N-Phenylglycine-(Thio)xanthene Dye Photoinitiating System and Application to Photopolymer for Visible Laser Exposure

TSUGUO YAMAOKA, YU-CHUAN ZHANG,* and
KEN'ICHI KOSEKI, *Department of Image Science and Technology,
Faculty of Engineering, Chiba University, Yayoi-cho,
Chiba 260, Japan*

Synopsis

It was found that the bimolecular type photoinitiators consisting of *N*-phenylglycine and (thio)xanthene dyes exhibited high initiating efficiency on irradiation of visible light. From the time-resolved spectroscopic study, the free radical is formed by the sensitized decarboxylation of *N*-phenylglycine in the presence of (thio)xanthene dye. By using these initiating systems, the visible laser sensitive photopolymer was prepared and the imaging characteristics were evaluated.

INTRODUCTION

Recently sensitivity enhancement of photopolymers is attracting interest from the viewpoint of laser direct imaging.[1-3] The development of a highly sensitive photopolymer based on photopolymerization requires a photoinitiator which is sensitive to visible light to generate initiating free radicals with high efficiency.

Several visible absorbing photoinitiators which have been reported so far are of the bimolecular type consisting of a radical generator and a sensitizing dye. For example, biimidazole acts as the visible light sensitive photoinitiator with the aid of arylketones.[4] Williams et al. reported that *N*-phenylglycine, in the presence of ketocoumarin dye, shows sensitivity in the visible region up to 550 nm.[5] In addition, diphenyliodonium salt-merocyanine dye[6] and trichloromethyltriazine derivative-cyanine dye[7,8] are also reported as highly sensitive initiating systems upon exposure to visible light. Although quite a few visible-light-sensitive initiators have been proposed, a detailed report on the imaging characteristics of the photopolymeric material using these initiators cannot be found.

In the present study, it was found that bimolecular type photoinitiators consisting of *N*-phenylglycine and a xanthene or thioxanthene dye exhibited high initiating efficiency. By using these initiating systems, laser sensitive photopolymers were prepared and imaging characteristics as well as the free radical forming photochemical processes were studied.

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*On leave of absence from Peking Institute of Chemical Engineering, Beijing, China.

TABLE I
Characterization of Poly(styrene-co-Maleic Anhydride) [p(St-co-MA)]
and Its Half-Esters by 2-HEMA

| | p(St-co-MA) | | | Half-ester of the copolymer by 2-HEMA |
Abbreviation	$\overline{M}_w$ ($\times 10^4$)	$\overline{M}_w/\overline{M}_n$	St : MA	molar content of 2-HEMA in the copolymer (%)
CP	5.85	1.8	1 : 1.6	0
CPA-1	5.85	1.8	1 : 1.6	59
CPA-2	4.19	2.3	1 : 1.4	52
CPA-3	5.31	2.3	1 : 1.4	41

EXPERIMENTAL

Photoinitiators

Commercially available N-phenylglycine (NPG) was used after purification by sublimation at 80°C, 10^{-3} mm Hg. Xanthene and thioxanthene dyes were supplied by the Nippon Kayaku Co.

Synthesis of the Reactive Copolymer

Ten grams poly(styrene-co-maleic anhydride), 3.2 g 2-hydroxyethyl-methacrylate (2-HEMA), 0.1 g imidazole, and 0.05 g hydroquinone were dissolved in 300 mL methylethylketone. The solution was reacted for 5 h at 60–65°C, and then poured into a large amount of 5% aqueous solution of acetic acid to precipitate the reactive copolymer [the half-ester of poly(styrene-co-maleic acid) by 2-HEMA]. The copolymer was obtained by filtration and purified by dissolving in MEK and precipitating from aqueous solution of acetic acid. The purification was repeated twice, followed by vacuum drying to constant weight.

The molecular structure was identified by IR spectrum and the degree of esterification was determined by elemental analysis. The characterization of the copolymer is shown in Table I.

Measurement of Sensitivity

The photosensitive layer was prepared by a coating 2-methoxyethanol solution of the photosensitive composition onto a grained aluminum plate and drying at 80°C to produce a 2-μm-thick film.

Spectral sensitivity was measured using a Narumi RM-23 monochromator equipped with a grating and a 500-W xenon arc lamp. The exposed photosensitive layer was developed in ethanol or an aqueous solution of sodium carbonate, depending on the binder polymer used, and the plate was toned by an aqueous solution of methyl blue or printing ink as required.

The photographic sensitivity was measured by exposing the photosensitive layer through a 21-step tablet (Kodak no. 2 step tablet) with a fluorescence chemical lamp (Toshiba FL-20BL) *in vacuo*. Selection of the wavelength of the exposing light was carried out by using an appropriate glass filter. The photosensitivity (E, mJ/cm^2) was defined as the minimum exposure energy

insolubilizing the layer, and is calculated

$$E = I_0 \times T \times t \tag{1}$$

where I_0 is the incident light intensity (mJ/cm²s), T is the transmittance of the step at which the photosensitive layer begins to be insolubilized and t is exposure time (s).

