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Photopolymerization System with Microgel Matrix: Application to Visible-Laser-Recording Materials and Effects of Microgel on Rate of Photopolymerization

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Microgels with ammonium ions on the surface are combined with acrylate monomers and visible light absorbing photoinitiators consisting of 3,3′-carbonylbis(7-(diethylamino)coumarin) (KCD, **1**) and 3,3′,4,4′-tetrakis(*tert*-butyldioxycarbonyl)benzophenone (BTTB, **2**). This results in a visible-laser-sensitive photopolymer. Photopolymers with a heterogeneous matrix are insoluble and provide oleophilic images when exposed to visible laser and developed in tap water. Its photosensitivity and rate of photopolymerization are investigated and compared with those of conventional photopolymers with homogeneous polymer matrices. Results show that microgel-based photopolymers exhibit a higher rate of photopolymerization as well as higher sensitivity levels than conventional ones. Its high sensitivity is attributed to the rapid photopolymerization of acrylate monomers in a microgel matrix with ammonium ions. The effects of several microgels made up of different compositions on the rate of photopolymerization of acrylate monomers are investigated. Results show that the rate of photopolymerization increases directly with increasing amounts of cationic groups on microgel surfaces. Microgels quaternized with tertiary amines with a lower pK_a are most effective in accelerating the rate of photopolymerization.

Introduction

Sensitivity increases in photopolymers may lead to better laser direct imaging.[1] Several highly sensitive photopolymers have been developed.[2] Using photoinitiators that are sensitive to visible light to generate efficient initiating free radicals. For example, one author reported that the photoinitiation system of the ketocoumarin dye-sensitized peroxyester yields high-quality photopolymers. This photoinitiating system when combined with acrylate monomers and a polymer matrix is highly sensitive to 488-nm Ar$^+$ laser light.[3] Nevertheless, most of the photopolymers that are sensitive to visible light cannot be used because they lack sufficient photosensitivity.

Several reports on photopolymers prepared by using microgels have appeared recently. Kanda reported that ultraviolet (UV) photosensitive films with microgels provide good coating and adhesive characteristics.[4] However, photosensitivity was not discussed. Michael et al. compared UV photosensitive films with microgels to a similar UV photopolymerization composition without them and found the former to have a higher level of photosensitivity.[5] However, the microgels used in the above report coalesce in the photopolymer layer because of poor dispersibility in the coating solution and must be used together with a homogeneous polymer matrix to obtain good resolution and developability. These factors decrease the sensitivity of the photopolymers, and render them unsatisfactory. Our previous paper[6] reported on a UV photopolymerization system based on a microgel matrix that exhibited significant increases in photosensitivity to UV light, compared with conventional photopolymers with homogeneous polymer matrices.

In the present study, visible-laser-sensitive photopolymers are developed by using the microgel matrix. We now describe the materials used as well as the characteristics and reaction mechanisms of these photopolymers.

Experimental Section

Materials. Styrene (St), chloromethylstyrene (CMS, meta and para mixture) and divinylbenzene (DVB, meta and para mixture, *ca.* 55% in ethylvinylbenzene + diethylbenzene) were purchased from Tokyo Chemical Ind. Co., Ltd., and were distilled under a reduced pressure of *ca.* 10^{-3}–10^{-4} mmHg before use. Commercially available 3,3′-carbonylbis(7-(diethylamino)coumarin) (KCD, **1**, (keto)coumarin dye, Nippon Kayaku Co.) and 3,3′,4,4′-tetrakis(*tert*-butyldioxycarbonyl)benzophenone (**2**, BTTB, Nippon Oil & Fats Co., Ltd.) were purified as reported in ref 3. The following materials were used as received: *N,N*-dimethylbenzylamine (DMBzA), trimethylamine (TMA), triethylamine (TEA), tri-*n*-propylamine (TPA), tri-*n*-butylamine (TBA), *N,N*-dimethyl-*n*-butylamine (DMBA), *N,N*-dimethyl-*n*-dodecylamine (DMDA), 2-(dimethylamino)ethanol (DMAE), and 3-(dimethylamino)propanol (DMAP) quaternizing agent (Wako Pure Chemical Industries, Ltd.), potassium persulfate and sodium hydrogen sulfite emulsion polymerization initiator (Wako Pure Chemical Ind., Ltd.), 2-methoxyethanol, 2-ethoxyethanol and isopropyl alcohol (IPA, Tokyo Chemical Industries Co., Ltd.)

