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Penetration-depth Dependence of Photochemical Conversions in the Dye-sensitized Heterogeneous Photopolymerization of Acrylamide

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The Amethyst violet-sensitized photolysis of *p*-tolyl *p*-anilinobenzenediazo sulfone initiated the polymerization of acrylamide in ethanol-water (9.3 : 0.7, v/v) to yield insoluble polymers. The polymer particles formed scattered the incident 546 nm light, leading to a change in the rate of photopolymerization. Using a 632.8 nm laser beam for viewing the sample at various penetration depths normal to the 546 nm light beam, a new method of determining the penetration-depth dependence of the yield of polymers was presented on the basis of the approximately linear relationship between the optical density at 632.8 nm and the polymer concentration. The method had the advantage that the progress of the photopolymerization, which takes place rapidly, can be easily followed with a high sensitivity below a 2.2% monomer conversion. From an evaluation of the magnitude of both the shadowing and forward scattering arising from the increasing number of polymer particles at various depths, it was confirmed that 546 nm light scattered by polymer particles brought about an effective photopolymerization over a wide range of the depths as a forward-scattering effect. Furthermore, the exposure to the 546 nm beam intensity range from 142 μW/cm^2 to 15.6 μW/cm^2 at sample depths up to 10 mm exhibited equal contributions of shadowing and forward scattering at the depth of $\sim$1.5 mm.

In photochemical experiments, the photoabsorbing properties of a sample vary with the irradiation time. This behavior may be due to change in the fraction of the photoexcited molecules during such photochemical reactions as the photobleaching of dye and photolysis. It is conceivable that the rate of the photochemical reaction varies as a function of the penetration depth as a result of the attenuation of the light transmitted through. In the photochemistry of solutions, most of the experimental data obtained by means of continuous irradiation have been concerned with the apparent reactions over the entire penetration depths in the sample solution, although the dependence of the rate on the incident light intensity has been measured. Unfortunately, there are very few published data on the penetration-depth dependence of photochemical reactions in samples, presumably because of the difficulty of measurements. We, therefore, undertook the evalution of the photochemical conversions at various penetration depths, using the dye-sensitized heterogeneous photopolymerization of acrylamide which was initiated by the amethyst violet (AV)-sensitized photolysis of the *p*-tolyl *p*-anilinobenzenediazo sulfone (TABS) formed by a reaction between sodium *p*-toluenesulfinate and *p*-anilinobenzendiazonium sulfate in ethanol–water (9.3 : 0.7, v/v). This report will describe the experimental techniques and presents the depth-dependence of photochemical conversions in the heterogeneous polymerization of acrylamide.

Experimental

Materials. The ethanol (Tokyo Kasei Co. GR grade) was used without further purification. The other materials, obtained from the Tokyo Kasei Co., were used after purification. The *p*-anilinobenzenediazonium sulfate was dissolved in a mixture of 100 ml of glacial acetic acid and 150 ml of acetone and reprecipitated with 250 ml of ether. This salt was dried in a vacuum desiccator with phosphorus pentoxide. The sodium *p*-toluenesulfinate and AV were purified by recrystallizations from a water-ethanol mixture. The acrylamide was purified by recrystallization from ethanol.

Sample Preparations. Sample solutions were prepared in the dark by mixing 2 ml of a 2.1×10^{-3} M *p*-anilinobenzenediazonium sulfate aqueous solution, 5 ml of a 5×10^{-2} M sodium *p*-toluenesulfinate aqueous solution, and 4 ml of a 10^{-3} M AV ethanol solution, by adding 7.1 g acrylamide to the mixture, and by, then diluting it with ethanol to a total volume of 100 ml. It was confirmed that 4×10^{-5} M TABS was formed with an equilibrium constant[1] of 5.2×10^3 M^{-1} in the resulting solution; stock solutions during the experimental procedure showed no change in the absorbance at the absorption maxima of 450 and 546 nm for TABS and AV respectively. AV dye was found to obey Beer's law at the range of dye concentration employed ($\leq 4\times10^{-5}$ M).