Laser exposure was carried out with an argon ion laser (Spectra-Physics, Model 164-09, maximum power 5 W) with the TEM$_{00}$ beam diameter 1.25 mm, at which the energy is $1/e^2$ of the peak energy.

The sensitivity was determined by static and by scanning exposure.[9] In the static measurement, the sensitive layer was exposed with the laser beam spot by spot, by varying the exposure time at constant laser power. The incident energy required to insolubilize a spot size of the layer equal to the beam diameter was defined as the sensitivity. In the scanning measurement, the photosensitive layer was scan-exposed with the laser beam, which was focused to 25 μm in diameter, by varying the scanning speed at constant intensity. The sensitivity was determined by the incident energy with which the line width equal to the beam diameter is insolubilized.

Measurement

Infrared absorption spectra were measured on a Hitachi Infrared Spectrophotometer 260-10. ESR spectra were obtained by using a Japan Electron Optics Lab. Co. Ltd., JES-ME-3X. The molecular weight of polymers were measured by a Toyosoda high-speed liquid chromatograph HLC-802UR. The GPC columns (column: G-5000H$_6$ + G-3000H$_8$ + G-2000H$_8$) were calibrated with monodisperse standards of polystyrene (Waters Associates Inc.). The photon energy was measured with a Coherent power meter 210 for the argon ion laser and with an Eplay thermopile E-6 for the other light source.

RESULTS AND DISCUSSION

Photoinitiating System

The photoinitiating system consists of NPG and the sensitizing dye where NPG is the radical generator. As sensitizers, xanthene and thioxanthene dyes, having the general formula I and II, were used. The dyes used in this study are summarized in Table II and all of them have substantial absorption in visible wavelengths.
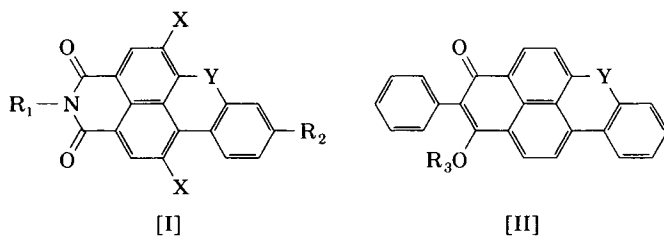
Scheme 1.

TABLE II
The Structure of Xanthene and Thioxanthene Dyes Used as Sensitizer

Dye no.	R_1	R_2	R_3	X	Y
XD-1	$CH_3CH(OH)CH_2$	MeO		H	O
XD-2	C_3H_7	$(Et)_2N$		H	O
XD-3	$MeO(CH_2)_3$	$(Et)_2N$		Cl	O
XD-4	$EtO(CH_2)_3$	$(Et)_2N$		Cl	O
XD-5	$HO(CH_2)_2$	$(Et)_2N$		Cl	O
XD-6	$(Et)_2N(CH_2)_3$	$(Et)_2N$		Cl	O
XD-7	$C_4H_9CH(Et)CH_2$	$(Et)_2N$		Cl	O
XD-8	$(Et)_2N(CH_2)_3$	$(Et)_2N$		Br	O
XD-9	$EtO(CH_2)_3$	$(Et)_2N$		Br	O
TXD-1*			Et		S
TXD-2*			MeCO		S
TXD-3	$i\text{-}C_3H_7O(CH_2)_3$	H		H	S

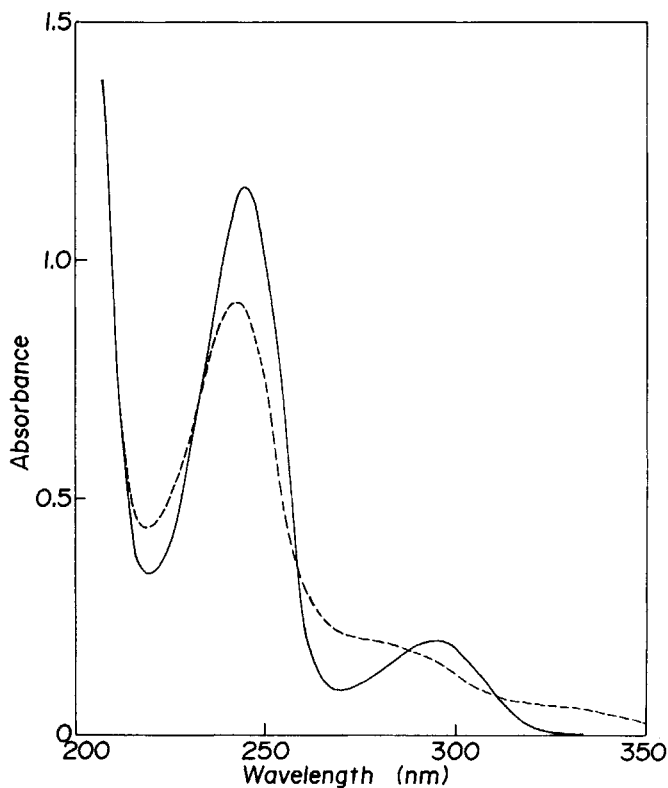*Refers to the general formula [II]. Others refer to [I].