[•] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

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(2) (a) Kondo, S.; Matsufuji, A.; Umehara, A.; Ukai, T. Japanese Kokai Patent No. 54-151024, 1979. (b) Dueber, T. E. U.S. Patent No. 4,162,162, 1979. (c) Ichimura, K. Japanese Kokai Patent No. 60-76735, 1985. (d) Nagasaka, H.; Takahashi, N. Japanese Kokai Patent No. 61-123603, 1986. (e) Kawabata, M.; Takimoto, Y. *Chem. Express* **1986**, *1*, 619. (f) Umehara, A.; Kondo, S.; Tamoto, K.; Matsuhuji, A. *Nippon Kagaku Kaishi* **1984**, 192.

(3) Yamaoka, T.; Nakamura, Y.; Koseki, K.; Shirosaki, T. *Polym. Adv. Technol.* **1990**, *1*, 287.

(4) Kanda, K. *Radcure 86' Proc.* **1986**, 5–31.

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Scheme I. Preparation of Microgel

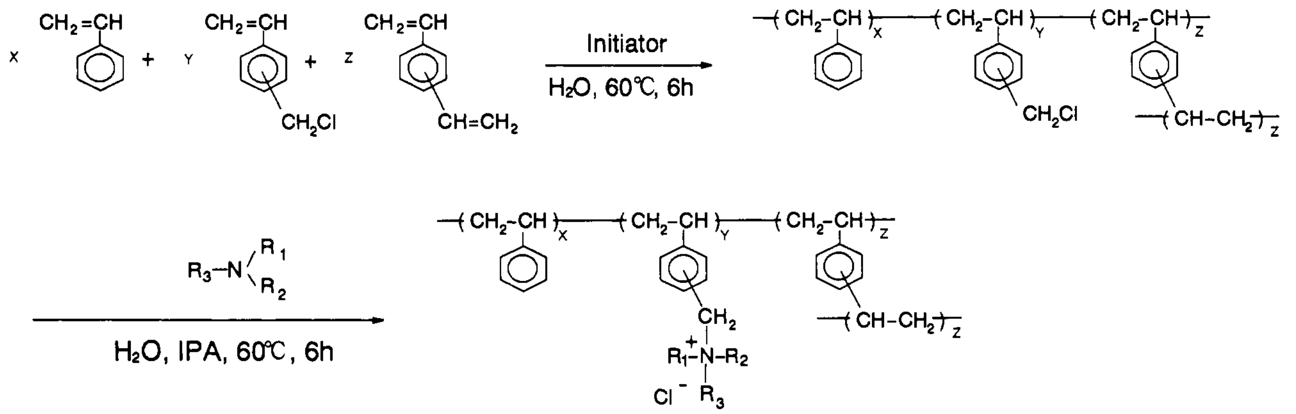


Table I. Preparation of Microgels and Characteristics of the Microgel

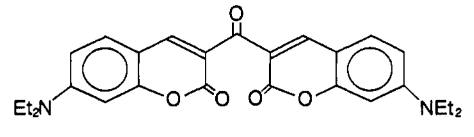
	monomer feed (mol %)			tertiary amine		ACS [N^+Cl^-][c] ($\times 10^{-4}$ mol/g)	yield[d] (%)	av diam (nm)	viscosity[e] (cps)
run no.	St	CMS	DVB	structure	pK_a				
MG 1	68.0	28.0	4.0	$PhCH_2N(CH_3)_2$		4.0	79	26	6.0
MG 2	58.0	38.0	4.0	$PhCH_2N(CH_3)_2$		5.6	80	30	6.0
MG 3	48.0	48.0	4.0	$PhCH_2N(CH_3)_2$		6.9	86	25	6.5
MG 4	48.0	48.0	4.0	$PhCH_2N(CH_3)_2$		7.2	75	25	7.0
MG 5	28.0	68.0	4.0	$PhCH_2N(CH_3)_2$	8.93[a]	9.5	70	35	7.5
MG 6	48.0	48.0	4.0	$N(CH_3)_3$	9.79[a]	9.4	84	32	13.5
MG 7	48.0	48.0	4.0	$N(C_2H_5)_3$	10.67[a]	9.3	60	30	12.2
MG 8	48.0	48.0	4.0	$N(n\text{-}C_3H_7)_3$	10.65[a]	9.2	52	26	11.0
MG 9	48.0	48.0	4.0	$N(n\text{-}C_4H_9)_3$	10.89[a]	9.0	60	20	5.4
MG 10	48.0	48.0	4.0	$(CH_3)_2NC_2H_4OH$	8.2[b]	9.0	79	30	10.3
MG 11	48.0	48.0	4.0	$(CH_3)_2NC_3H_6OH$		7.2	75	24	11.0
MG 12	48.0	48.0	4.0	$(CH_3)_2N(n\text{-}C_4H_9)$	10.02[a]	9.0	80	28	11.4
MG 13	48.0	48.0	4.0	$(CH_3)_2N(n\text{-}C_{12}H_{25})$		5.4	74	25	7.3

