Dye-sensitized Photopolymerization of Vinyl Compounds. Polymerization of Styrene by Cyanine Dyes. II.

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Introduction

As reported in the preceding paper[1], the photosensitized polymerization occurs when the solution of cyanine dye in a mixture of styrene and *n*-butanol is irradiated at 60°C. In this reaction, the dye molecule is decomposed most probably by its interaction with styrene, when the former is in the excited state, producing one or two kinetic chains of polymerization per one dye molecule decomposed. Now in order to know the features of the reaction in more detail, the effects of various factors upon the reaction such as temperature, the wave lengths of the incident light, and the concentrations of dye, have been examined, chiefly employing pinacyanol iodide as a sensitizer.

Further, the probable scheme of the reaction has been proposed and on its basis suitable corrections have been given to the α-values reported in the previous paper.

The apparatus and the experimental procedures are the same as in the previous paper.

Experimental Results

1. Effect of Temperature.—Two series of experiments were performed at 40°C and 60°C, using a 6×10^{-6} mol./l. solution of pinacyanol iodide in a mixture of 15 parts styrene and 1 part of *n*-butanol. A Matsuda color filter VO-2, which transmits the wave lengths of the two absorption maxima of dye, was used, and the number of photons entering the reaction cell was measured to be about 10^{16} per sec.·cm².

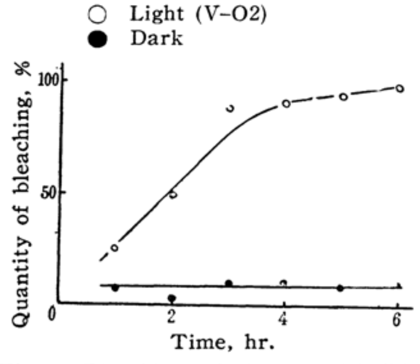

Fig. 1. Bleaching of pinacyanol iodide at 40°C.

The bleaching curves and the polymerization curves both in light and dark at 40°C are given in Figs. 1 and 2, respectively. The results at

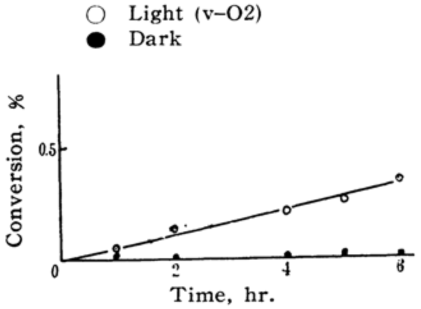

Fig. 2. Polymerization of styrene at 40°C.

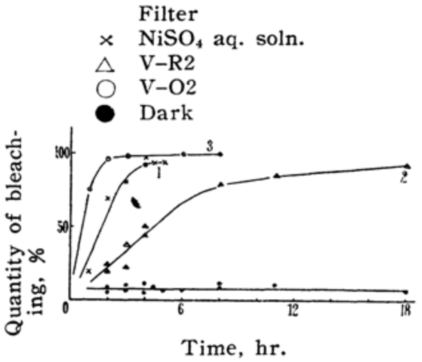

Fig. 3. Bleaching of pinacyanol iodide at 60°C.

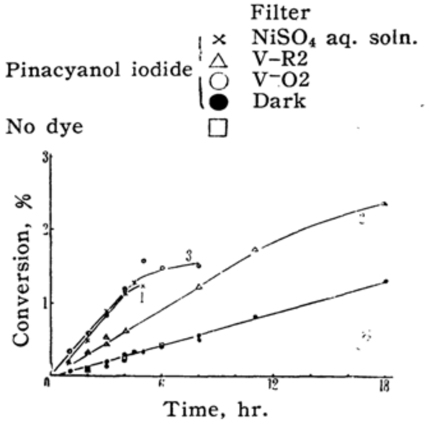

Fig. 4. Polymerization of styrene at 60°C.

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[1] M. Koizumi and A. Watanabe, This Bulletin, 28, 136 (1955).

60°C are shown by the curves, (3) in Figs. 3 and 4, which include the other results obtained when the different filters were used.

As seen from Figs. 1 and 3, the bleaching of dye occurs even in the dark both at 40°C and 60°C, but its quantity is small and independent of time, and moreover in the same order of magnitude in both cases. The photobleaching is much faster at 60°C than at 40°C.

As for the polymerization, thermal polymerization scarcely occurs, and only photopolymerization proceeds at 40°C; the latter seems to continue even after the completion of photobleaching. At 60°C, thermal polymerization takes place, but its rate is not affected by the addition of dye as already reported in the previous paper. A remarkable fact is that a new band, which will be shown later, appears in the region of shorter wave lengths, and this is more marked at 40°C than at 60°C.