Methods. The absorption spectra were recorded on a Hitachi 624 spectrophotometer. Unless specified otherwise, all the results were obtained with quartz cells (10 mm internal path length) containing oxygen-free solutions obtained by the usual freeze-pump-thaw cycles. The molecular weights of the polyacrylamide obtained were measured by viscosity measurements at 29.4 °C in 1 M NaCl using the following relationship:[2] $[\eta]=3.73\times10^{-4}\times(\mathrm{Mw})^{0.66}$. The schematic diagram of the apparatus used for the depth-distribution experiments is given in Figure 1. The 546 nm and 632.8 nm

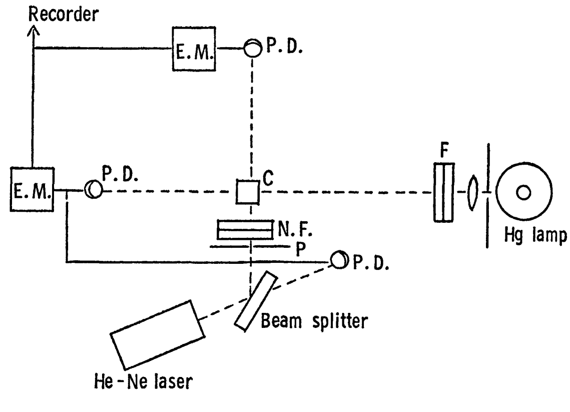

Fig. 1. Apparatus used for the depth distribution experiments.
F: 546 nm filters, N.F.: neutral density filters, P.D.: photodiode, E.M.: electrometer, C: sample cell, P: pinhole.

beam intensities were measured by means of a Coherent Radiation Laboratories Power Meter, Model 212. A 500-W super high-pressure Hg lamp was the source of the 546 nm light beam. A 2-mm aperture, a lens, and Toshiba Interference filters (KL-54+VO-52) were placed in the optical path before the cell to obtain the 546 nm light beam, which was focused at the range of the cell position with a beam diameter of 3 mm. The sample cell was positioned ~50 cm from the Hg lamp. The 632.8 nm beam from a He-Ne laser (Nippon Electric Co. GLB 2026B 1.2 mW output) was used as the analyzing light beam; its beam intensity was reduced by a beamsplitter (1 : 1), a 0.2 mm pinhole, and neutral density filters before entering the sample to prevent the photopolymerization of the sample. It was confirmed that the reduced 632.8 nm beam intensity of 0.32—0.40 μW (1.0—1.3 mW/cm^2) brought about no chemical change in the sample during the experimental procedure. The intensities of the 546 and 632.8 nm light beams transmitted through the cell were monitored by means of Sharp SBC-102 photodiodes, and photocurrent signals obtained by the use of a Takeda Riken Co. electrometer TR-8651 were read out simultaneously on a Riken Denshi Co. Sp-H recorder. The calibration of the photodiode was accomplished with neutral density filters relating the electrical output of the photodiode to the fraction of light transmitted across the gap. The photocurrent output of each photodiode was directly proportional to each light-beam power. The reference beam passing through the beam splitter was converted to a signal in order to monitor the fluctuation in the beam intensity. Figure 2 shows the coordinate system for the sample. The 632.8 nm-analyzing-light beam interesects the 546 nm light beam at 90° in the sample solution. Various penetration depths up to 10 mm can be obtained by translating the sample cell in steps of 1 mm in the x direction in the stage of microscopy. When the 632.8 or 546 nm light beam is passed through the dispersion of the polymerizing medium, the beam is attenuated by diffraction, reflection, and refraction. If one polymer particle is considered, each of the three scattering mechanisms prevents the rays from maintaining their original direction. If the photodiode as a light detector is placed at a large distance from the dispersion so that it receives only parallel light, the refractive index will have little effect on the amount of light received. Thus, each photodiode was positioned ~30 cm from the sample cell. Multiple scattering occurs when light which has been scattered by one polymer particle is scattered again by another particle. This causes the photodiode to receive an excess amount of light. However, the error introduced by multiple scattering will be minimized if the photodiode has a high angular resolution and if the diameters of the light beams are small-3 mm and 0.2 mm for 546 and 632.8 nm respectively. The above possibility was confirmed by the following result: during the photopolymerization, a 632.8 nm beam detector may receive the 546 nm light scattered by the sample dispersions, too. However, the error due to the multiple scattering could be made negligible for the sample dispersions under the present experimental conditions, since no photocurrent arising from 546 nm scattered light was detected in the range of 10^{-8}—10^{-7} A corresponding to the 632.8 nm-analyzing-light-beam signal.