[a] Cited from the literature.[17-19] [b] Determined according to the literature: Patai, S., Ed. *The chemistry of the amino group*; Interscience: New York, 1968. [c] Determined by the colloidal titration. [d] Polymer yield [product/(polymer + tertiary amine)]. [e] Measured at 10 wt % in 2-methoxyethanol at 25 °C.

solvent, pentaerythritol triacrylate (PETA) polymerization monomer (Shin-Nakamura Kagaku Co., Ltd.), anion surfactant (Trax H-45) emulsifier (Nippon Oil & Fats Co., Ltd.) and polymer matrices such as poly(*N*-vinyl-2-pyrrolidone) (PVP, $K = 90$, $M_w = 360\,000$, GAF), poly(styrene-*co*-*N*,*N*-dimethylbenzylvinylbenzylammonium chloride) (PSA, 0.3:0.7 copolymer, $M_w = 30\,000$ and poly(methyl methacrylate-*co*-methacrylic acid-*co*-*tert*-butyl methacrylate-*co*-cyclohexyl methacrylate) (HSP-621, 0.27:0.8:0.40:0.25 copolymer, $M_w = 150\,000$).

Water was purified by ion exchange.

Synthesis of Microgels. Synthesis and characterization of poly(styrene-*co*-*N*,*N*-dimethylvinylbenzylammonium chloride-*co*-divinylbenzene) (MG 1–5) were carried out in the same way as described in the previous paper.[6] A new series of microgels comprising quaternary ammonium ions were prepared by emulsion polymerization and successive quaternization as described in Scheme I. Eight microgels of different composition (MG 6–13) were prepared by quaternization with various tertiary amines. These are summarized in Table I.



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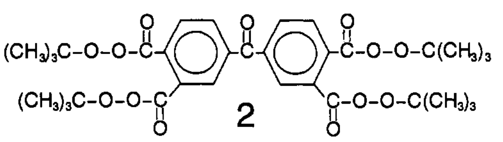

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Characterization of Microgels. Microgel size was observed by transmission electron microscopy (TEM, JEOL, JEM-2000FX). The TEM sample was prepared as follows. A copper mesh was coated with a thin carbon film, and then one drop of a dilute microgel solution (5×10^{-4} g/mL) was applied to it. The sample was then dried at room temperature. The size of the microgels was measured from TEM photographs by using a digitizer. Average diameters was calculated from three points on the outer surfaces of the microgel particles. In all, 20 microgels were measured.

The composition of the microgel particles was qualitatively confirmed by proton nuclear magnetic spectroscopy (^1H NMR, JEOL, JNM-GX400) and infrared spectroscopy (IR, JASCO, FTIR 5300). The amount of cationic groups on the particle surface, abbreviated ACS[N^+Cl^-], was determined by the colloid titration[7] of purified microgels. Viscosity determination was carried out in 2-methoxyethanol using a Brookfield viscometer at 25 °C.

Sensitivity Measurement. A photosensitive layer was prepared by coating a 2-methoxyethanol solution for the photosensitive composition onto an aluminum plate and drying it at 80 °C, producing a 2-μm film. In addition, it was given an overcoat of 2 μm poly(vinyl alcohol) (PVA). The exposed photosensitive layer was developed in tap water (with 2 wt % aqueous solution of sodium metasilicate for an HPS-621 matrix) and the plate was toned with printing ink.