The influence of temperature upon the polymerization degree, α-value and upon the quantum yield will be given later.

2. Effect of the Dye Concentration.—The polymerization curves at 60°C for three different concentrations of dye are given in Fig. 5. It is to be noted that styrene in this case was not distilled directly before the experiment and that the thermal polymerization proceeded faster than in the other cases. In spite of this fact, it is certain that the photopolymerization continues longer in the more concentrated solution, and that at least in the initial stage the reaction goes on at almost the same rate at three different concentrations of dye. Judging from the molar extinction coefficient of dye, the effective light is absorbed almost completely in the initial stage of the reaction so that it is very probable that the rate depends only on the number of excited dye molecules rather than on the total concentration of dye.

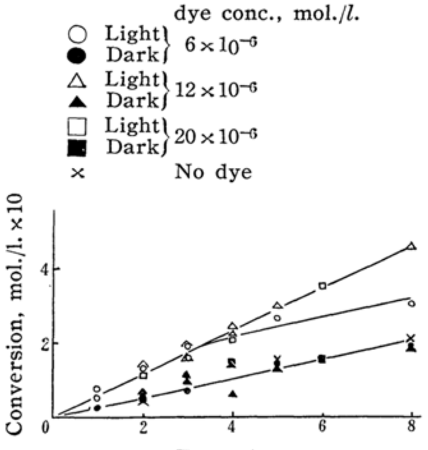

Fig. 5. The effect of dye concentration on the quantity of polymerization.

3. Effect of the Wave Lengths of Incident Light.—Pinacyanol iodide has two maxima at 580 mμ and at 630 mμ. In order to investigate the effect of different wave lengths, the three series of experiments were done using the following filters; 1) 200 g./l. aqueous solution of $NiSO_4$ 2.5 cm. in thickness, which transmits only the maximum of shorter wave length, 2) Matsuda color filter V-R2 which selects the light longer than about 600 mμ and 3) Matsuda color filter V-O2 which transmits the wave lengths at the two absorption maxima. The results are shown in Figs. 3 and 4.

It is remarkable that the rate of photobleaching in (2) is much slower than in (1) and (3), though the exact comparison can not be given on account of the difference of the light intensity in the three cases. The number of photons absorbed in the initial stage of the reaction are approximately 1×10^{15}, 2×10^{15} and 6×10^{15} quanta per sec.·cc. for the above three cases, respectively.

In addition, it is observed that in case 3) the photopolymerization continues even after the almost complete destruction of the dye. In cases 1) and 2), the photobleaching and photopolymerization proceed seemingly in a parallel manner. Now the appearance of a new absorption band mentioned in section 1 and the survival of the photopolymerization after the completion of photobleaching in case 3) could be successfully correlated in the following way.

In case (1) the absorption curve of the sample after the reaction declines throughout the whole visible region as the bleaching proceeds, while in case (2) a new absorption band appears accompanied by the fall of the two original maxima. A typical example is shown in Fig. 6. In case 3), this new absorption band, which appears in the proper stage of reaction though less markedly than in case 2), gradually drops as time goes on. It was ascertained by another experiment that this new absorption band does not decline when the sample is maintained in the dark at 60°C for a long time. Thus it becomes quite clear that the reaction product which produces this new absorption band is decomposed only by irradiation.

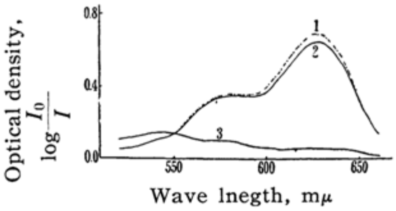

Fig. 6. Absorption spectra of 6×10^{-5} mol./l. pinacyanol iodide in styrene and butanol (15: 1) in 1 cm. silica cell.
(2) After the reaction in dark for 18 hrs. at 60°C.
(3) After the reaction in light for 18 hrs. at 60°C.

