*Dye-sensitized Photopolymerization of Vinyl Compounds. Polymerization of Acrylonitrile by Stannous Chloride and Acriflavine. II**

By Ai WATANABE**

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In the previous paper[1], the present author and Koizumi studied the polymerization of acrylonitrile (AN), which takes place when a solution of AN, acriflavine (D) and stannous chloride in the mixed solvent of water and dimethylformamide (DMF) is illuminated by visible light. They found that neither oxygen nor water is of primary importance for the initiation of polymerization, as a mechanism they proposed that a transient tin ion of odd valency is produced and that this, by interacting with the monomer, initiates the polymerization.

The aim of the present work is to make the proposed scheme more definite by ascertaining whether it also fits the photosensitized polymerization of AN in DMF (with no addition of water and in vacuo) in the presence of stannous chloride and acriflavine.

Experimental

Materials.—AN from the Union Carbide Corporation was distilled at atmospheric pressure and was further distilled twice in an atmosphere of nitrogen under reduced pressure. Commercial acriflavine was recrystallized twice from water and dried in vacuo. Stannous chloride dihydrate (G. R) was dehydrated in vacuo at room temperature. DMF from Du Pont was purified as has been described previously[1].

Procedure.—As the light source, a tungsten projection lamp 100 V.-500 W was operated at 80 V., as has been described in Part I. The distance between the light source and the reaction cell in a thermostat was 10 cm. A Matsuda color filter V-Y3C and a heat-cutoff filter were put between the reaction cell and the light source. The reaction cells and dilatometers were the same as have been described in Part I except for the one shown in Fig. 1, which was used to study the influence of oxygen upon the rate of polymerization. The solution to be studied was poured into cell A and then degassed after being frozen in a dry-ice bath. When the degassing was complete, a definite quantity of air was introduced through B and the dilatometer was sealed off at constricted Part B. When the contents thawed, the air was dissolved by shaking the cell, and the solution was poured through capillary C into the reaction cell D by tilting the unit. The drop of meniscus in the capillary, E, was followed by the use of a travelling microscope. All the experiments were done at 30°C, and the solutions were degassed by repeating the vacuum distillation except when otherwise described.

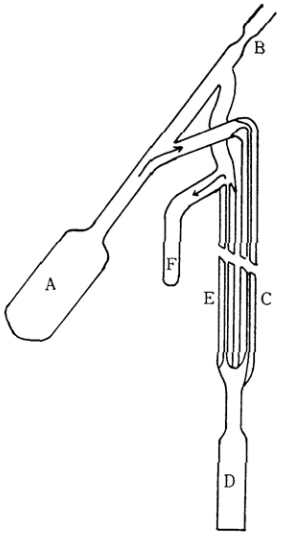

Fig. 1. Dilatometer.

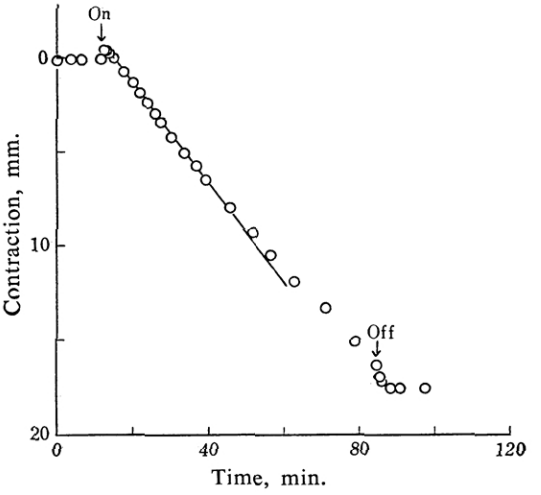

Fig. 2. The polymerization~time curve. $[D]=1.0\times10^{-4}$ M; $[SnCl_2]=1.25\times10^{-2}$ M; $[AN]=5.0$ M

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1) A. Watanabe and M. Koizumi, This Bulletin, **34**, 1086 (1961).