Photosensitivity was measured by passing the photosensitive layer through a 21-step tablet (Kodak no. 2 step tablet) and exposing it to a high pressure mercury lamp (Oak, Jet printer) *in vacuo*. Wavelength selection was determined with a glass filter. Photosensitivity (E, mJ/cm^2) was defined as the minimum exposure energy needed to insolubilize the layer, and is calculated as

$$E = I_0Tt \qquad (1)$$

where I_0 is the incident light intensity (mJ/cm^2 s). Here T is the

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[7] Senshu, R. *Koroido Tekitei-Ho*; Nankodo Publishers: Tokyo, 1969.

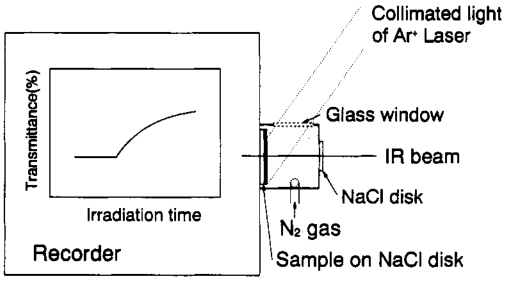

Figure 1. Apparatus for the measurement of the rate of photopolymerization.

transmittance for the step at which the photosensitive layer begins to become insolubilized and t is the exposure time (seconds).

Laser exposure was carried out with Ar^+ laser (Spectra-Physics, Model 164-09, maximum power 5 W) containing a TEM_{00} with a beam diameter of 1.36 mm, at which the energy is $1/e^2$ of the peak energy. Sensitivity was determined by static exposure.[8] The sensitive layer was exposed to the laser beam spot by spot with varying exposure time at constant laser power. The incident energy required to insolubilize a spot size equal to the beam diameter was defined as the sensitivity.

Photopolymerization Rate Measurement.[9] The photosensitive layer was prepared by coating a 2-methoxyethanol solution of the photosensitive composition on a NaCl disk resulting in a 2-μm film. The coated disk was placed into an infrared spectrometer (IR, Hitachi, IR 260-10), fixed at 810 cm^{-1} where the acrylic double bond exhibits sharp and distinct absorption when operated in the transmittance mode. The sample was exposed to a collimated Ar^+ laser light. Figure 1 provides a schematic description of the simple apparatus devised to expose the sample simultaneously to the polymerizing Ar^+ laser beam and the analyzing IR beam. The Ar^+ laser irradiance at the sample position was measured by actinometry and was in the order of 5×10^{-4} W/m^2. Photopolymerization was carried out in a controlled atmosphere by flushing an airtight chamber with nitrogen gas. As soon as the sample was exposed to Ar^+ laser radiation, the transmittance at 810 cm^{-1} increased rapidly as a result of the reaction of acrylic double bonds. This increase, which accurately reflects the extent of the polymerization process, was monitored continuously and in real time on the spectrophotometer recorder. Figure 2a shows a recorded curve as well as the IR transmittance spectrum of the acrylic double bond at 810 cm^{-1} for the photosensitive film. A_0 and A_t, which are the absorbances at 810 cm^{-1} before and after exposure for time t, were calculated from the equations

$$A_0 = \log(T_0/T_1) \qquad (2)$$

$$A_t = \log(T_0/T_2) \qquad (3)$$

where T_1 and T_2 represent the transmittance at 810 cm^{-1} of the sample before and after exposure for time t. T_0 represents the transmittance of the base line at 810 cm^{-1}. The degree of conversion is related directly to the decrease in IR absorbance and can be calculated from the equation