Fig. 1. The electronic spectra of NPG (—) and its change by irradiation (---) in ethanol solution.

Figure 1 shows the absorption spectrum of NPG in solution. NPG has its absorption band in the ultraviolet region and decomposes by the irradiation of ultraviolet light.

The Photoinduced Reaction of Thioxanthene Dye and NPG

Figure 2 shows the absorption spectrum of thioxanthene dye (TXD-1) in 2-methoxyethanol. The spectrum does not exhibit any change on irradiation, indicating that, by itself, TXD-1 is photochemically stable in the solution. When NPG was added to the solution and then degassed, the spectrum of TXD showed a remarkable change due to irradiation with visible light, while it did not change at all by irradiation in the presence of oxygen. As shown in Figure 3, the absorption of TXD-1 at 508 nm was decreased by irradiation, and a transient absorption band appeared in the 380–450 nm region. The transient absorption is stable in the absence of oxygen, but disappears rapidly by exposing the solution to air, and the spectrum of TXD-1 is recovered.

The photoinduced spectral change of TXD-1 was studied by using other aromatic amines in place of NPG. TXD-1 and an aromatic amine such as N,N-dimethylaniline, p-dimethylaminobenzoic acid, p-aminobenzoic acid, or p-nitro-N,N-dimethylaniline were dissolved in oxygen-free 2-methoxyethanol, and the change of the absorption spectrum due to irradiation was measured. In the case of p-nitro-N,N-dimethylaniline, the spectrum of TXD-1 did not show any change. On the other hand, the spectrum of TXD-1 in the presence of N,N-dimethylaniline, p-dimethylaminobenzoic acid, or p-aminobenzoic acid showed a change due to irradiation similar to that which is obtained for the TXD-1-NPG combination. Figure 4 shows the spectral change for TXD-1-N,N-dimethylaniline as an example. The transient absorption is assigned to
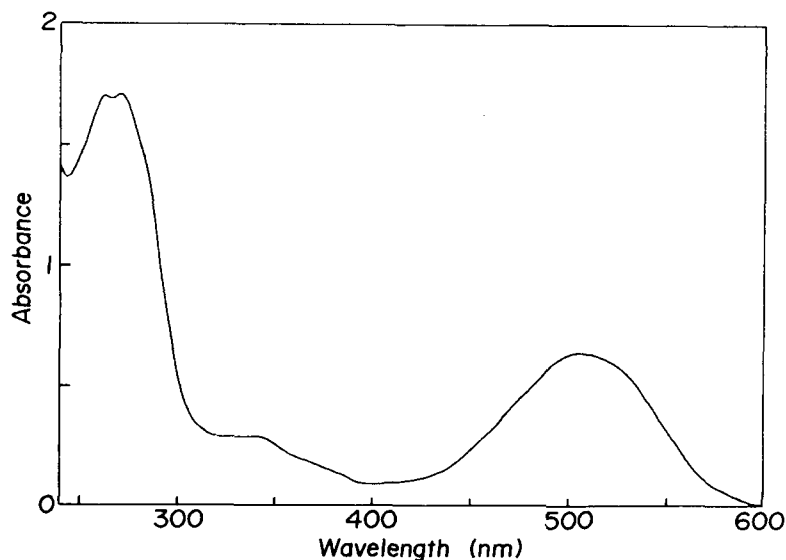

Fig. 2.   The electronic spectrum of TXD-1 ($4.83 \times 10^{-5}M$) in 2-methoxyethanol.
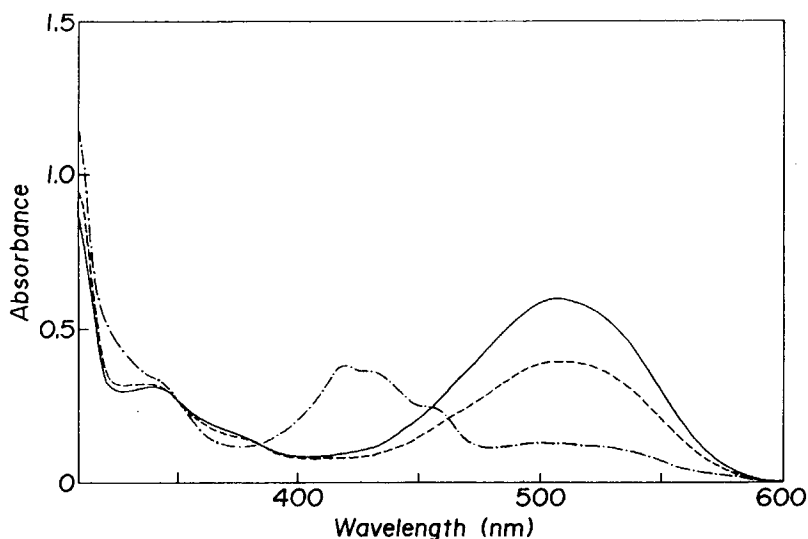
Fig. 3. The change of the electronic spectrum of 2-methoxyethanol solution containing TXD-1 $(4.83 \times 10^{-5}M)$ and NPG $(7.53 \times 10^{-4}M)$ due to irradiation. Before (—) and after irradiation (— · — · —), and after contacting with air (---).

the reaction intermediate originating from TXD-1, since its wavelength and shape are the same with variation of the amine.