The apparatus employed for making a sample of a bleaching reaction was almost the same as that used for the polymerization. The solutions were thoroughly degassed and were poured into two reaction cells in vacuo. They were sealed off, separately; one was used for the dark-reaction, and the other for the photo-reaction. At various time intervals during the reaction, reaction cells were taken out and the dye concentration of solutions was measured by a spectrophotometer.

Results

The Polymerization.—Induction periods were observed in almost none of the experiments, and after a short period of constant rate the rate fell off gradually. Figure 2 shows a typical curve for the polymerization. During the course of polymerization, the polymer did not deposit. In all cases, the rate was evaluated from the initial linear portion of the curve. The reproducibility of experiments was not excellent enough to correlate the data of a different series of experiments.

The Effect of Dye Concentration.—In Fig. 3 is shown the variation of the rate with the concentration of acriflavine. It is apparent from the figure that, at a concentration of dye of less than 1×10^{-5} M, the rate increases linearly with the square root of the dye concentration and that the log(rate)~log[D] curve gives the slope of 0.4. The rate decreases when the concentration of dye exceeds 1×10^{-4} M.

The Effect of the Concentration of Stannous Chloride.—The effect of the concentration of stannous chloride on the rate is shown in Fig.

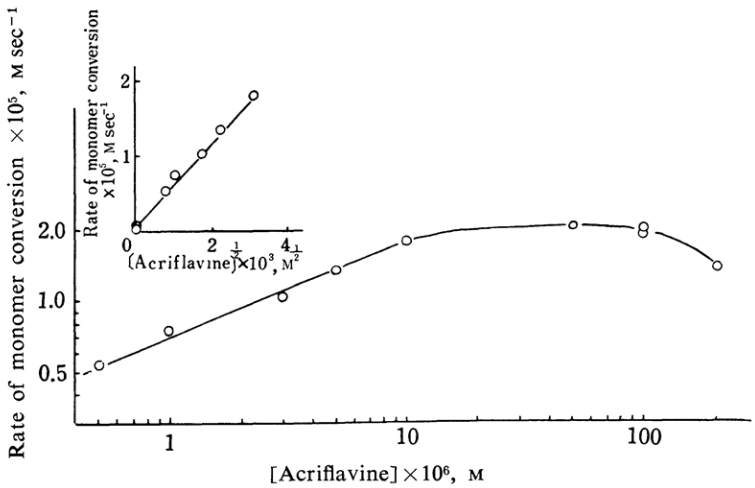

Fig. 3. The dependence of the initial polymerization rate on acriflavine concentration.
$[SnCl_2]=1.25\times10^{-2}$ M; [AN]=5.0 M

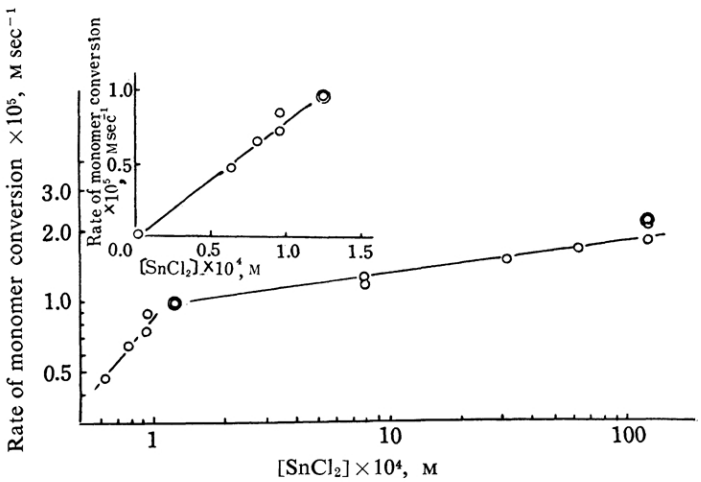

Fig. 4. The dependence of the initial polymerization rate on $SnCl_2$ concentration.
$[D]=1.0\times10^{-4}$ M; [AN]=5.0 M

4. When the concentration of stannous chloride is less than 1×10^{-4} M, the linearity holds between the rate and the concentration of stannous chloride, this being also confirmed by the slope of 0.95 for the log(rate)~log[$SnCl_2$] plot, although there exists some scattering of the experimental points. In the region where the concentration of stannous chlorde is more than ca. 1×10^{-4} M, the rate increases at a lower rate.

