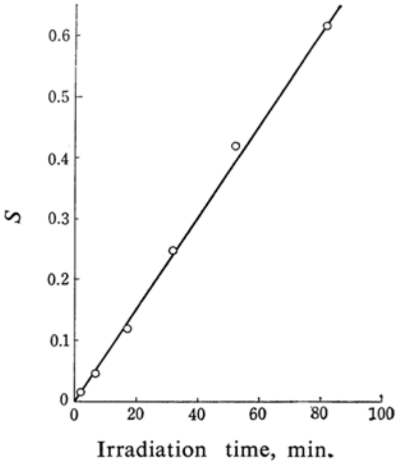

Fig. 3. S vs. irradiation time in acrylonitrile. S is the left side of Eq. 3

In view of the fact that the photobleaching of the dye did not occur in the absence of the monomer but did in its presence, the monomer must play a part in the photobleaching of the dye. However, the relation of the rate of bleaching to the monomer concentration could not be examined, since the monomer concentration was not allowed to increase owing to the precipitation of polymers. Therefore in order to understand more clearly the relationship between photobleaching and polymerization, other vinyl monomers than acrylonitrile were chosen for the following experiments.

Photobleaching in the System of Vinyl Acetate.—The absorption maximum of this system did not shift at various irradiation times, similarly as in the case of acrylonitrile. The optical densities at the maximum wavelength (456 mμ) are plotted against the irradiation time in a series of monomer concentrations in Fig. 4. It has been examined whether or not these photobleachings obey the simple rate formula, Eq. 3. As is seen from Fig. 5, linear relationships between S and t can not be always obtained. However, it may be considered that at the initial stage of irradiation the slopes of these lines correspond to the apparent overall rate constants in various monomer concentrations. Then, these rate constants seem to be roughly proportional to the monomer concentrations. Therefore, it may be concluded that the apparent overall rate constant is also a function of the monomer concentration, and that the photobleaching is not due to the self-decomposition of the dye but to the

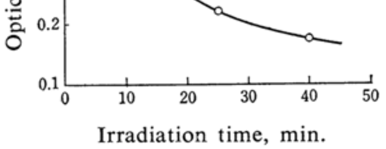

Fig. 4. Variation of optical densities at 456 mμ of the dye in various concentrations of vinyl acetate with irradiation time.
Monomer concn. (mol./l.)
○ 8.13, △ 5.42, □ 2.71

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[2] M. Imamura and M. Koizumi, ibid., **28**, 117 (1955); M. Imamura, *J. Inst. Polytech. Osaka City Univ.*, 6C, 85 (1956).

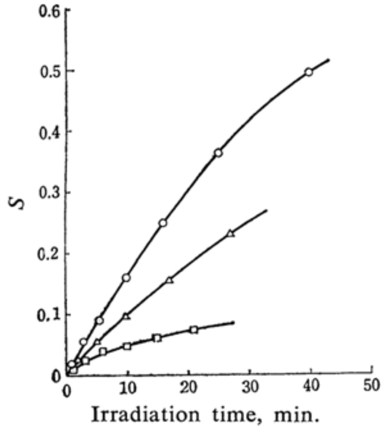

Fig. 5. Variations of S in various concentrations of vinyl acetate with irradiation time.
Monomer concn. (mol./l.)
○ 8.13, △ 5.42, □ 2.71

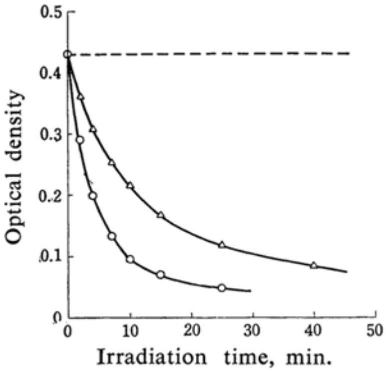

Fig. 7. Variations of optical densities at 460 mμ of the dye under various light-intensities in the system of styrene.
Monomer concn. 6.40 mol./l.
Relative light intensity ○ 1
△ 0.305 --- 0 (dark)