$$\frac{A_0 - A_t}{A_0} \times 100\% \qquad (4)$$

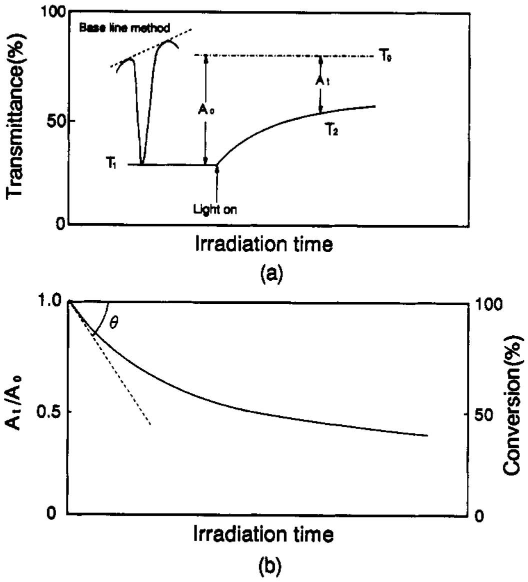

Figure 2. Method for the measurement of the rate of photopolymerization: (a) The decrease of the sharp peak at 810 cm^{-1} (CH_2═CH— twisting of the acrylate group) due to light irradiation. (b) Typical per cent conversion vs time curve of the polymerization of acrylate monomer.

Figure 2b shows a typical kinetic curve. One can readily evaluate how many acrylic bonds have polymerized, and determine the initial rate of polymerization from

$$R_p = -d[M_0]/dt = [M_0] \tan\theta \qquad (5)$$

where $[M_0]$ is the original concentration of acrylate double bonds ($\approx$5 mol/L) and $\tan\theta$ is the slope at zero irradiation time.

Results and Discussion

Characteristics of Microgels. The structures of the synthesized microgels were characterized by ^1H NMR (DMSO-d_6) and IR (KBr disk). Typical ^1H NMR (DMSO-d_6) signals δ for these microgels appeared as follows: MG 6: 3.4 (N–CH_3), 5.0 (N–CH_2); MG 7: 1.3–1.6 (CH_3, triplet), 3.0–3.5 (CH_2, quartet), 4.4 (N–CH_2); MG 8, 9: 1.0–1.2 (CH_3, triplet), 3.2–3.5 (CH_2), 4.8 (N–CH_2); MG 10, 11: 3.3 (N–CH_3), 3.4–3.7 (CH_2), 4.1 (OH), 5.0 (N–CH_2); MG 12, 13: 1.0–1.2 (CH_3), 3.4–3.7 (CH_2), 3.3 (N–CH_3), 5.0 (N–CH_2). Respective aromatic protons of the benzene ring and methylene protons of the polymer backbone appear at δ = 7.3–7.7 ppm and at δ = 1.7–2.5 ppm in all microgels. The exhibition of signals caused by N–R (R = CH_3, C_2H_5, C_3H_7, or C_4H_9) in all microgels indicates a successful quaternization reaction. The IR peak at 1260 cm^{-1}, which is caused by the chloromethyl group, disappears. Instead, absorption peaks due to quaternary groups are observed.

In poly(styrene-*co*-*N*,*N*-dimethylvinylbenzylammonium chloride-*co*-divinylbenzene), the original CMS content was varied from 28 to 68 mol %. The ACS[N^+Cl^-] for MG 1–5 is presented in Table I. ACS[N^+Cl^-] increased with increases in the amount of CMS monomer used. Characteristics for microgels MG 6–13 quaternized with various tertiary amines are presented in Table I. The yields, viscosities and ACS[N^+Cl^-] vary with the tertiary amine used, in spite of constant synthetic conditions. This suggests that the reactivity toward quarternization and the hydrophilic properties of the ammonium ion groups in the microgels are different from the tertiary amines.

The average diameter of microgels ranged from 20 to 35 nm. All microgels dispersed in common solvents, such as 2-ethoxyethanol and 2-methoxyethanol, without use of a surfactant or protective colloid polymer and miscible with

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[8] Yamaoka, T.; Zhang, Y. C.; Koseki, K. *J. Appl. Polym. Sci.* **1989**, *38*, 1271.

[9] (a) Koseki, K.; Miyaguchi, S.; Yamaoka, T.; Yamada, E.; Goto, Y. *Nippon Kagaku Kaishi* **1985**, 119. (b) Koseki, K.; Miyaguchi, S.; Yamaoka, T. *Nippon Kagaku Kaishi* **1986**, 1234.

[10] Goto, Y.; Nakayama, M.; Hirano, J.; Nishibu, S.; Asano, T.; Nagamatsu, G. *The 78th Fall Spr. Conf. Prepr. Jpn.* **1987**, 66.