The ESR spectrum of a 2-methoxyethanol solution containing TXD-1 and NPG gave a signal due to a free radical, as is shown in Figure 5, when it was irradiated with visible light at room temperature in the absence of oxygen. The signal is stable when air is excluded, and shows fine structure indicating that the π-radical was formed by photoirradiation. A similar ESR spectrum
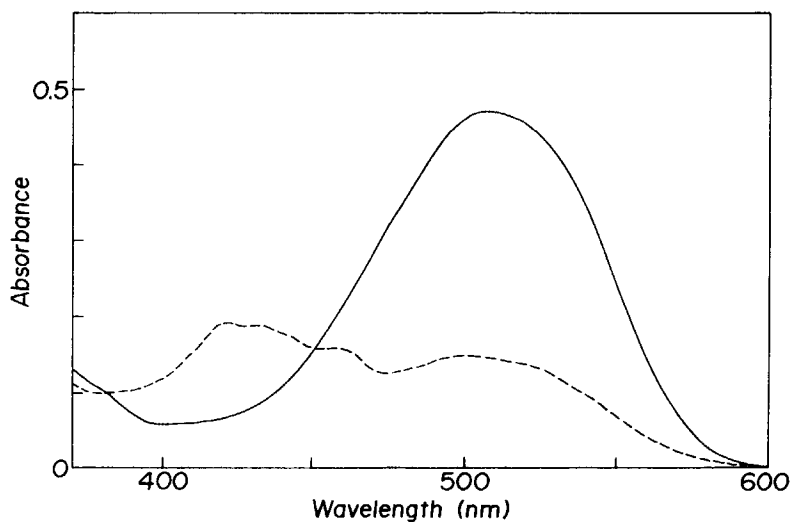

Fig. 4. The change of the electronic spectrum of 2-methoxyethanol solution containing N,N-dimethylaniline $(2.07 \times 10^{-3}M)$ and TXD-1 $(3.70 \times 10^{-5}M)$ due to irradiation. Before (—) and after irradiation (---).
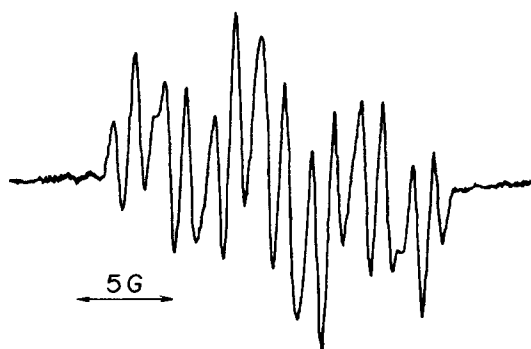
Fig. 5.   ESR spectrum of the irradiated 2-methoxyethanol solution containing NPG and TXD-1 at room temperature.
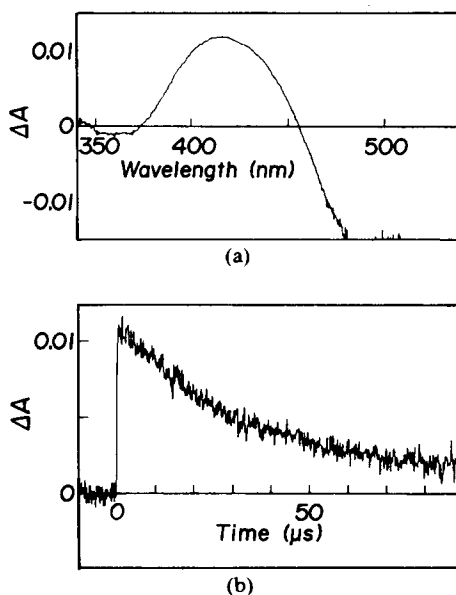

Fig. 6.   (a) The transient difference spectrum of TXD-1 after 533 nm laser pulse (5 ns) excitation in 2-methoxyethanol solution. The delay time is 100 ns. (b) The time dependence of absorbance change (ΔA) at 400 nm for TXD-1 in 2-methoxyethanol solution.

was also observed for a poly(*N*-vinyl-2-pyrroridone) (PVP) matrix containing TXD-1 and NPG. The free radical species is postulated to be anion radical of TXD-1, since it is formed only in the presence of NPG and other aromatic amines which have low ionization potential and act as electron donors.