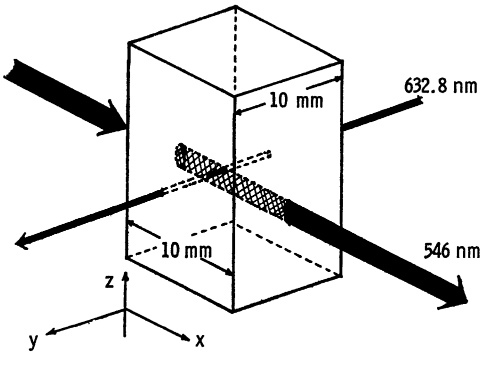

Fig. 2. Sample orientation.

Results

Fraction of 632.8 nm Laser Beam Transmission. While the deaerated sample solution was being continuously irradiated, the formation of the insoluble polyacrylamide produced a scattering of the incident light and resulted in a decrease in the fraction of the light transmitted. During the photopolymerization of acrylamide, no significant change occurred in the AV concentration. The polyacrylamide particles obtained seemed to be immovable during the irradiation (≤10 min) unless the solution was agitated. This result may be ascribed to equal specific gravities (~0.80) between the polymer particle and the solution. A long duration of the 546 nm light irradiation caused the polyacrylamide zone to bend down at the deep penetration depth in the cell. After the separation of the polymer particles produced in the 4-ml sample solution on a fine sintered glass filter, the filtrate was dumped into 200 ml of methanol, but no more polymers were precipitated as long as the monomer conversion was within 15%. This result confirmed that the amount of insoluble polymers observed in the irradiated sample cell covered sufficiently most of the polymers formed by dye sensitization, at least within a monomer conversion of 15%. The dependences of the molecular weight of the polyacrylamide on the monomer conversion and the incident 546 nm light intensity were also investigated. The experimental results are listed in Table 1. The molecular weight of 7—11×10^3 was slightly affected by both the monomer conversion (within 15%) and the incident 546 nm light intensity in the range from 17.5 to 350 μW/cm^2.

To prepare dispersions consisting of various polymer concentrations, dispersed solutions obtained by the above irradiation were diluted with ethanol. As-

Table 1. Dependences of molecular weight of polymer on monomer conversion and incident 546 nm light intensity[a)]

546 nm light intensity (μW/cm^2)	Monomer conversion (%)	Molecular weight of polyer
350	14.1	7×10^3
350	11.2	9×10^3
350	6.3	8—10×10^3
87.5	13.5	7—11×10^3
35.0	15.4	9—10×10^3
17.5	8.6	9×10^3

a) All systems contain 4×10^{-5} M AV, 4×10^{-5} M TABS, and 1 M acrylamide in ethanol-water (9.3 : 0.7, v/v).

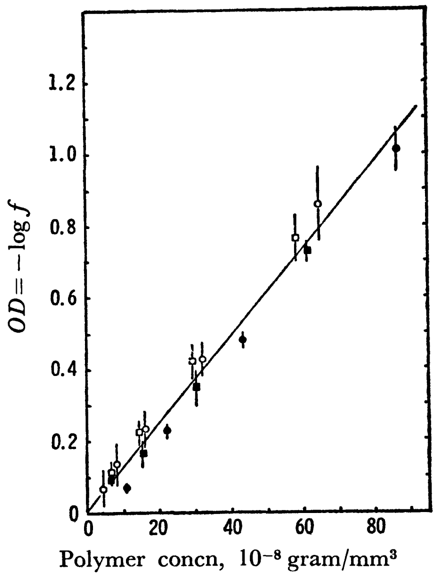

Fig. 3. Optical density ($OD = -\log f$) at 632.8 nm *vs.* concentration of polymer (10^{-8} gram/mm^3) in the dispersion obtained under various incident 546 nm light intensities. Cell thickness corresponding to the optical path length of the dispersion is 5 mm. ○: 350, ●: 87.5, □: 35.0, ■: 17.5 μW/cm^2.