[11] Eto, K.; Nanpei, M.; Miyagi, M. German Patent No. 2,454,676, 1975.

Table II. General Composition of the Photopolymer (in Parts by Weight)

matrix polymer	100
polyfunctional monomer (PETA)	100
photoinitiator (BTTB)	8
photosensitizer (KCD)	6

Table III. Sensitivity and the Rate of Polymerization R_p of the Photopolymer

matrix polymer	sensitivity ($\times 10^{-3}$ mJ/cm^2) mercury lamp (488 nm)[a]	sensitivity ($\times 10^{-3}$ mJ/cm^2) Ar laser (488 nm)	R_p ($\times 10^{-2}$ mol/L s)
MG 1	90	90	8.5
MG 2	80	70	10.5
MG 3	60	55	12.0
MG 4	60	55	12.5
MG 5	65	60	15.0
MG 6	90	85	11.5
MG 7	90	90	9.5
MG 8	85	85	9.0
MG 9	90	80	9.0
MG 10	85	75	16.5
MG 11	80	70	13.0
MG 12	85	85	10.5
MG 13	80	75	10.0
PVP	150	140	5.5
HSP-621	240	250	2.5
PSA	150	150	6.0

[a] Y-47 (sharp-cut filter), KL-49 (interference filter), and HA-30 (heat-absorbing filter).

various acrylate monomers. In addition, this solution is spin-coatable on an aluminum substrate, resulting in a clear and transparent film.

Photosensitivity. The photosensitive layer consists of microgel as the matrix, PETA as the monomer, BTTB as the photoinitiator and KCD as the sensitizer. It was prepared by coating a 2-methoxyethanol dispersion and solution of the composition shown in Table II onto a grained aluminum plate and drying it, resulting in a film about 2 μm thick. Sensitivity values of the microgel-based photosensitive layers for visible and laser light are summarized in Table II. The microgel-based photopolymers have sensitivities ranging between 5.5×10^{-2} and 9.5×10^{-2} mJ/cm^2. Among these microgels, MG 3 and 4 exhibited the highest sensitivity, while MG 1 and 7 exhibited the lowest. The sensitivities of the photopolymers prepared in a homogeneous matrix, such as PVP, HSP-621, and PSA, are also summarized in Table III. By comparing these sensitivities, it becomes obvious that microgel provides higher sensitivity than the homogeneous polymer matrix.[3,8-11] This suggests that a heterogeneous microgel matrix promotes a concentration of monomers which, in turn, increases the rate of polymerization.

Dependence of sensitivity on the ACS[N^+Cl^-] was investigated. Tables I and III show the ACS[N^+Cl^-] as well as the sensitivities for MG 1–5. The ACS[N^+Cl^-] was controlled by varying the concentration of CMS in the synthesis of microgels and keeping the concentration of DVB at a constant 4 mol %. It was found that sensitivity is dependent on ACS[N^+Cl^-] and increases with increases in a concentration of ACS[N^+Cl^-] up to *ca.* 7×10^{-4} mol/g. Further increases in ACS[N^+Cl^-] do not increase sensitivity.

The effects caused by the microgel were shown in a UV photopolymer system reported earlier[6] and are now confirmed in visible and laser-sensitive photopolymers.

Rate of Photopolymerization. It is easy to evaluate the rate of photopolymerization (R_p) from the slope of the IR kinetic curves. The R_p values obtained are summarized in Table III. The microgel-based photopolymerization system has R_p values ranging between 8.5×10^{-2} and 10.5×10^{-2} mol/L·s. Among these microgels, MG 10 exhibited the higest R_p value, while MG 1 exhibited the lowest. The R_p values for photopolymers prepared from a homogeneous matrix, such as PVP, HSP-621, and PSA, are also summarized in Table III. Comparing these R_p values shows that the microgel has a higher R_p value than the homogeneous polymer matrix. R_p can be increased by increasing the monomer concentration, shown by the equation[12]