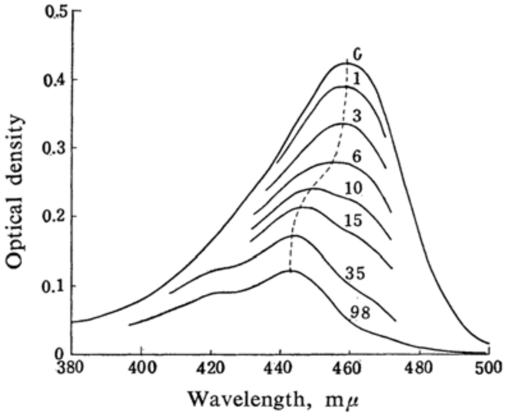

Fig. 8. The change of spectra of acridine yellow in styrene with irradiation time.
Monomer concn. 2.13 mol./l.
Relative light intensity 0.30
Numbers beside curves indicate the irradiation time in minute.

interaction of the excited dye molecule with the monomer.

Under aerobic conditions, neither photobleaching nor polymerization could be brought about. This might be because oxygen deactivated the excited state of the dye.

Photobleaching in the System of Styrene.— The experiment was further extended to the system involving styrene. In various concentrations of styrene, the change in optical density at the initial absorption maximum (460 mμ) was plotted against time, as is shown in Fig. 6. From the results, it can be seen that the bleaching of the dye was very rapid and that its rate was nearly independent of the styrene concentration if it was higher than about 2 mol./l. When the light intensity was reduced to 30.5% by inserting a blackened metallic net, the rate of bleaching decreased as compared with that carried out under full intensity, as is shown in Fig. 7.

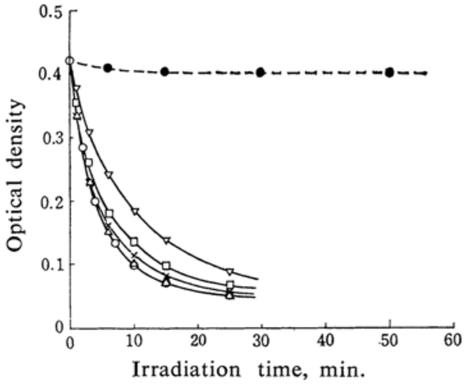

Fig. 6. Variations of optical densities at 460 mμ of the dye in various concentrations of styrene with irradiation time.
Styrene concn. (mol./l.)
○ 6.40 △ 4.24 × 2.13
□ 1.06 ▽ 0.53 ● 0

When the absorption spectra in the range of 400$\sim$500 mμ were followed in the order of the irradiation time (Fig. 8), it was unexpectedly found that the optical density decreased rapidly in spite of the reduced intensity of light and that, at the same time, an absorption maximum appeared at the shorter wavelength. This new absorption did not change in the dark, but disappeared only on irradiation. This phenomenon was soon observed whenever both photobleaching and polymerization occurred in these experiments, but it was observed only after a time in the presence of air or hydroquinone, where the polymerization was hardly able to occur. Since it is well known that hydroquinone can not inhibit polymerization without the coexistence of air and that it is a good quencher for a phosphorescent state, it is clear that the effect of hydroquinone in this case does not result from the inhibition of polymerization but from the quenching of a triplet state of the dye.

The addition of polystyrene to the reaction system in the dark did not lead to the shift in absorption maximum. This result may indicate that the shift does not result from the mere adsorption or binding of the dye on the polymer.

From these reasons, the photobleaching and the shift in the absorption maximum do not always accompany the polymerization of styrene but may be realized prior to it.

Analysis of the Absorption Spectra in the System of Styrene.—Although a gradual shift in the absorption maximum was observed during irradiation in the above system, its limiting position in every case was in the neighborhood of 443 mμ. Since the above results strongly suggest the formation of a coloring product from acridine yellow, identification of the product was attempted from an analysis of absorption spectra. The method is entirely the same as that reported by Imamura[3].