suming uniform polymer concentrations in the resultant dispersions, the fraction (f) of the 632.8 nm laser beam transmitted through a dispersion (5-mm internal optical-path length) was measured. The attenuation of the incident 632.8 nm light was related to the polymer amount per unit volume of dispersion, since the AV absorption of 632.8 nm light could be neglected at low AV concentrations (below 4×10^{-5} M). The concentration of polyacrylamide, C, in 10^{-8} gram per cubic millimeter is plotted against the optical density OD ($=-\log f$) in Fig. 3. The error (vertical bars) in Fig. 3 was reflected in the fluctuation in the laser-beam intensity. An approximate linearity was shown by the curve up to $OD\approx1.1$. Above this value the experimental error was at its maximum because of the small photo-to-dark current signal ratio. The fact that the values corresponding to four different incident 546 nm light intensities seemed to lie on the same line may be explained in terms of the similar distribution of the polymer-particle size for all the dispersions, as was also suggested by the small effects of both the conversion and the incident-light intensity on the molecular weight. The slope of the rectilinear portion of the curve implied that OD was given by:

$$OD = -\log f = 2.4\times10^{-3}\,Cl = 0.17\,C'l \qquad (1)$$

where l and C' were an optical path length of the dispersion in mm and a monomer conversion in % respectively.

Recently, the light-transmission theory has been applied to non-uniform dispersions in an attempt to determine the relationship between the transmitted light and the characteristics of the dispersion. According to studies of liquid-liquid dispersions by McLaughlin and Rushton,[3] and fraction (f) of the parallel light transmitted through the liquid-liquid dispersion was independent of the drop-size distribution for all the cases studied and was expressed by the exponential relationship: $f=\exp(-al/4)$ (a is the interfacial area per unit of volume of dispersion).

It is interesting to note that Eq. (1) for our dispersions may be connected with the mathematical model simulating light transmission through liquid-liquid dispersions which was developed by McLaughlin and Rushton[3] although we have little information about the sizes and shapes of the polymer particles obtained.[4] At any rate, Eq. (1) allowed us to determine the penetration-depth dependence of the monomer conversion in the sample cell.

Photopolymerization at Various Depths. A 546 nm light beam with a diameter of 3 mm was used as an exciting light to measure monomer conversions at various penetration depths. The fraction (f) of the 632.8 nm laser beam passing through the sample at various depths normal to the 546 nm light beam was assumed to provide a one-dimensional representation of the optical-path variations in the sample as a function of x. The optical density ($=-\log f$) near the irradiated cell surface at $x\approx0.1$ mm was considered to provide the amount of the polymers obtained under a constant fraction of the incident 546 nm light beam, since there was no scattering medium in front of the cell surface during the irradiation. Figure 4 represents the variation in the optical densities at the depth of $x\approx0.1$ mm for various 546 nm light-beam intensities.

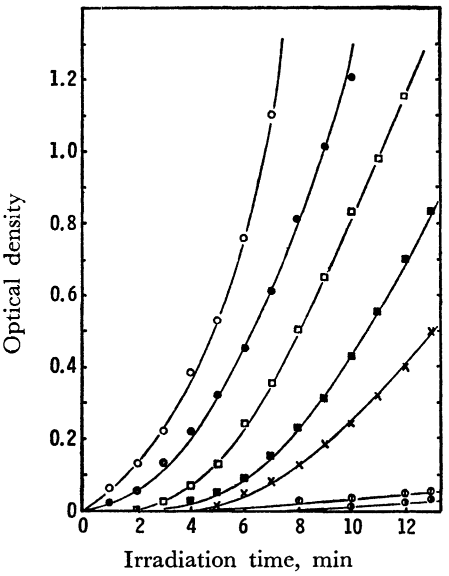

Fig. 4. Optical density at $x\approx0.1$ as a function of incident 546 nm beam intensity and irradiation time. ○: 142, ●: 99, □: 35.5, ×: 14.2, ⦶: 9.9 ◑: 7.1 μW/cm^2.

Figure 4 shows that the rate of the photopolymerization increased with the irradiation time up to the optical density of about 1.1, corresponding to a ~2.2% monomer conversion, and increased with an increase in the 546 nm-light-beam intensity. The results of the depth dependence of the optical density are shown in Fig. 5, where optical densities expressing the monomer conversions (Eq. (1)) are plotted against the irradi-