Further, it was found in case (2) that, when the polymer is dissolved in benzene and reprecipitated by use of methanol, the polymer still has a tint of pink, while the polymer obtained in the dark reaction, when treated in the same way, becomes completely colorless. The analogous and still more marked results were obtained at 40°C;

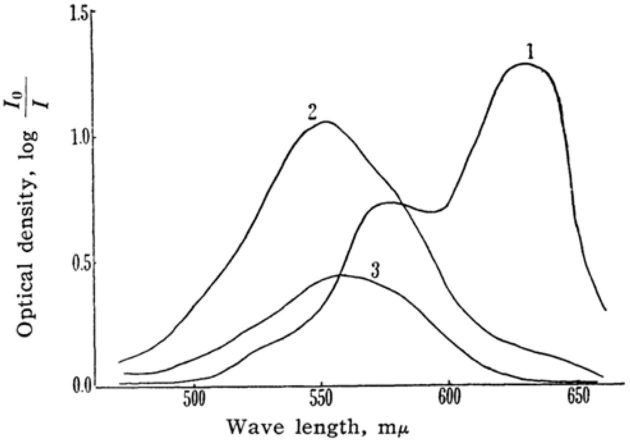

Fig. 7. Absorption spectra of the sample and the polymer.
(1) 1.2×10^{-5} mol./l. pinacyanol iodide in styrene and butanol (15 : 1) in 1 cm. silica cell.
(2) After light reaction (filter V–O2) for 16 hrs. at 40° C.
(3) The polymer separated from the sample in (2).

thus when the concentration of dye is made two fold and the illuminated portion of the cell is increased, the polymer obtained has a marked pink color which can never be eliminated by the above treatment. In Fig. 7, the absorption curve of the sample after 16 hours irradiation through V–O2 at 40°C and that of the polymer separated and dissolved in a mixture of styrene and butanol (15 : 1) are compared with the original curve. All these facts demonstrate quite strongly that a fragment of decomposed dye molecule is attached to the polymer.

An experiment similar to the above was tried for pinacyanol chloride, but in this case it was not possible to recognize the same phenomenon.

4. The Average Polymerization Degree.—The average polymerization degree under various experimental conditions is tabulated in Table I. It is about 12000 for the thermal reaction at 60°C. and for the reaction in light it seems that the value, approximately half of that in the dark, becomes less the faster the reaction.

5. Quantum Yields for Photobleaching and for the Initiation Process in Polymerization. The Value of α.—Quantum yields for photo-

TABLE I

THE AVERAGE POLYMERIZATION DEGREE

Temperature (°C)	Time (hr.)	Dark $\bar{P}$ (10^3)	Light $\bar{P}$ (10^3)	Light Filter
60	1		6.9	NiSO$_4$aq. soln.
	2		5.0	
	3	12	5.4	
	4	10	6.7	
	1		5.0	V–O2
	2	14	5.3	
	3	14	5.2	
	4	12	5.5	
	5	12	5.7	
	2	10	5.6	V–R2
	3	13	7.1	
	4	11	6.7	
	8		6.5	
40	2		5.4	V–O2
	4		5.6	
	4.7		5.6	
	5		4.3	

TABLE II

QUANTUM YIELD

Time (hr.)	Quantum yield for bleaching (10^{-4}) 40°C. V–O2	60°C. NiSO$_4$ aq.soln.	60°C. V–O2	60°C. V–R2	Quantum yield for initiation process in polymerization (10^{-4}) 40°C. V–O2	60°C. NiSO$_4$ aq.soln.	60°C. V–O2	60°C. V–R2
1	0.78	4.7	4.8		0.40	10	4.3	
2	1.5	12	5.5	0.7	1.2	15	6.8	2.4
3		11	4.5	1.0		21	8.4	2.5
4	1.5	8.7	2.9	1.9	0.91	18	8.2	2.8
5	1.1	10			0.85	23		
6	1.2		4.2		0.90		12	
8			4.2	2.0			12	3.5

TABLE III
THE VALUE OF α

Time (hr.)	α				α'			α_0		
	40°C.	60°C.			60°C.			60°C.		
	V–02	$NiSO_4$ aq.soln.	V–O2	V–R2	$NiSO_4$ aq.soln.	V–O2	V–R2	$NiSO_4$ aq.soln.	V–O2	V–R2
1	0.52	2.0	0.91		2.4	1.1		1.8	0.93	
2	0.79	1.3	1.2	3.5	2.0	1.5	4.4	1.6	1.2	3.2
2		1.0	0.86	2.3	1.7	1.3		1.4	1.0	
3	0.70	2.0	1.9	2.7	2.8	2.3	3.3	2.3		2.4
3				2.4			2.5			1.7
4	0.60	2.0	2.8	1.5	2.3	3.2	2.3			1.7
4.5		2.5			3.6					
4.7	1.0									
5	0.77	2.3	3.8		2.7	4.4				
6	0.77		2.8			3.3				
8			2.8	1.8		2.7	2.9			
11				2.5			3.6			
18				2.4						

bleaching and for the initiation process in polymerization under various conditions are shown in Table II, and the values of α in Table III. α was calculated by using the P-value averaged for each filter. This procedure is of course not exact and the rigorous treatment will be given below. It is further to be added that α-value in the later stage of reaction in case of V-O2 can not be adopted, since the decomposed fragment of dye attached to the polymer still accelerates the reaction photochemically even after the complete fall of the original maximum of absorption utilized for determining the dye concentration. The order of the quantum yields is 1)>3)>2) both for the photobleaching and the photopolymerization.