An example of absorption curves obtained for a coloring product by such an analysis is given in Fig. 9, from which it can be seen that the optical density of the product increases with irradiation time, moderately at the initial stage and more slowly at the intermediate stage, and then begins to decrease, though slowly. The absorption band of the coloring product is quite broad and has a maximum at 443 mμ which is not displaced with time.

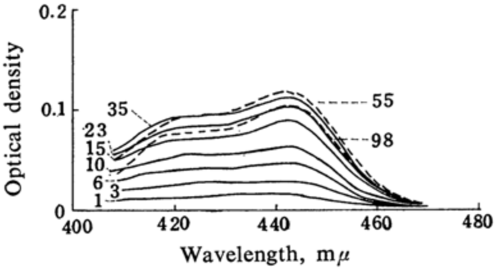

Fig. 9. The change of spectra estimates for a intermediate product in styrene from Fig. 12 with irradiation time

Estimation of the Coloring Product in the System of Styrene.—An attempt was undertaken to decide if the coloring product was a substance produced photochemically by a direct interaction of the excited dye with the styrene monomer. After the reaction system was irradiated for a suitable period, it was poured into a proper amount of methanol. The polystyrene thus precipitated was separated by filtration. The filtrate showed the same spectra, with an absorption maximum at 443 mμ, as that obtained by the above-mentioned analysis. The polystyrene thus obtained had spectra with a broad absorption maximum at ca. 450 mμ in the benzene solution, in spite of the repeated treatment of successive precipitation and dissolution, as is shown in Fig. 10.

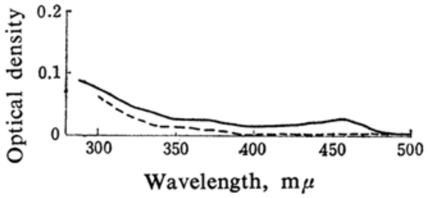

Fig. 10. The absorption spectra of the benzene solutions of the polystyrene obtained photochemically and thermally in the presence of the dye.
Full line; Photochemically
Dotted line; Thermally

On the other hand, when the same reaction system was polymerized thermally in the dark, the filtrate obtained by the same procedure as before showed essentially the same absorption spectra as those of the original reaction system. The polystyrene obtained in this case did not show an absorption maximum near 450 mμ (Fig. 10).

Therfore, it may be concluded that the coloring product was photochemically produced only by a direct interaction of the excited dye with the styrene monomer, and that it was bound to the polymer in the course of the polymerization.

Rate of Photobleaching in the System of Styrene.—It is therefore clear that the optical density at the initial absorption maximum (460 mμ) does not obey Eq. 3, but that on the other hand, at the initial stage of irradiation the decrease in the optical density at 460 mμ may be taken to represent the bleaching of the initial dye. The values of k_{init} thus obtained correspond to the apparent overall rate constants of the bleaching. By plotting them against the monomer concentration, as in Fig. 11, it is found that k_{init} increases rapidly with the monomer concentration but is nearly independent of it in the region higher than about 2 mol./l., even though the conditions of irradiation is different. In addition, it is shown that k_{init} is approximately proportional to the light intensity. These results suggest that the bleaching of the dye is so rapid that the rate of bleaching is

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[3] M. Imamura and M. Koizumi, This Bulletin, 29, 913 (1956).

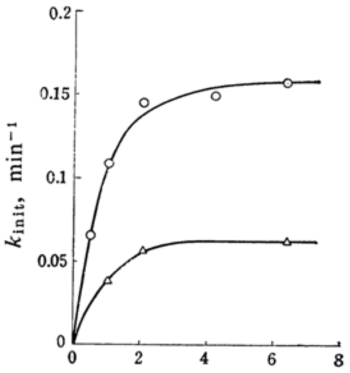

Fig. 11. Dependence of k_{init} on the concentration of styrene.
Relative light intensity
○ 1, △ 0.305

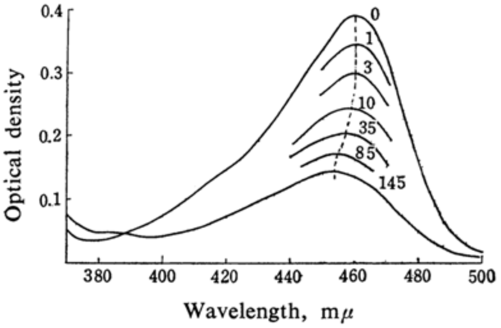

Fig. 12. The change of spectra of acridine yellow in α-MS with irradiation time.