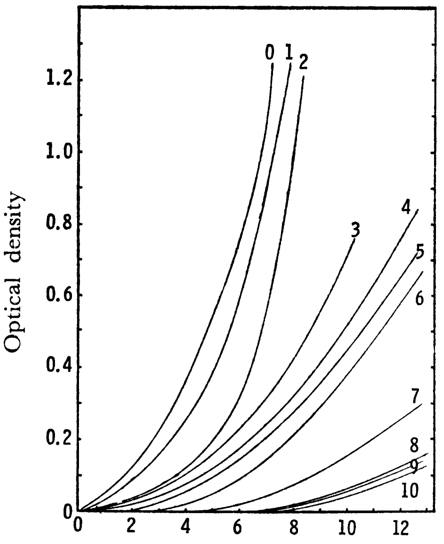

Fig. 5. Optical density as a function of irradiation time and the depth.
Numbers indicate the depth, x in mm. 546 nm light beam intensity incident on the sample is 142 μW/cm^2.

ation time or the corresponding values of the depth parameters. The plots show that the rate of photopolymerization decreases with an increase in the depth, x. The acceleration of the polymerization rate with the irradiation time at each depth may result from the accumulation of solid polyacrylamide in the system, as was discussed in connection with the heterogeneous thermal polymerization of acrylonitrile and vinyl chloride by Bamford and Jenkins[5] and Bengough and Norrish[6] respectively. When the exciting 546 nm light beam was turned on and off, the optical density at each depth showed a tendency to increase in the dark, but this dark reaction due to an after-effect was sluggish in comparison with the previous photo-reaction rate. The after-effect may be explained in terms of the occluded radicals observed in polyacrylamide particles, which induce continued polymerization and an increase in the optical density. The increase in the optical density during a period (≤ 10 min) measured from the end of the 546 nm-light irradiation excluded the possibility of the significance of the diffusion of polymer particles to the outside of the 546 nm-light-beam path, since the optical density should decrease with an increase in the standing time after irradiation if the above possibility is operative. Therefore, most of the polyacrylamide particles may be considered to remain within the pathway of the exciting 546 nm light, at least during the irradiation time (≤ 10 min). This implies that the dispersion length for the 632.8 nm laser beam is kept constant during the irradiation and that it is equal to a 546 nm-light-beam diameter of 3 mm.

Discussion

During the photopolymerization of acrylamide, the formation of insoluble polymers produced a scattering of the incident light, leading to a change in the rate of photopolymerization. The rate of the photopolymerization obviously increases when light which has been scattered by praticles induces the polymerization again ("scattering effect"). However, scattering by particles prevents a part of the exciting beam from maintaining its original direction, resulting in a less effective photopolymerization in the background ("shadowing effect"). To evaluate the magnitude of these effects of scattering and shadowing from the increasing number of polymer particles at various penetration depths, we first undertook an evaluation of the optical densities derived on the basis of the assumption that neither scattering nor shadowing occurred during the photopolymerization. This optical density will be represented by $d_1(x, t)$ as a function of the penetration depth (x) and the irradiation time (t); the optical densities without subscripts $d(x, t)$ represent the experimental values, as is shown in Fig. 5. We observed no significant permanent AV bleaching during the photopolymerization. Therefore, the 546 nm light intensity absorbed was assumed to be independent of t. Thus, the local 546 nm-light-beam intensity could be calculated, based on Beer's law, as a function of the x into the sample. When an aerobic sample solution[7] was exposed to the 546 nm light beam with its diameter of 3 mm, which would establish a beam-intensity range from 142 to 15.6 μW/cm^2 at sample depths up to 10 mm, the local 546 nm-light-beam intensity was given by Eq. (2):

$$\log I(x) = 2.152 - 0.096\,x \tag{2}$$

where $I(x)$ was the beam power in μW/cm^2 at a certain depth, x mm.

By reference to the experimental conditions for the data acquisition of Fig. 4, the optical density in Fig. 4, $d(x \approx 0.1, t)$ was assumed to represent $d_1(x \approx 0.1, t)$. When the 546 nm light-beam intensity incident on the sample was 142 μW/cm^2, the $d_1(x, t)$ estimation was made by calculating $I(x)$ for each depth, x, by Eq. (2) and by using the optical density-beam intensity curves obtained by replotting the optical densities in Fig. 4 against the incident-beam intensities for different times. A typical set of $d_1(x, t)$