The Effect of the Monomer Concentration.—As is shown in Fig. 5, the rate depends on the second power of the monomer concentration. The log(rate)~log[AN] plot gives a straight line of the slope of 2.2.

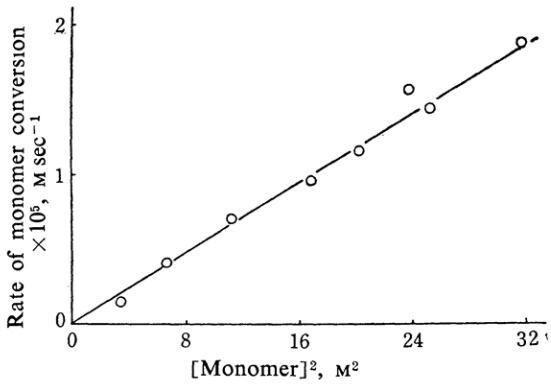

Fig. 5. The dependence of initial polymerization rate on acrylonitrile concentration.
[D]=2.0×10^{-4} M; [$SnCl_2$]=1.25×10^{-2} M

The Effect of the Pressure of Oxygen.—In Fig. 6, the rate is plotted against the pressure of oxygen. It is evident that the polymerization in the degassed solution has a rate somewhat smaller than that in the non-degassed solution, the ratio of the rate in the two cases being about 0.5. Thus, the presence of oxygen is not of primary importance for the occurrence of the reaction.

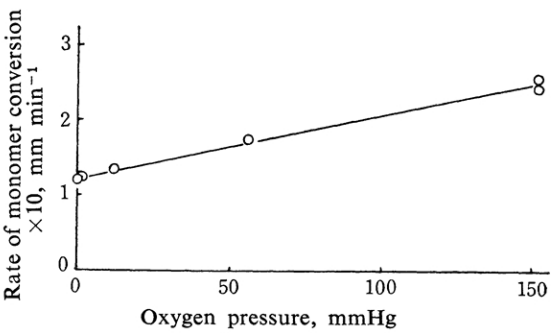

Fig. 6. The dependence of the initial polymerization rate on oxygen pressure.
[D]=1.0×10^{-4} M; [$SnCl_2$]=1.25×10^{-2} M;
[AN]=5.0 M

The Effect of the Light Intensity.—The intensity of the exciting light was changed to 50, 25 and 12% of the standard light by the use of neutral filters. The samples used in these experiments contained a quantity of dye large enough to absorb almost all the effective light. As is shown in Fig. 7, the intensity exponent is about 0.35.

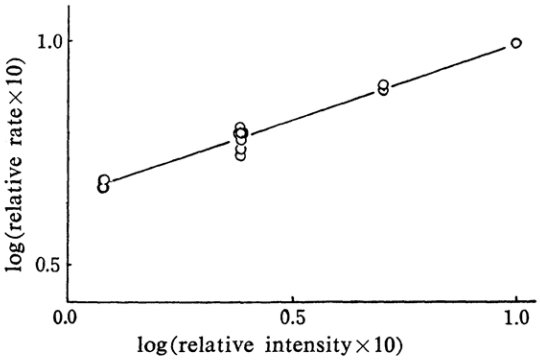

Fig. 7. The intensity exponent.
[D]=1.0×10^{-4} M; [$SnCl_2$]=1.25×10^{-2} M;
[AN]=5.0 M

The Bleaching.—*The Bleaching of Dye in the DMF Solution.*—When the degassed solution of dye in DMF was illuminated, the bleaching occurred, whereas not a slight bleaching was observed in the dark. In Fig. 8 the absorption spectrum of the sample after illumination is (2), and that of the original sample is (1). A slow restoration of the absorption curve was realized even in vacuo when the illuminated sample was kept in the dark (3). On the