Discussion

At first, let us consider how to obtain the correct value for α or the number of initiation processes per one dye molecule decomposed. The values hitherto tabulated were calculated according to the following formula and must be corrected accordingly.

$$\frac{\begin{pmatrix}\text{Quantity of polymer}\\ \text{in light reaction}\end{pmatrix}-\begin{pmatrix}\text{Quantity of polymer}\\ \text{in dark reaction}\end{pmatrix}}{(\text{The average polymerization degree in light})}\Bigg/\begin{pmatrix}\text{Quantity of}\\ \text{photobleaching}\end{pmatrix} \tag{1}$$

For this correction, there are two facts to be taken into consideration. One concerns the experimental condition and the other is related to the reaction mechanism.

Now, scrutinizing the experimental condition, it was found that only 1.6/5 of the sample is irradiated. Hence one must consider that the polymerization in light takes place only in this part, while in the remaining part only the pure dark polymerization proceeds at the same time. It may, therefore, be plausible to admit that the whole reaction is a mere superposition of the two, and the average polymerization degree $\bar{P}$, which was hitherto tabulated, is a weighted mean of the two separate reactions occuring in the different parts of the cell.

Thus if one puts the quantities of polymerizations in dark and in light respectively as D and L, then $\bar{P}$ will be expressed as follows:

$$P=\frac{L}{\dfrac{L-\dfrac{3.4\bar{D}}{5}}{P_L}+\dfrac{\dfrac{3.4\bar{D}}{5}}{\bar{P}_D}} \tag{2}$$

where $\bar{P}_D$ and $\bar{P}_L$ are respectively the degree of polymerization in dark and in light space. If one uses $\bar{P}_L$ value calculated from (2) the more plausible values of α would be obtained, which are tabulated as α' in Table III.

Another fact to be criticized in equation (1) is the assumption that the polymerization in light is a simple sum of the dark-and photo-polymerization. This assumption will perhaps be wrong, and in order to treat the problem it is necessary to put forth a correct mechanism for the reaction, which will require a more detailed kinetic investigation. All that can be done in the present stage of research is to propose a plausible mechanism and develop a deduction on the basis of it.

In view of the facts that the dye molecules in the ground state do not affect the dark polymerization and that the number of excited dye molecules in the stationary state is very small, the most plausible scheme of the polymerization in light will be just the one in which only the initiation process is the sum of the dark and light processes. Thus,

1. Initiation $V_{ta}+V_{tl}$
2. Propagation $k_p[R][M]$
3. Monomer transfer $k_{tr\cdot M}[R][M]$
4. Solvent transfer $k_{tr\cdot s}[R][S]$
5. Termination $k_t[R]^2$,

where V_{ta} and V_{tl} are respectively the rates of thermal- and photochemical-initiation, and k_p, $k_{tr\cdot M}$, $k_{tr\cdot s}$ and k_t are the rate constants respectively for propagation, monomer transfer, solvent transfer and termination. All the other notations have the usual meaning.

Now, it is worthy to state that the above mechanism can be supported to some extent on the basis of the data already obtained as follows.

Thus if the above mechanism is correct, the average polymerization degree in light is easily given by the following formula

$$P_L=\frac{k_p[R][M]}{k_t[R]^2+k_{tr\cdot M}[R][M]+k_{tr\cdot s}[R][S]} . \quad (3)$$

Combining (3) with the overall rate

$$V=k_p[R][M] , \quad (4)$$

one gets

$$\frac{1}{\bar{P}_L}=\frac{k_t V}{k_p^2[M]^2}+\frac{1}{k_p[M]}\left[k_{tr\cdot M}[M]+k_{tr\cdot s}[S]\right] . \quad (5)$$

Thus $\frac{1}{\bar{P}_L}$, when plotted against V, must give a straight line. If one takes V, as a quantity of the polymer produced in 1.6/5 of the cell per one hour, one can test the above relation with the data for the various dyes described in the previous paper and with those in various conditions including the dark reaction.

The result is satisfactory to some degrees, as shown in Fig. 8.