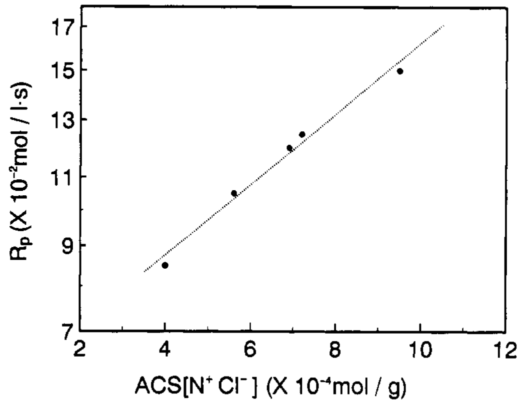

Figure 3. Dependence of the rate of photopolymerization R_p on the amount of cationic groups on the microgel surface (ACS[N^+Cl^-]).

$$R_p = \frac{k_p}{(k_t)^{0.5}}[M]\{2.303 \times 10^3 \phi f I_0 \epsilon [I]\}^{0.5} \qquad (6)$$

where k_p is the rate constant of propagation, k_t is the rate constant of termination, ϕ is the quantum yield, f is the initiation efficiency of the free radicals, I_0 is the incident light intensity, [I] is the concentration of the initiator of extinction coefficient ϵ, and [M] is the concentration of monomers. This suggests that the microgel matrix promotes a concentration of monomers, which in turn increases R_p. It also suggests that photopolymers with a microgel matrix show higher sensitivity than those with a homogeneous polymer matrix. Therefore, higher valued R_p followed by increasing monomer concentration is cause for higher sensitivity in a microgel-based photopolymer.

Figure 3 shows the dependence of R_p on the amount of cationic groups found on the microgel surface (ACS[N^+Cl^-]) for MG 1–5. Here, the ACS[N^+Cl^-] was controlled by varying the concentration of CMS in the synthesis of the microgel and keeping the concentration of DVB at a constant 4 mol %. It was found that value for R_p increases directly with the concentration of ACS[N^+Cl^-]. This suggests that the ammonium ion on the microgel surface accelerates the photopolymerization reaction. The reason for the activity increases by ammonium ions has not been determined. Recently, Fouassier et al. reported on the photoinitiating function of analogous compounds.[13] They suggest that iodonium salt may decrease the concentration of the ketyl radical (this type of structure acts as a terminating agent for growing polymer chains[14]), which is generated from ketocoumarin

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(12) Oster, G.; Yang, N. L. *Chem. Rev.* **1968**, *68*, 2, 125.

(13) (a) Fouassier, J. P.; Wu, S. K. *J. Appl. Polym. Sci.* **1992**, *44*, 1779. (b) Fouassier, J. P.; Ruhlmann, D.; Graff, B.; Takimoto, Y.; Kawabata, M.; Harada, M. *J. Imaging Sci. Technol.* **1993**, *37*, 208.

(14) Block, H.; Ledwidth, A.; Taylor, A. R. *Polymer* **1971**, *12*, 271.

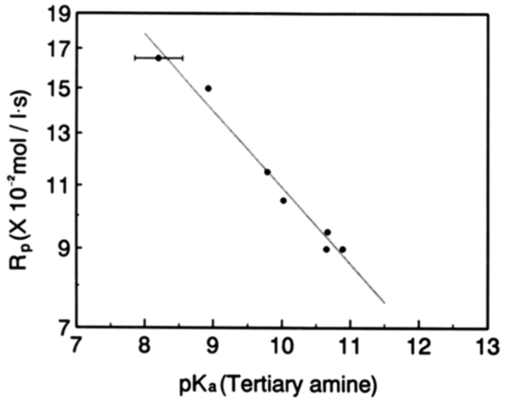

Figure 4. Dependence of the rate of photopolymerization R_p on the pK_a of tertiary amine.

and forms a new reactive radical. The same type of reaction may occur in the system ammonium/ketocoumarin and may be another basis for the increase in sensitivity as well as R_p of photopolymer based on a microgel with ammonium ions. However, sensitivity reaches a plateau when ACS[N^+Cl^-] is *ca.* 7 × 10^{-4} mol/g. This result indicates that ACS[N^+Cl^-] has an effect on both the sensitivity and the dispersibility of microgels in water. Increasing the concentration of ACS[N^+Cl^-] increases dispersibility of microgels in water as well as sensitivity.