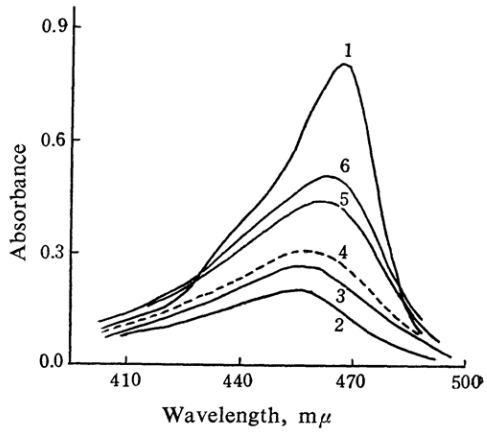

Fig. 8. Spectrum changes of acriflavine in DMF solution degassed.
1 Initial ([D]=1.4×10^{-5} M)
2 1.2 hr.-illumination at 30°C
3 15 hr.-standing of (2) in the dark
4 Aeration of (3)
5 5.4 hr.-standing of (4) in the dark
6 47.5 hr.-standing of (4) in the dark

introduction of air into the illuminated sample, the absorption curve was further restored to some extent.

The rate of photobleaching was reduced by the addition of stannous chloride, and it was found that the bleached solution in this case never completely regains its color upon the introduction of air. The bleaching did not occur in the dark. The reversible photobleaching was scarcely observed at about 6.25×10^{-3}M stannous chloride and the absorption spectrum showed a slight shift of λ_{max} toward a longer wavelength.

In Fig. 9, the absorbance at the wavelength corresponding to the maximum of the original sample is plotted against the reaction time. This figure does not allow a rigorous comparison of the rates of photobleaching because of the superposition of the reversible and irreversible bleaching, the latter especially giving an absorption curve due to the remaining dye and the product. However, the rates can be compared semiquantitatively from this figure, and it is clear that the rate decreases as the concentration of stannous chloride is increased.

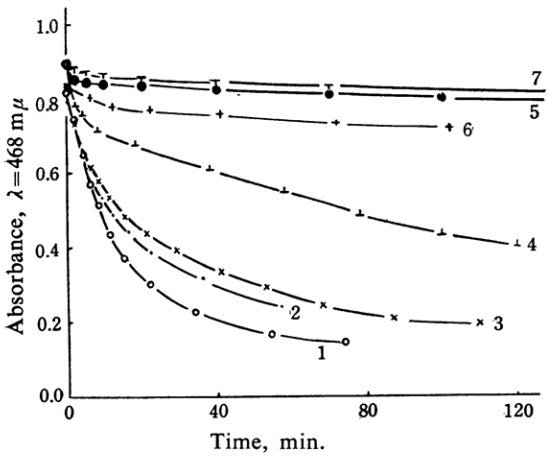

Fig. 9. The photobleaching~time curves of acriflavine in DMF solution degassed.
[D]≈1.4×10^{-5} M

	[$SnCl_2$], M
1	0
2	6.25×10^{-6}
3	1.25×10^{-5}
4	2.50×10^{-5}
5	1.25×10^{-4}
6	1.25×10^{-3}
7	1.25×10^{-2}

The Bleaching of Dye in the DMF-AN Solution. —When AN is added to the DMF solution, the spectrum of dye showed little change, but the rate of photobleaching was reduced. Furthermore, the photobleaching of dye in the degassed DMF-AN solution was irreversible, and the absorption spectra of the illuminated solution showed a shift of λ_{max} to longer wavelengths. When stannous chloride is added, the rate of photobleaching is appreciably

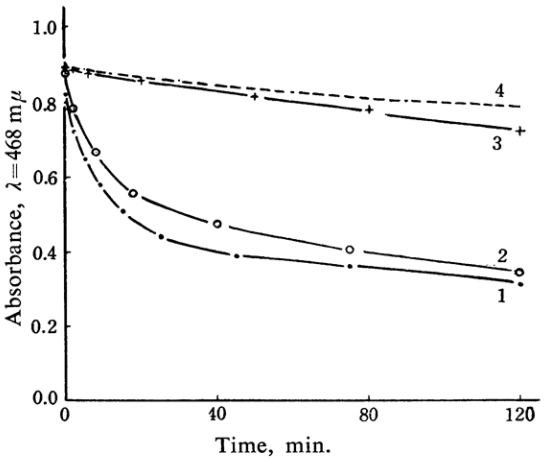

Fig. 10. The photobleaching~time curves of acriflavine in DMF-AN solution degassed in the presence of $SnCl_2$.
Volume ratio, DMF/AN=9;
[D]≈1.4×10^{-5} M