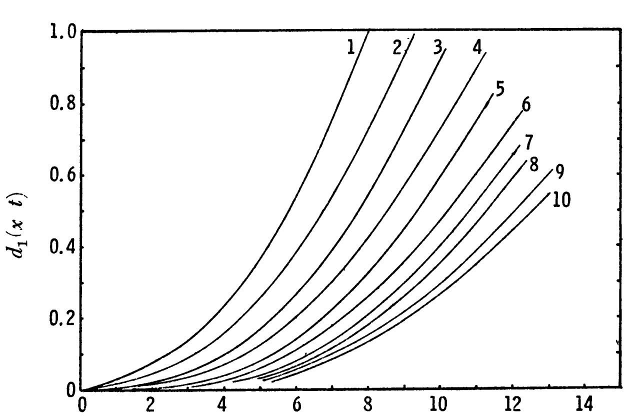

Fig. 6. $d_1(x, t)$ estimated as a function of irradiation time and depth.
Numbers indicate the depth, x in mm.

curves is shown in Fig. 6. It should be noted that the estimated set, $d_1(x, t)$, includes the contribution of the photopolymerization induced by the backscattered light from the dispersion layer with a thickness of 9.8 mm (=10−0.2), as represented by the experimental conditions in Fig. 4; therefore, the estimated set, $d_1(x, t)$, in Fig. 6 denotes the optical density derived on the basis of the assumption that neither forward scattering nor shadowing occurred. Actually, the thickness $(10-x)$ of the dispersion layer which induces a backscattering effect decreases with an increase in x. This may imply that the $d_1(x, t)$ estimated in Fig. 6 includes an excess contribution of backscattering as the x increases. However, the error introduced by this excess of backscattering becomes negligible if the backscattering effect is considered to decrease with an increase in x, since $d_1(x, t)$ decreases with an increase in x. The $d_1(x, t)$ data obtained provided the information necessary to determine the $d_{sh}(x, t)$, denoting the optical density which would be derived using the assumption that backscattering and shadowing, but not forward scattering, occurred during the photopolymerization. $d_{sh}(x, t)$ was given by Eq. (3) on the basis of the assumption of equal 546 nm light-energy densities at x:

$$d_{sh}(x, t) = -\int_0^t d_1(x, t')\frac{\partial F_1(x, t')}{\partial t'}dt' + d_1(x, t)F_1(x, t) \tag{3}$$

with $$F_1(x, 0) = 1 \tag{4}$$

where $F_1(x,t)$ was the fraction of the 546 nm light beam entering x. It should be noted that, in the estimation of $d_{sh}(x,t)$, forward scattering by polymer particles was left out of consideration. For the purpose of the approximate calculations of $d_{sh}(x,t)$, it was assumed that $dt \approx 1$(min), so Eq. (3) became:

$$\begin{aligned} d_{sh}(x, t) \approx\ & d_1(x, 0)\{F_1(x, 0)-F_1(x, 1)\} \\ & + d_1(x, 1)\{F_1(x, 1)-F_1(x, 2)\} \\ & + d_1(x, t-1)\{F_1(x, t-1)-F_1(x, t)\} \\ & \cdots\cdots\cdots\cdots\cdots\cdots \\ & \cdots\cdots\cdots\cdots\cdots\cdots \\ & + d_1(x, t)F_1(x, t) \end{aligned} \tag{5}$$

Assuming equal optical densities at the depth range from $x-0.5$ to $x+0.5$ mm (x=*integral*), $F_1(x,t)$ was given by:

$$F_1(x, t) = f_1(0, t)^{1/2l}\cdot f_1(1, t)^{1/l}\cdot f_1(2, t)^{1/l}\cdots\cdots f_1(x-1, t)^{1/l}$$
$$(l=3 \text{ and } x=0, 1, \cdots\cdots, 10) \tag{6}$$

with: $$F_1(0, t) = 1 \tag{7}$$
$$f_1(x, 0) = 1 \tag{8}$$

and:

$$d_1(x, t) = -\log f_1(x, t) = 2.4 \times 10^{-3}\, Cl = 0.17\, C'l \tag{9}$$

where $F_1(x,t)$ denoted the fraction of the 546 nm light beam entering the sample layer from $x-0.5$ to $x+0.5$ (x=*integral*) with a thickness of 1 mm (for $x=0$ and 10, entering the sample layer with a thickness of 0.5 mm), $f_1(x,t)$ was the fraction of the 632.8 nm laser beam transmitted through the dispersion of $d_1(x,t)$ at x, and l was the dispersion length in the y direction and was assumed to be independent of x and t. From this assumption l should be equal to the 546 nm light-beam diameter of 3 mm. We computed $d_{sh}(x,t)$ using Eqs. (5)—(9). The results of these calculations for $d_{sh}(x,3)$, $d_{sh}(x,4)$, $d_{sh}(x,6)$ and $d_{sh}(x,7)$ are shown in Fig. 7, along with $d_1(x,t)$ and $d(x,t)$ for each t value. The horizontal hash marks for $d_{sh}(x,t)$ represent the equal values of this quantity, arising from the approximate calculation of $F_1(x,t)$ by means of Eq. (6). Figure 7 represents both the shadowing and forward-scattering effects on the photopolymerization as a function of x for each t value. The decrease in the optical density arising from the shadowing effect was represented by $d_1(x,t)-d_{sh}(x,t)$, while the increase in the optical density by the forward scattering was given by $d(x,t)-d_{sh}(x,t)$. For $t \leq 3$, neither significant shadowing nor forward scattering was apparently observed, as was represented by $d(x,t) \approx d_{sh}(x,t) \approx d_1(x,t)$, while for $t \geq 4$ both shadowing and forward-scattering effects on the photopolymerization were observed at various depths where the photopolymerization occurred and their magnitudes at each of the depth increased with an increase in t. Some values of the optical densities for $t \leq 3$ were larger than that for $t \geq 4$, as represented by $d(x \leq 1,3) \geq d(x \geq 4,6)$ or $d(x \geq 5,7)$. If the forward-scattering effect at each value of $x \geq 4$ for $t=6$ arose from polymer particles produced at the neighboring depth, the observation of the forward-scattering effect should be expected also at $x \leq 1$ for $t=3$, because of $d(x \leq 1,3) \geq d(x \geq 4,6)$. The observation of small effects of shadowing and forward scattering for $t \leq 3$ led us to the conclusion that the 546 nm scattered light due to the increasing number of polymer particles in the foregrounds brought about the forward-scattering effect

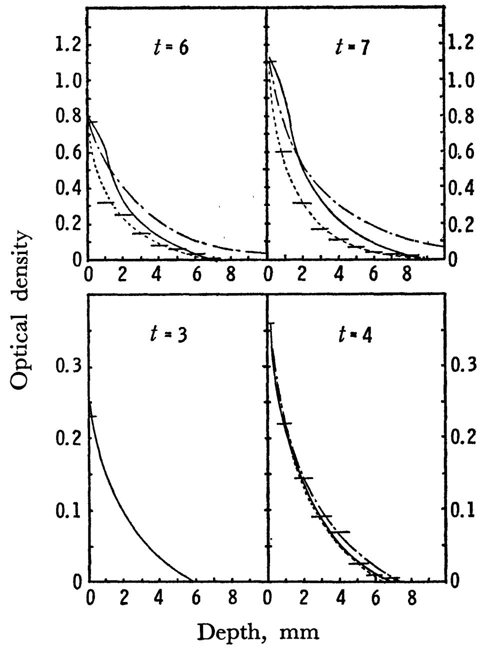

Fig. 7. Depth distribution of optical density for each of irradiation time t, in min.
—— $d(x, t)$, —·— $d_1(x, t)$, ---- $d_{sh}(x, t)$
For $t \leq 3$ three curves were identical.

at deep penetrations. When the monomer conversion at $x \approx 0$ became higher than 0.8% corresponding to $d(0,4)=0.4$, both shadowing and forward-scattering effects were apparently observed and increased with an increase in the monomer conversion, at least up to 2.2% corresponding to $d(0,7)=1.1$. $d(x,t) \approx d_1(x,t)$ at $x \approx 1.5$ for $t=6$ or 7 could be explained by equal contributions of the shadowing and forward-scattering effects.