Having thus shown the above scheme to be quite probable, one can, on the basis of it, obtain the more reliable values of α in the following way. Combining the relation

$$V_{ta}+V_{tl}=k_t[R]^2 \quad (6)$$

with (4), one can rewrite the formula (5) in the following way,

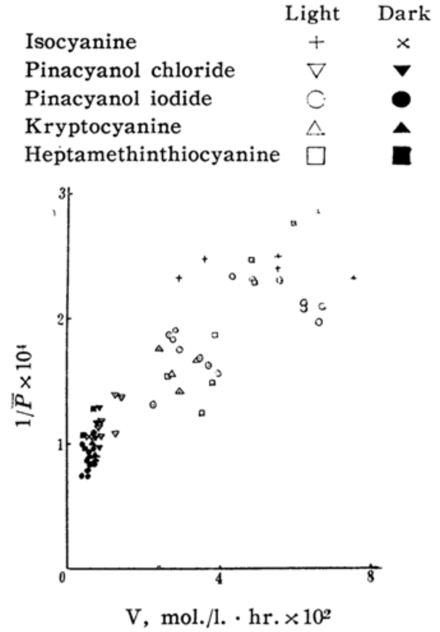

Fig. 8. Variation of the average polymerization degree with the overall rate.

$$\frac{V}{\bar{P}_L}=(V_{ta}+V_{tl})+\left[\frac{k_{tr\cdot M}}{k_t^{1/2}}[M]+\frac{k_{tr\cdot s}}{k_t^{1/2}}[S]\right](V_{ta}+V_{tl})^{1/2} . \quad (7)$$

In this equation V, $\bar{P}_L$, $[M]$ and $[S]$ are the known quantities. Hence if the values of $k_{tr\cdot s}$, $k_{tr\cdot M}$ and k_t are given, one can easily calculate $(V_{tl}+V_{ta})$. V_{ta} can also be calculated if one employs the data for V and $\bar{P}_D$ in the thermal polymerization. Thus one gets V_{tl} which is just the quantity necessary to obtain the correct α-values.

Now it is fortunate that the necessary constants for our system were already given in previous literature. They are

$$C_m=\frac{k_{tr\cdot M}}{k_p}=6\times10^{-5}\,{}^{2)} \quad \text{at } 60°\text{C}$$

$$C_s=\frac{k_{tr\cdot S}}{k_p}=0.6\times10^{-5}\,{}^{3)} \quad \text{at } 60°\text{C for } n\text{-butanol}$$

$k_p=60$ l. mol.$^{-1}$ sec.$^{-1}$ 4)

$k_t=4.6\times10^6$ l. mol.$^{-1}$ sec.$^{-1}$ 4)

In most cases, the value of V_{ta} is a few percent or less compared with that of V_{tl}. Using the values of V_{tl} obtained by the above

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2) F. R. Mayo, R. A. Gregg and M. S. Matheson, *J. Am. Chem. Soc.*, 73, 1691 (1951).

3) R. A. Gregg and F. R. Mayo, *J. Am. Chem. Soc.*, 75, 3530 (1953).

4) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.*, A192, 309 (1948).

procedure, one can get the most reliable α-values, which are given in Table III and denoted as α_0. It is quite probable that α_0 does not exceed 2.

In order to discuss the mechanism of the reaction one must make further investigations, particularly kinetic in nature, but, from the results already obtained, one may give the following outline of the reaction.

The excited dye molecule interacts with the monomer molecule and initiates the polymerization, and at the same time it decomposes partially. Broadly speaking, the two reactions run parallel, but the process of decomposition of the dye molecule and that of initiation of polymerization are not necessarily an identical process in view of the fact that α_0 value is smaller than 1 at 40°C while it is approximately 2 at 60°C. Activation seems to be necessary for the both reactions.

Summary

Choosing pinacyanol iodide as a sensitizer, the authors studied the effects of temperature, concentration of dye and the wave lengths of incident light upon the photopolymerization of styrene in a mixture of styrene and butanol (15:1). It was found that the number of initiation processes as for polymerization produced by one decomposed dye molecule is decidedly less than 1 at 40°C, while it is about 2 at 60°C, and, from this result and other facts, it was concluded that the initiation of polymerization and the photobleaching are not necessarily an identical process though the two processes are related quite closely. As for the probable scheme of the polymerization in light, it was proposed that the addition of dye and illumination only increases the initiation process without any effects upon the remaining processes in the polymerization.

It was further found that, in favorable conditions, the fragment of decomposed dye molecule is attached to the polymer, which can also initiate the polymerization photochemically.

A more detailed account of the experiments will be reported in Journ. Instit. of Polytech., Osaka City Univ.

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