	[$SnCl_2$], M
1	0
2	1.25×10^{-5}
3	1.25×10^{-4}
4	1.25×10^{-2}

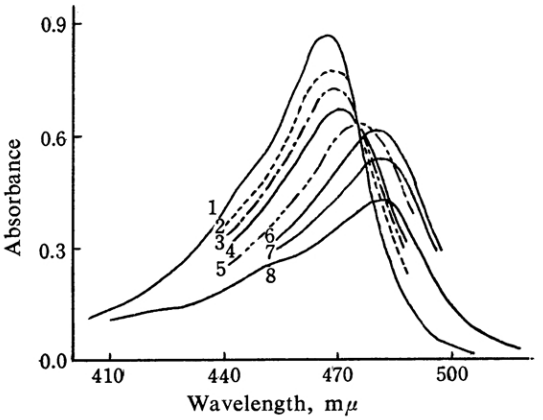

Fig. 11. Spectrum changes of acriflavine in DMF-AN solution degassed in the presence of $SnCl_2$.
Volume ratio, DMF/AN=9; [$SnCl_2$]=1.25×10^{-5} M; [D]=1.4×10^{-5} M
1 Initial
2 2 min.-illumination
3 4 min.-illumination
4 8 min.-illumination
5 18 min.-illumination
6 40 min.-illumination
7 75 min.-illumination
8 120 min.-illumination

reduced, as is shown in Fig. 10; the bleaching is irreversible. The bleaching does not occur in the dark. An example of the spectral change caused by illumination is shown in Fig. 11.

Though the feature of photobleaching is complicated and it is desirable to study it more quantitatively, some qualitative discussion may be given about the relation between photobleaching and photopolymerization on the basis of the above results. In broad outline, the photobleaching of dye occurs in the absence of stannous chloride though the photopolymerization does not occur. The rate of photobleaching is reduced by the addition of stannous chloride which, on the other hand, causes the photopolymerization to occur. Consequently, it may be concluded that the photobleaching of dye does not occur parallel with the photopolymerization.

Discussion

As expected, the polymerization of AN was initiated by visible light in the presence of stannous chloride and acriflavine in vacuo. It will be discussed below whether the experimental results can be interpreted on the basis of the schemes proposed in the previous paper. One of the schemes proposed for the initiation process involves the assumption that a complex is formed between the Sn^{2+} ion and the dye. However, this seems rather implausible in view of the finding that the shift of the absorption spectrum of dye in the visible region was not observed by the addition of stannous chloride in a DMF-AN or a DMF-AN-H_2O solution. Moreover, the essential steps are common in the two schemes. Hence, to avoid confusion, the discussion is limited to the other scheme, which is described below:

$$\mathrm{D} \xrightarrow[(1)]{h\nu} \mathrm{D}^* \xrightarrow[(3)]{\mathrm{D}} \mathrm{D}^t \xrightarrow[(5)]{Sn^{2+}} (\mathrm{D}^- \cdots \mathrm{Sn}^{3+}) \xrightarrow[(7)]{Sn^{2+}}$$

$$\downarrow(2) \quad \downarrow(4) \quad \downarrow(6') \quad \downarrow(6)$$

$$\mathrm{D} \quad \mathrm{D} \quad \mathrm{D}+Sn^{2+} \quad \mathrm{Leuco}+Sn^{4+}$$

$$\mathrm{D} + Sn^{+} + Sn^{3+} \xrightarrow[(8)]{} \mathrm{D} + 2Sn^{2+}$$

$$(\text{or } \mathrm{D}^- + Sn^{3+}) \qquad (\text{or } \mathrm{D} + Sn^{2+})$$

$$Sn^{3+} + \mathrm{M} \xrightarrow{k_i} \mathrm{R}$$

$$(\text{or } Sn^{+} + \mathrm{M} \rightarrow \mathrm{R})$$

The essential points in this scheme are that the two kinds of ionic species of a radical nature produced by process (7) react almost exclusively in such a way as to produce stable ions, and that only a small fraction of them react with the monomer to initiate the polymerization. It is assumed, in addition, that the reaction attains the steady state and that the termination of the growing polymer is spontaneous.