Figure 6(a) shows the transient difference spectrum of TXD-1 in oxygen-free 2-methoxyethanol at 100 ns after a 533 nm laser pulse (5 ns) excitation. The spectrum has its absorption peak at 420 nm and decays within 100 μs. Figure 6(b) shows the time dependence of the absorbance change at 400 nm. The decay kinetics of the transient species is first order, and the rate constant was determined to be $k_d = 3.4 \times 10^4$ s^{-1}. The life time of the transient species is very sensitive to the presence of oxygen in the solution, and it is shortened
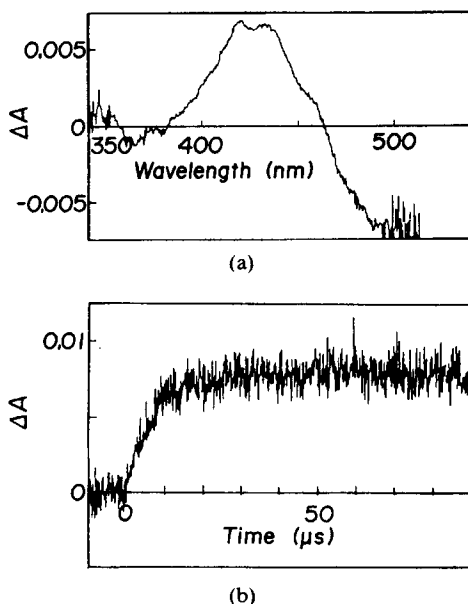
(a)

(b)

Fig. 7. (a) The transient difference spectrum of 2-methoxyethanol solution containing TXD-1 and NPG after 533 nm laser pulse excitation. The delay time is 100 μs. (b) The time dependence of absorbance change (ΔA) at 430 nm for TXD-1/NPG in 2-methoxyethanol solution.

from 29.5 μs in the absence of oxygen to 0.25 μs in the presence of oxygen. From these facts, the transient species is deduced to be the triplet state of TXD-1, and the transient spectrum is due to triplet–triplet absorption.

When NPG is added to the solution, the spectrum due to the triplet–triplet absorption of TXD-1 is not detected. Instead, another absorption with vibrational structure appeared at 380–470 nm as is shown in Figure 7(a). Figure 7(b) shows the time dependence of the formation of the transient species. The formation of the transient species is slow, and reaches a constant absorbance at 20 μs after laser pulse excitation. The transient species is stable in the absence of air, and its wavelength and shape are very similar to that which was observed in the stationary light exposure.

From these facts, the transient absorption is assigned to the anion radical of TXD-1.

Brimage et al. reported[10] that acids of the type Ar—X—CH$_2$COOH (X=O, S, or NH) undergo decarboxylation on irradiation in the presence of acridine, phenazine, and methylene blue. The sensitized decarboxylation process was proposed as follows:
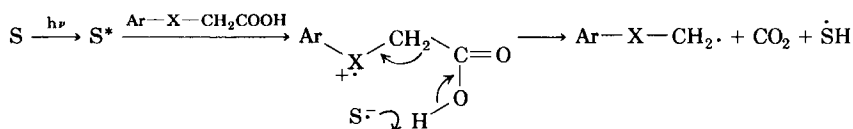
Based on the experimental facts mentioned above, together with the decarboxylation scheme proposed so far, the mechanism of the photoinduced

reaction between NPG and TXD-1 is proposed as follows.

$$\text{TXD-1} \xrightarrow{h\nu} {}^1\text{TXD-1*} \longrightarrow {}^3\text{TXD-1*}$$
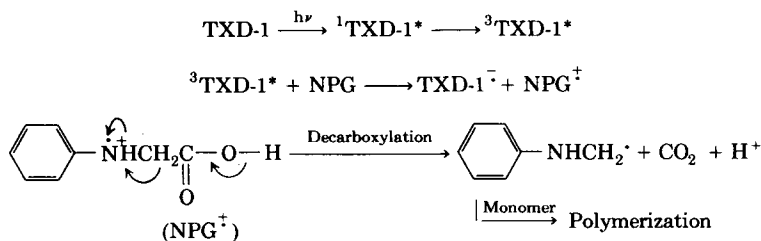
$${}^3\text{TXD-1*} + \text{NPG} \longrightarrow \text{TXD-1}^{\cdot -} + \text{NPG}^{\cdot +}$$

The excited triplet of TXD-1 interacts with NPG to give the TXD-1 anion radical and NPG cation radical. The long-lived transient species observed in the electronic and the ESR spectrum of the photoirradiated solution of TXD-1-NPG is considered to be the anion radical of TXD-1. The slow formation of the anion radical in Figure 7(b) suggests that the electron transfer occurs via the triplet state of TXD-1. The cation radical of NPG may decompose to give a radical fragment which initiates the photopolymerization of a monomer. The electron transfer via the excited singlet is being examined.