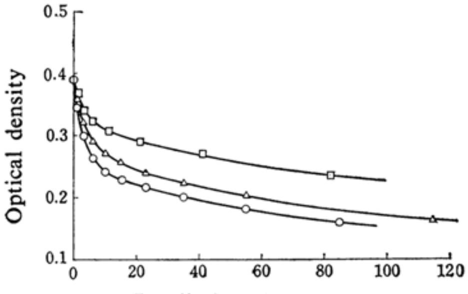

Fig. 13. Variation of optical densities at 460 mμ of the dye in various concentration of α-MS with irradiation time.
Concn. of α-MS (mol./l.)
○ 5.56, △ 3.82, □ 1.96

mainly determined in the case of concentrated monomer concentrations by the intensity absorbed, while it depends both upon the light intensity and upon the monomer concentration in the case of more dilute solutions. Therefore, it may be concluded that the decrease in optical density at the initial absorption maximum (460 mμ) of the dye is attributed to the interaction of the dye molecule, excited to the triplet state, with the monomer to produce a new coloring product which will be destroyed by further irradiation.

Photobleaching in the System of α-Methylstyrene. — The photobleaching in α-methylstyrene (α-MS) was found to closely resemble that in styrene. The absorption curves of a reaction system, as is shown in Fig. 12, shifted towards a shorter wavelength with irradiation time. For the sake of convenience, the optical densities at 460 mμ at various monomer concentrations are plotted against irradiation time in Fig. 13. It can be seen that the rate of bleaching is smaller than that in styrene. On the same assumption as in the case of styrene, the apparent overall rate constants k_{init} were calculated from Eq. 3. The dependence of k_{init} on the monomer concentration appears to be proportional to the square root of the concentration in this region, as is shown in Fig. 14. The efficiencies in polymerizing this monomer were very low. This may be attributable to the low polymerizability of α-MS. It is interesting the features of the photobleaching of acridine yellow are alike in styrene and α-MS. This may be due to the production of coloring products similar in their structure.

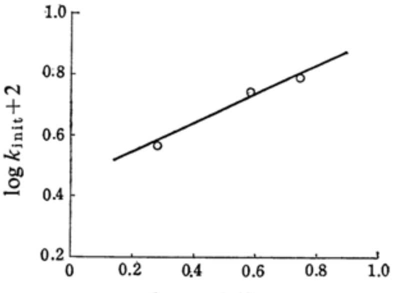

Fig. 14. Logarithm of k_{init} vs. logarithm of the concentration of α-MS.

Photobleaching in the System of Methyl Methacrylate.—In view of the fact that the apparent behaviors of the bleaching of acridine yellow may be differentiated in two groups (acrylonitrile and vinyl acetate; styrene and α-MS), it is attractive to extend the experiments to the system involving methyl methacrylate (MMA), which is one of the most well-known vinyl monomers. Contrary to the author's expectation, it was found that the bleaching ceased after an initial slight photobleaching, the rate of which depended upon the monomer concentration and the extent of which was nearly always in the same ratio to the initial dye concentration even though the concentra-