R_p values were investigated for the photopolymers prepared with microgels quaternized with various tertiary amines. Figure 4 shows the dependence of R_p on the pK_a for the tertiary amines used as quaternizing agents for the synthesis of microgels, where MG 5–10 and 12 are used as the polymer matrix and the ACS[N^+Cl^-] for these microgels is within a range between 9.0 and 9.5 mol/g. The R_p values are in good agreement with the pK_a order for corresponding tertiary amines, where lower pK_a promotes the R_p. This suggests that decomposition ability is in agreement with the pK_a order for corresponding tertiary amines, i.e., the leaving ability.

Various techniques for kinetic investigation of solid photopolymerizable materials have been studied and presented.[15] One author introduced an IR method for measuring the R_p value of photopolymers with a homogeneous polymer matrix.[9] Decker et al. reported on similar kinetic studies using the IR method.[16-19] The present study confirms that the IR method is useful for kinetic investigation of solid photopolymerizable materials.

Lithographic Evaluation. A photopolymerizable layer based on the microgel matrix was evaluated as an offset printing plate. Photopolymers with compositions shown in Table II were coated on a grained aluminum plate, resulting in an overcoat of about 2 μm of PVA to prevent the sensitive layer from coming in contact with oxygen in the air. They were then scan exposed to a 488-nm Ar^+ laser beam. Laser exposure conditions are summarized in Table IV. After exposure the plate was developed in tap water to dissolve the photopolymer layer in unexposed areas. Good patterns were obtained for the thin photopolymer layer (2–3 μm). A photograph of images in Figure 5 shows that 25-μm lines were clearly resolved.

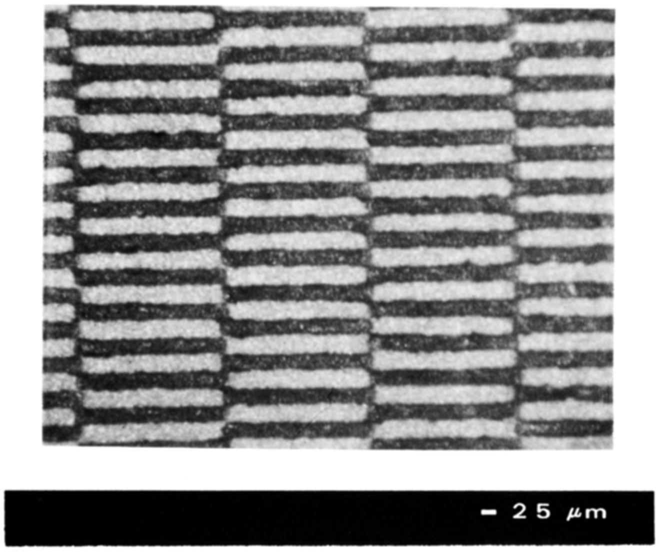

Figure 5. Photograph of laser-exposed image on an aluminum plate.

Table IV. Specification of Laser Exposure

laser (wavelength)	argon ion, 488 nm
scanning speed	9.8 m/s
beam diameter	25 μm
line density	600 lines/in.
scanning time (41 × 59 cm)	9.7 min

A photopolymer layer can be developed in tap water at temperatures between 15 and 35 °C. This indicates a wide process latitude. Developing time between 20 and 120 s resulted in almost the same sensitivity, which shows a wide latitude in development.

The shelf life of a photopolymer is an important aspect of practical use. A photopolymer consisting of MG 4 as the matrix, pentaerythritol triacrylate as the monomer, KCD/BTTB as the initiator, and 0.3 wt % hydroquinone as the inhibitor was kept under high temperatures and sensitivity was measured every 3 days. No sensitivity change was observed for up to 9 days. This indicates good thermal stability.

These results show that the photopolymer developed in this study offers a high-sensitivity material for presensitized plates that can be exposed to Ar^+ lasers.

Conclusion

A microgel-based photopolymer combined with acrylate monomer and visible light absorbing photoinitiators provides oleophilic images when exposed to visible Ar^+ laser and developed in tap water.

Photopolymers with a heterogeneous matrix exhibit a higher rate of polymerization as well as higher levels of sensitivity than conventional ones with homogeneous polymer matrices. The rate of photopolymerization increases directly with an increase in the amount of cationic groups on microgel surfaces. In addition, microgels quaternized by tertiary amines with lower pK_a are especially effective in accelerating the rate of photopolymerization.

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