The experimental overall rate formula in the present case may be expressed as follows,

$$v \propto [\mathrm{D}]^{1/2} [SnCl_2] [\mathrm{M}]^2 \qquad (\mathrm{I})$$

provided that [D] and [$SnCl_2$] are small. Thus, the rate is 1/2-order with respect to the dye concentration, whereas it is first order in the previous system, containing water and oxyen, which was treated in Part I. This difference in the order of reaction with respect to the dye concentration can be explained on the assumption that the transition from a singlet (D^*) to a triplet (D^t) excited state occurs in this case as is described below, whereas this is induced by the ground state dye molecule[2] in the previous system, as was discussed in Part I:

$$\mathrm{D} \xrightarrow[(1)]{h\nu} \mathrm{D}^* \rightarrow \mathrm{D}^t \rightarrow \text{same as the above scheme}$$

$$\downarrow(2)(3) \quad \downarrow(4)$$

$$\mathrm{D} \quad \mathrm{D}$$

From this scheme, the initiation rate (v_i) and v can be derived as follows:

$$v_i = \left[\left(\frac{I_0 k_1 k_3}{k_2 + k_3}\right)\left(\frac{k_5 [Sn^{2+}]}{k_4 + k_5 [Sn^{2+}]}\right) \times \left(\frac{k_7 [Sn^{2+}]}{k_6 + k_6' + k_7 [Sn^{2+}]}\right)\right]^{1/2} \frac{k_i}{k_8^{1/2}} [\mathrm{M}] \qquad (\mathrm{II})$$

and

$$v = \frac{k_i k_p}{k_t k_8^{1/2}} [\mathrm{M}]^2 \left[\left(\frac{I_0 k_1 k_3}{k_2 + k_3}\right)\left(\frac{k_5 [Sn^{2+}]}{k_4 + k_5 [Sn^{2+}]}\right) \times \left(\frac{k_7 [Sn^{2+}]}{k_6 + k_6' + k_7 [Sn^{2+}]}\right)\right]^{1/2} \qquad (\mathrm{III})$$

From Eq. III, the following relations are obtained, satisfying the experimental results:

i) When [D] is small, $I_0 k_1$ may be put as approximately proportional to [D]. Hence, $v \propto [\mathrm{D}]$.
ii) When $[Sn^{2+}]$ is small, $v \propto [Sn^{2+}]$.
iii) In all cases, $v \propto [\mathrm{M}]^2$.
iv) $v \propto I_0^{1/2}$

It is regrettable that the value of the intensity exponent experimentally obtained, i.e., 0.35 (which is much less than 0.5), can not be explained satisfactorily.

To sum up, all the features of the present reaction, except a single point mentioned above, can well be interpreted on the basis of a scheme quite similar to that proposed in the previous paper. In addition, the rate of the photobleaching of dye decreases with the increasing stannous chloride concentration, whereas the rate of the photopolymerization increases appreciably with it. This result also supports the view that the photopolymerization

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

does not accompany the transient photobleaching of dye, which finding is naturally expected according to the proposed scheme.

Summary

The photosensitized polymerization of AN in DMF by acriflavine and stannous chloride in vacuo was investigated. The reaction rate was shown as: $v \propto [D]^{1/2}[SnCl_2][M]^2$, where [D] and $[SnCl_2]$ were small. The experiments performed examining the photobleaching of dyestuff in various conditions led to the finding that the photopolymerization does not occur by virtue of the transiently-reduced dye. The scheme proposed in Part I, in which the transient tin ion of odd valency (Sn^{3+} and/or Sn^{+}) initiates the polymerization by interacting with the monomer, was further substantiated.

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