Sensitivity of the Poly(*N*-Vinyl-2-Pyrrolidone) (PVP) Based Photopolymer System

The photosensitive layer was prepared by coating a 2-methoxyethanol solution of the composition given in Table III onto a grained aluminum plate and drying to a finish of about 2 μm thickness. It consists of PVP of molecular weight 360,000 as the binder, pentaerythritoltriacrylate (PETA) as the monomer, NPG as the photoinitiator, and xanthene or thioxanthene dye as the sensitizer.

Figure 8 shows the spectral sensitivity of the photosensitive layer in which the photoinitiator is varied. When NPG was used as the photoinitiator by itself, without sensitizer, the sensitivity appeared only in ultraviolet wavelengths shorter than 370 nm. On the other hand, when the sensitizing dye was used as the photoinitiator without NPG, the sensitivity appeared over a broad wavelength region from ultraviolet to visible light, which corresponds to the absorption spectrum of the dye. These facts show that both NPG and the sensitizing dye act as photoinitiators by themselves, but the initiating efficiency is low and a long exposure time is required to insolubilize the layer. However, when NPG was combined with the sensitizing dye, the photosensitivity is remarkably enhanced over a wide spectral region ranging from ultraviolet to near 600 nm.

TABLE III
Fundamental Composition of the Photosensitive Layer

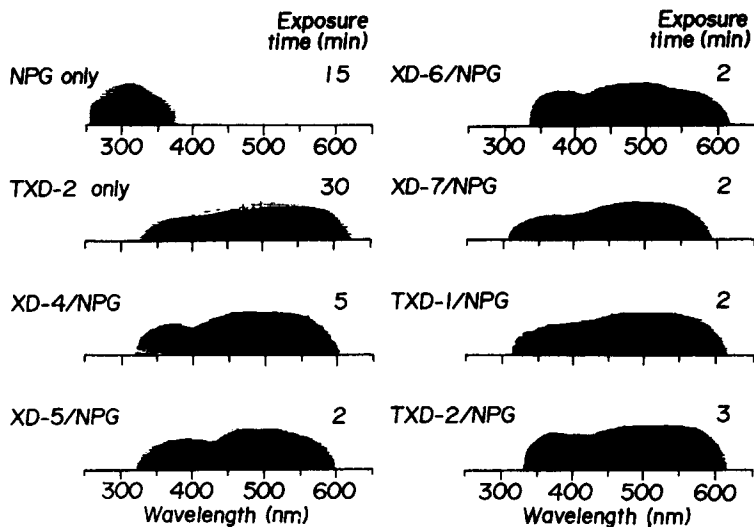| Component	
Binder polymer	100 parts
Multifunctional acrylate monomer	100 parts
Initiator	8 parts
Sensitizing dye	6 parts

Fig. 8. The spectral sensitivities of the PVP-based photosensitive layer measured by varying the initiator.

The sensitivity values of the photosensitive layers for ultraviolet, visible and argon laser light are summarized in Table IV. The photosensitive layer containing only NPG as the photoinitiator showed a sensitivity of 49 mJ/cm^2 to ultraviolet light. As mentioned above, the sensitizing dyes act as photoinitiators by themselves, and some of them have relatively high sensitivities of some mJ/cm^2. However, when NPG was combined with the sensitizing dye, a very high sensitivity up to a few μJ/cm^2 was obtained for light filtered with an Y-43 filter. Especially for the combination of NPG and xanthene dye XD-5, a highest sensitivity of 60 μJ/cm^2 was obtained for visible light, and 200 μJ/cm^2 for 488 nm light of an argon laser. These values were much higher than those which have been reported for photopolymers in practical use.[11]

Sensitivity in high speed scanning exposure by the laser beam was measured by varying the laser power, and the characteristic curve for the scanning exposure was obtained by plotting the line width after development against the incident laser energy. It is shown in Figure 9 that the characteristic curves determined at different laser powers overlap each other, indicating that the sensitivity of the photosensitive layer follows the reciprocity law.

It must be noticed that PVP binder gives particularly higher sensitivity in comparison to other polymeric materials such as poly(methyl methacrylate), polystyrene or poly(vinyl acetate).[12] The higher sensitivity shown for PVP is responsible for the higher photopolymerization rate of the monomer in PVP compared to the other polymers.[13] The reason for the higher polymerization rate of the monomer in PVP is not elucidated at present.

Application to Presensitized Plate for Laser Exposure

The photosensitive layer was also applied to a presensitized printing plate. Although PVP shows high sensitivity as mentioned in the previous section, it

TABLE IV
Sensitivity Values of the PVP-Based Photosensitive Layer by Use of NPG
and Various Sensitizing Dyes as Photoinitiator