The observation of photopolymerization by the scattered light caused us to question whether the length of the dispersions in the y direction was unchanged during the irradiation, since the polymer particles in the 546 nm-light-beam path radiated 546 nm light in the form of scattered radiation to all directions, with angular distributions of its intensity, so that polymer particles might be formed also outside the original pathway of the transmitted light beam. To see if the assumption of an unchangeable length (l) of the dispersion in the y direction was realistic during the photopolymerization, the values of l were estimated for each t value. Assuming that the optical density was nearly uniform in the range from $x-0.5$ to $x+0.5$ (x=*integral*) in the x direction, the fraction of 546 nm light transmitted through the dispersion up to 10 mm in the x direction, $F(t)$, was given by Eq. (10):

$$F(t) \approx f(0,t)^{1/2l} \cdot f(10,t)^{1/2l} \cdot f(1,t)^{1/l} \cdots\cdots f(9,t)^{1/l} \quad (10)$$

with

$$d(x,t) = -\log f(x,t) \quad (11)$$

where $f(x,t)$ represented the measured fraction of the 632.8 nm laser beam transmitted through the dispersion, with a length of l mm in the y direction. It must be noted that the estimation of $F(t)$ in Eq. (10) is based on the assumption that equal dispersion densities exist at the position of the dispersion in the y direction. For data analysis, Eq. (10) was written in optical density forms:

$$\begin{aligned} -\log F(t) = D(t) &= \{d(0,t)/2 + d(10,t)/2 + d(1,t) \\ &\quad + \cdots\cdots + d(9,t)\}/l \\ &= d(t)/l \end{aligned} \quad (12)$$

with

$$d(t) = d(0,t)/2 + d(10,t)/2 + d(1,t) + \cdots\cdots d(9,t) \quad (13)$$

Eq. (12) predicted that a plot of $D(t)$ *vs.* $d(t)$ should be a straight line whose slope is related to $1/l$. Figure 8 is a plot of the experimental data of $D(t)$ and $d(t)$ for each t value. This figure shows that an approximate linear relation ($l=3$) was obtained up to $t \leq 3$. Furthermore, it was pointed that, for $t \geq 4$, l increased with an increase in t (for example, $l=6$ for $t=7$). The linear relationship up to $t \leq 3$ seemed to be ascribable to no significant observation of the effects of shadowing and forward scattering, as is shown in Fig. 7. The observation of $d(x \leq 1.5, t \geq 6) > d_1(x \leq 1.5, t \geq 6)$ (Fig. 7) seemed to be evidence for the enlargement of l due to the forward-scattering effect from the increasing number of polymer particles at $x \approx 0$, although the assumption that l was independent of x during the photopolymerization was not realistic. It is clear that the scattered light from the polymer particles which were positioned within the pathway of the 546 nm light beam (with a diameter of 3 mm) propagating in the x direction through the dispersion induced the polymer formation outside the original pathway of the 546 nm light beam transmitted. Therefore, it does not matter if the measured optical density $d(x,t)$ is regarded as an amount corresponding to the dispersion of $l=3$, no matter how the dispersion lengthened in the y direction during the photopolymerization.

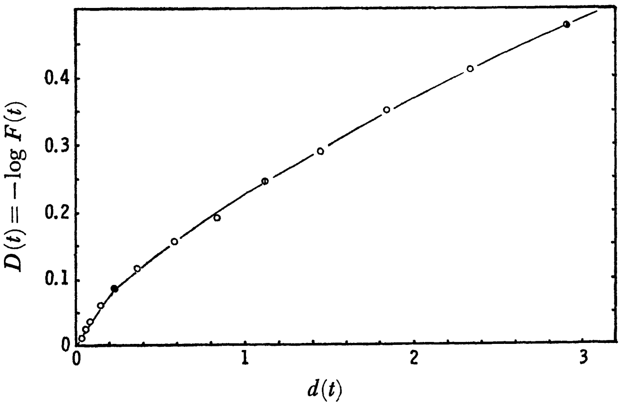

Fig. 8. $D(t)$ *vs.* $d(t)$ for each irradiation time (Ex. ● 3, ⦶ 5, ◑ 7 min).

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4) The microscopic examination showed that our dispersions consisted of particles of various sizes smaller than 0.1 mm in diameter. According to studies of the heterogeneous polymerization by Bamford and Jenkins[5] a growing polymer radical becomes insoluble at a relatively low degree of polymerization, and the aggregation of polymer molecules by coiling leads to the formation of polymer particles.

5) C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc., Ser. A*, **216**, 515 (1953).

6) W. I. Bengough and R. G. W. Norrish, *ibid.*, **200**, 301 (1950).

7) The exposure of the aerobic sample to 546 nm light induced no observable polymerization of acrylamide, although the sensitized photolysis of TABS was observed without any of the permanent bleaching of AV previously reported[1].