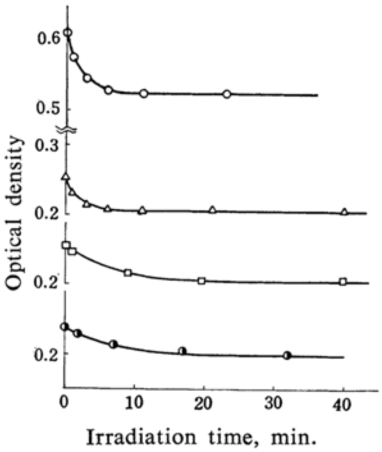

Fig. 15. Variations of optical densities at 457 mμ of the dye in various concentration of methyl methacrylate with irradiation time.
Concn. of MMA (mol./l.) ○, △ 7.01
□ 4.68 ◑ 2.34

tions of the dye and the monomer differed (Fig. 15.), while the monomer continued to polymerize as long as the system was irradiated[4]. In this case, no shift in the absorption maximum of the dye was observed. In the presence of air or hydroquinone, the photobleaching was very slight, without polymerization even in the light; moreover, the optical density of the reaction system could be restored to its initial value after a long period in the dark. This may be evidence for the transient production of a comparatively stable intermediate. Furthermore, the bleaching could not occur in the dark at 30 and 60°C, irrespective of the presence of azobisisobutylonitrile. This leads to the conclusion that acridine yellow can not be attacked by radicals produced thermally from the radical source and, so, perhaps not by polymer radicals.

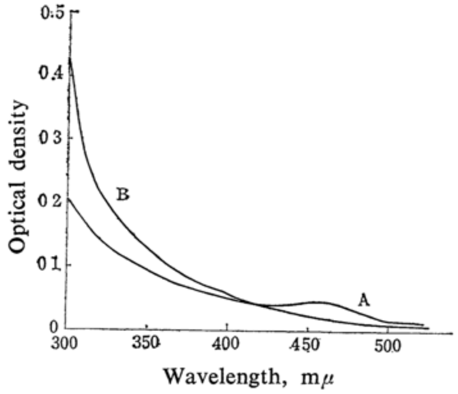

Fig. 16. The absorption spectra of the solution of poly-MMA obtained photochemically (A) and thermally (B) in the presence of the dye.

The absorption spectra of the solution of polymers, which were obtained photochemically in the light and thermally in the dark, are shown in Fig. 16. In spite of the treatment of these polymers by a procedure similar to that described before, the polymers obtained photochemically showed a broad absorption maximum near 460 mμ, while those obtained thermally did not. It is sure that the broad absorption near 460 mμ may be attributed to the dye bound to the polymer and not to the dye merely adsorbed on it, and that the bonding of the dye to the polymer is caused by the action of light in the course of the sensitization of the polymerization.

General Discussion

Acridine dyes are characterized by their resistance to reduction in the dark. Millich and Oster[5] reported that those acridines which had amino groups in both the 3- and 6-positions underwent photoreduction rapidly in the presence of a suitable reducing agent such as allylthiourea. It has now been found that acridine yellow, which was also included in their research, underwent photobleaching in the presence of various vinyl monomers in vacuo without any reducing agent and at the same time, sensitized their polymerizations.

It has been shown that the photobleaching of acridine yellow was apparently different in feature depending on the type of monomer: a) the absorption curves of the dye declined monotonously without any shift in absorption maximum in such monomers as acrylonitrile and vinyl acetate; b) the photobleaching was brought about rapidly with a shift towards shorter wavelengths in both styrene and α-MS, and c) the decreases in its optical density at the absorption maximum with irradiation ceased after a decrease of about 20% from the initial values in the reaction system containing MMA, and even thereafter the polymerization continued as long as irradiation was carried out.

In view of the fact that the intermediate coloring products, which are produced by an interaction of the excited dye with the monomer, seem to be bound to the polymers only in the cases of the photopolymerization of styrene and MMA but not in the dark thermal polymerization, it seems likely that the intermediate products are produced only under the influence of light and play a role in initiating

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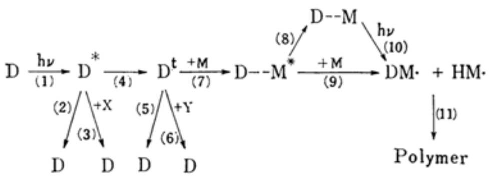
[4] The Kinetic experiments involving this sensitize polymerization will be reported on in a forthcoming paper.