		Sensitivity (mJ/cm^2)		
		Chemical lamp		Laser
	Dye Initiator	No filter	Y-43 filter	(488 nm)
XD-1	—	2.0	0.77	
	NPG	0.65	0.49	0.50
XD-2	—	150		
	NPG	17	19	
XD-3	—	6.2	2.0	8.0
	NPG	2.3	2.4	1.7
XD-4	—	8.9	6.8	
	NPG	1.2	0.44	0.37
XD-5	—	8.9	3.4	
	NPG	0.22	0.060	0.20
XD-6	—	8.9	4.8	
	NPG	0.87	0.24	0.23
XD-7	—	2.4	1.3	
	NPG	1.2	0.44	0.30
XD-8	—	49	29	
	NPG	2.4	1.3	0.40
XD-9	—	69	58	
	NPG	3.2	1.8	0.90
TXD-1	—	75	29	
	NPG	0.65	0.49	0.40
TXD-2	—	6.2	2.7	
	NPG	0.88	0.33	1.3
TXD-3	—	9.7	3.8	
	NPG	0.65	1.7	0.17

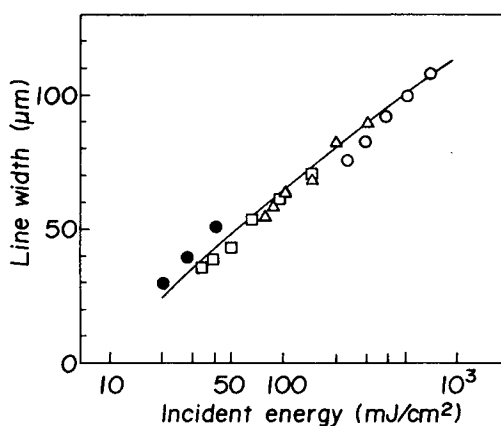

Fig. 9. The characteristic curves of the PVP-based photosensitive layer measured by scanning exposure in air by varying the incident beam power: (○) 6.1×10^4 mJ/cm^2 s; (△) 2.0×10^4 mJ/cm^2 s; (□) 8.2×10^3 mJ/cm^2 s; (●) 1.6×10^3 mJ/cm^2 s.

TABLE V
Sensitivities of the Photosensitive Layers in Which the Reactive Polymers
Were Used as the Binder

| Polymer | Sensitivity (mJ/cm^2) | |
	Chemical lamp (Y-43)	Laser (488 nm)
CP	3.7	44
CPA-1	0.90	2.3
CPA-2	0.90	1.3
CPA-3	3.5	7.8

is not appropriate for the presensitized plate, since PVP is too hydrophilic to be ink-receptive.

Instead of PVP, a reactive copolymer was synthesized as described in the experimental section. The copolymer is expected to show higher sensitivity as a binder polymer, owing to the reactivity of the methacryloxyethyl group.

Table V shows sensitivities for a series of photosensitive layers in which the copolymers, having a different amount of methacryloxyethyl groups, are used as the binder. The composition of the photosensitive layer is the same as given in Table III, except that PVP was replaced with the copolymer. NPG (4 wt%) and TXD-1 (4 wt%) are added as photoinitiator. While poly(styrene-co-maleic anhydride) has a low sensitivity of 44 mJ/cm^2, it shows a remarkably enhanced sensitivity of 1.3–7.8 mJ/cm^2, depending on the amount of 2-HEMA introduced in the copolymer.

Table VI shows the effect of photoinitiator on the sensitivity of the photosensitive layer in which CPA-1 was used as the binder. It is noticed that the bimolecular type initiator, consisting of a mixture of dye (TXD-1) and NPG, has a high sensitivity of 2.1 mJ/cm^2 to the argon laser visible line, while neither show sensitivity by themselves in this wavelength region. The trimolecular type initiator consisting of TXD-1, NPG, and peroxide (3,3',4,4'-tetrakis(t-butyldioxycarbonyl) benzophenone (BTTB)), exhibited the highest sensitivity (1.2 mJ/cm^2) among the initiators investigated in this study.

Figure 10 shows the relationship between the sensitivity and the concentration of TXD-1 and NPG, where the binder polymer is CPA-1 and the concentration of TXD-1 or NPG was varied by keeping that of the other

TABLE VI
Dependence of the Sensitivity Values of Photopolymer on the Photoinitiator
for Visible and Laser Light (488 nm)

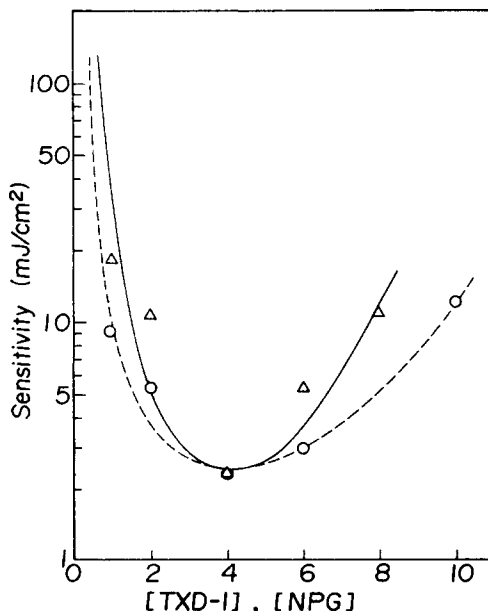| Initiator | Sensitivity (mJ/cm^2) | |
	Chemical lamp (Y-43)	Laser (488 nm)
TXD-1	195	—
NPG	48	—
TXD-1 + NPG	0.9	2.3
TXD-1 + NPG + BTTB	0.7	1.2
TXD-1 + NPG[a]	> 213	—

[a] No PETA monomer.

Fig. 10. The relationship between the laser sensitivity and the concentration of TXD-1 (—△—) and NPG (---○---).

constant at 4 wt %. The effect of the concentration on the sensitivity is almost the same for NPG and TXD-1, rendering the highest sensitivity at a concentration of 4 wt %.

The sensitivity is affected by the atmosphere, since the photopolymer is based on radical polymerization. Figure 11 shows the effect of oxygen on the sensitivity, which was measured in a vacuum box with controlled air pressure. It is noticed that the sensitivity is very sensitive to the concentration of oxygen, changing from 2 mJ/cm^2 at 2.7 × 10^3 Pa to 70 mJ/cm^2 at 14.7 × 10^3 Pa. This fact means that, when this polymer is put to practical use, a top coating will be required to prevent the air from contacting the sensitive layer.

The development was carried out with an aqueous solution of sodium carbonate of a concentration higher than 0.1 wt %. The sensitivity value after development was almost constant for concentrations between 0.1 and 1 wt %, and for temperatures between 10 and 55°C. The developing time between 2 and 10 min gave almost the same sensitivity, showing a wide latitude in the development.

The shelf life of the photopolymer is an important point for its use as a practical material. The shelf life of the polymer was measured by keeping it in a high temperature atmosphere. The photopolymer, consisting of TXD-1, NPG as the initiator, and 0.3 wt % hydroquinone as the inhibitor, was kept in this atmosphere at 80°C, and the sensitivity change was measured every 15 min. No sensitivity change was observed up to 75 min, indicating good thermal stability.

Figure 12 shows the laser exposed image, which was formed with the photopolymer consisting of CPA-2 as the binder and the trimolecular type initiator, TXD-1/BTTB/NPG. The exposing conditions are as follows: wave-
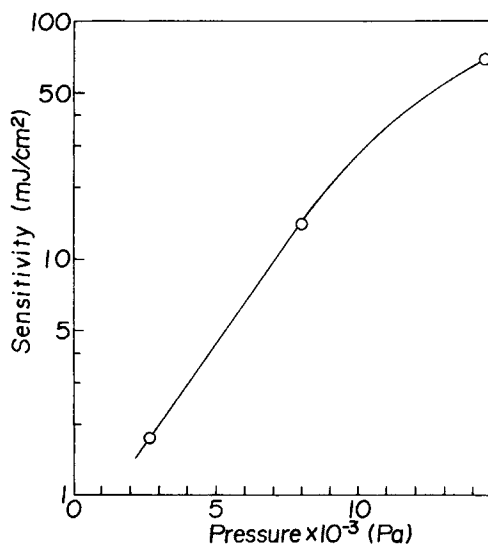
Fig. 11.   The oxygen effect on the sensitivity of the photosensitive layer containing TXD-1 and NPG.
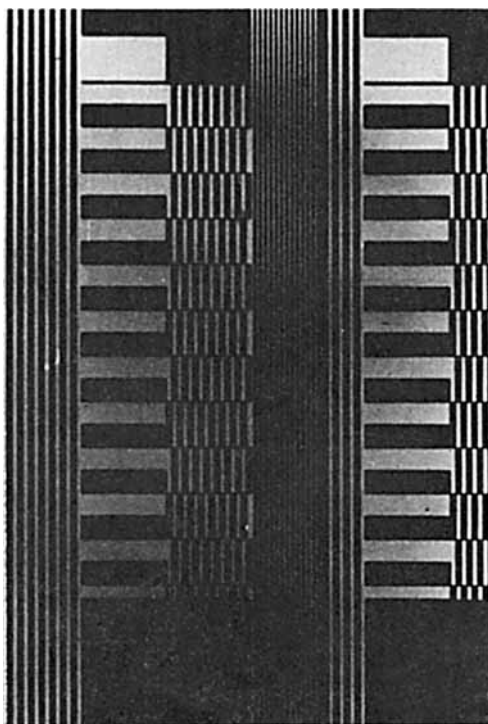

Fig. 12.   The photograph of laser exposed image on aluminum plate obtained by laser scanning exposure using the photosensitive layer containing trimolecular type initiator, TXD-1/BTTB/NPG.

length 488 nm; laser output power 100 mW; scanning speed 9.8 m/s; beam diameter 25 μm; the line density 23.6 1/mm. The first diffraction light of the argon laser was modulated with an AO modulator. The efficiency of the optical system was 0.3. The sensitivity of the polymer was calculated as 7 mJ/cm^2, based on Kaplan's equation[14] at the exposing condition described above.

The printing test was carried out with this plate on an offset printing machine, and good prints with high resolution and density were obtained.

These results show that the photopolymer developed in this study offers a sensitive material for a presensitized plate which can be exposed with a 100 mW Ar laser.

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