[5] F. Millich and G. Oster, *J. Am. Chem. Soc.*, **81**, 1357 (1959).

polymerization either for themselves or in the course of their production. The apparent features of the photobleaching of the dye in various monomers may be attributed to such properties of the intermediates as optical properties and their photochemical stabilities. Thus, although the photobleaching in vinyl acetate seemed to be simple, it obeyed Eq. 3 only incompletely. After a long period of irradiation, the absorption curves of the system involving vinyl acetate seem to shift slightly towards shorter wavelengths. In this case, an intermediate coloring product would be gradually produced by irradiation and be rather rapidly lost by further irradiation. Therefore, the polymers thereby obtained did not have an absorption band in visible regions. On the contrary, the poly-MMA obtained photochemically in the presence of the dye had a relatively clear absorption band near the same wavelength as the absorption maximum of the original dye. This shows the intermediate products to have absorption spectra similar to those of the dye itself and probably to be rather stable.

Considering the effects of such quenchers as potassium iodide and hydroquinone, it may be concluded that the first singlet and triplet-excited states of the dye are involed in the course of interaction between the dye and monomers. In the acridine yellow-sensitized polymerization of an aqueous solution of methacrylic acid[6], it has been found that potassium thiocyanate, which is well-known as a quencher for fluorescence, can retard the photosensitized polymerization and that the efficiency of the retardation is of the same magnitude as that of the quenching of fluorescense,

Accordingly, the over-all reaction scheme of the photobleaching of acridine yellow in various monomers and the sensitization of polymerization may be expressed by the following:



(1) absorption of light with excitation to the first excited singlet state; (2) reversion to the ground state by a radiationless transition or by emission of fluorescence; (3) fluorescence quenching by potassium iodide or probably by oxygen; (4) transition to the triplet state; (5) transition from the triplet state to the ground state; (6) quenching of the triplet state by hydroquinone or probably by oxyen; (7) production of an activated intermediate product by the interaction of the triplet state with the monomer; (8) transformation to a stable coloring product; (9) initiation of polymerization; (10) re-absorption of light by the stable coloring product, which may lead to polymerization and to photobleaching of the coloring product; and (11) growth of polymer chains, which may be retarded or inhibited by oxygen. For styrene process (7) seems to be very rapid and process (1), a rate-determining step in the concentration range of more than 2 mol./l. For vinyl acetate, process (7) is the rate-determining step. For MMA the coloring product is so stable that it may induce the polymerization, probably by the energy transfer mechanism, without further bleaching.

Watanabe[7] has discussed, in the sensitized polymerization of styrene, the state activated by the use of cyanine dyes and has estimated that an electon transfer from X^- to D^+ was involved in the process of activation, where D^+ and X^- were a dye cation and a halogen anion respectively. In the present cases, it is difficult to decide whether or not such a electron transfer is involved, but it may be reasonable to assume that the intermediate product, which is produced by the direct interaction of the triplet state of the dye with the monomers, is responsible for the photobleaching and leads to the polymerization.

Summary

The photobleaching of acridine yellow has been studied in various vinyl monomers, such as acrylonitrile, vinyl acetate, styrene, α-methylstyrene and methyl methacrylate.

It has been found that (a) the photobleaching is apparently different in featue depending on the type of monomer; (b) the absorption maximum of the dye in the reaction systems shifted rapidly to a shorter wavelength in the cases of both styrene and α-methylstyrene by the irradiation of light, while it did not in the cases of acrylonitrile, vinyl acetate and methyl methacrylate; (c) a new absorption maximum at a shorter wavelength may result from the production of a relatively stable intermediate from the dye and styrene.

Considering also the effects of such quenchers as potassium iodide and hydroqinone on the photobleaching and the polymerization, it has been concluded that the interaction of the triplet state of the dye molecule with the monomers is responsible for both the bleaching and the polymerization.

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[6] This will be reported on in a forthcoming paper.

[7] A. Watanabe, This Bulletin, 32, 557 (1959).

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