

A Novel Dry Photopolymer for Volume-Phase Holograms

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ABSTRACT: A novel photopolymer for the fabrication of high-resolution volume-phase holograms, which primarily are used for holographic optical elements, is reported. This photopolymer consists of a thermosetting resin as a polymeric binder, a polyfunctional monomer, a photoinitiator, and a sensitizing dye. The chemistry to form images is based on the polymerization of an acrylic monomer initiated by radical species while making the holographic exposure, and accelerated diffusion transfer of the polymerized monomer with postexposure baking, and of a bisphenol-type epoxy resin as a binder initiated by cations with UV exposure, which are generated through photodecomposition of a diaryliodonium salt-sensitized 3-ketocoumarin dye. Exposure of these photopolymer films to an Ar⁺ laser beam emitting 514.5 nm light at 60–150 mJ/cm² and subsequent heat treatment resulted in a refractive index alteration according to the light intensity. With this dry process, high diffraction efficiency and heat-stable holograms can be formed. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2189–2200, 2000

Key words: volume-phase hologram; recording material; dry processing; high diffraction efficiency; heat stable

INTRODUCTION

Holograms enable the reproduction of three-dimensional stereoscopic images, and hence, have been frequently used in covers of books, magazines, or the like, pop art display, gifts, and so forth because of their attractive designability and decorative effect. In particular, in volume-phase holograms, spatial interference fringes with differences not in optical absorption but in refractive indexes are formed in photosensitive recording mediums, whereby phases can be modulated without absorption of light beams passing through images. Hence, in recent years, they are not only used for display applications but are also

expected to be applied as holographic optical elements (HOEs) as typified by an automotive display of a stand-alone type head-up display system¹ and a holographic reflector on reflective liquid crystal display.²

Now, recording materials for forming the volume-phase holograms are required to be highly sensitive to laser light, having a visible oscillation wavelength and also showing a high resolution (spatial frequency). When actually used in forming holograms, they are also required to provide holograms having characteristics such as diffraction efficiency, wavelength reproducibility of reconstructed light, spectral bandwidth (half-width of peak of reconstructed light), and so forth suited for their purpose, as indicated in Table I. In particular, recording mediums for HOEs are also required to have good stability, for example, heat resistance, humidity resistance, light resistance,

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Table I Specifications of Recording Materials for Volume-Phase Holograms

Light source	Laser (single mode, coherency) blue, green, red
Sensitivity	< 100 mJ/cm ²
Resolution	Transmission type; ~ 1500 lines/mm Reflection type; > 5000 lines/ mm
Latitude	Broad
Film thickness	~ 30 μm
Stability	Heat resistance Humidity resistance
Manufacturing	Dry processing
Others	High refractive index modulation Transparency

environmental stability, and so on, over a long period of time.

As a value for comparing holographic characteristics formed as images, refractive index modulation (Δn) is used. This is a value calculated from the measured diffraction efficiency and recording medium thickness, the former being the proportion of incident light diffracted by a diffraction grating that is prepared while directly irradiating a recording medium in the manner that dual light fluxes are at the same angles to the recording medium. The Δn is a quantitative measure of the changes in refractive index that occur at exposed areas and unexposed areas of a volume hologram, i.e., the portions where light rays interfere with one another to become strong or weak in intensity, and can be found by Kogelnik's formula.³ In general, the reflection holograms have more interference fringes formed per 1 mm than the transmission holograms, and hence, make it difficult to carry out recording, so that it is difficult to obtain a high Δn .

As recording materials for such volume phase holograms, photosensitive materials of bleached silver salt⁴ and dichromated gelatin type⁵ have been commonly used. Such photosensitive materials, however, have so short a storage lifetime that they must be prepared just before the time the hologram is produced, or have inferior environmental properties as exemplified by humidity resistance and weatherability. Also, because the development is carried out by the wet process, holograms may undergo deformation in the course of swelling and shrinking of the gelatin required. To overcome such problems, as materi-

als having superior environmental and holographic properties, hologram recording materials making use of poly(*N*-vinylcarbazole)^{6,7} or poly(*N*-vinylpyrrolidone)⁸ as a polymer matrix have been proposed. However, these materials still also require the wet-process development. These materials are chemically stable, and have a high resolution and a high sensitivity, but are accompanied by formation of holes or pores because of the wet processing.⁹ Hence, they have a problem in that the presence of a large number of holes or pores in the hologram results in poor thermal resistance and thermopressure resistance.

As a measure for overcoming such problems, photopolymerization-type materials that enable production of a hologram through a single processing step without any wet processing have been proposed.^{10,11} A typical representative material comprises a polymer matrix incorporated with a photopolymerizable ethylenic monomer and photopolymerization initiator, according to which a permanent volume-type phase hologram can be obtained by one-time exposure to actinic radiation is known in the paper.¹²

On the other hand, we propose a novel photopolymer system for volume-type phase holograms having superior chemical stability, for example, environmental resistance, in particular, thermal resistance, produced by dry processing, and having high resolution, high diffraction efficiency, high transparency, and a superior reconstructed wavelength reproducibility.

EXPERIMENTAL

Materials

Diphenyliodonium (DPI) salt as a photoinitiator was prepared by the method of Crivello.¹³ Other diaryliodonium salts were synthesized through corresponding diaryliodonium chloride with ion exchange. 4,4'-bis(*tert*-butylphenyl)iodonium hexafluorophosphate (Midori Kagaku, BBI), 2,4,6-tris(trichloromethyl)-1,3,5-triazine (Midori Kagaku, TCT), (1,6- η -cumene)(η -cyclopentadienyl) iron(II) hexafluorophosphate (Ciba-Geigy, IRGACURE-261, IAC) and 3,3',4,4'-tetrakis(*tert*-butylperoxycarbonyl)benzophenone (25% toluene solution, Nippon Yishi, BTTB) as an initiator, 3,3'-carbonylbis(7-diethylaminocoumarin) (Kodak, KCD) as a sensitizer, a thermosetting bisphenol-type epoxy resin (Yuka Shell Epoxy, EP series) as a polymeric binder, acrylic monomers (e.g., Toagosei, ARO-

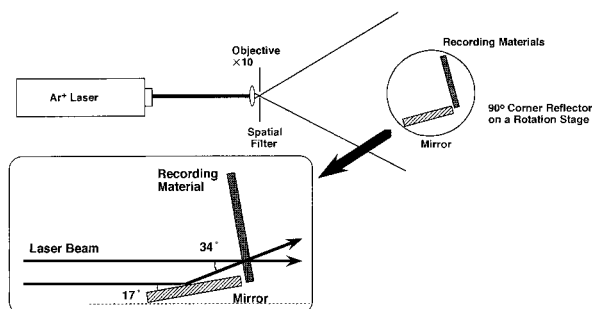


Figure 1 Optical setup for transmission holograms.

NIX M series or Nippon Kayaku, KAYARAD series) and 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate (Chiba-Geigy, CY-179, CEP) were used from commercial origin.

Preparation of Photosensitive Layer

To a 35% solution of the epoxy resin in 2-butanone (MEK) was added 40–60 wt % of a radical polymerizable aliphatic monomer based on the epoxy resin. After the solution was considerably stirred, a compound formed with 0.1–0.5 wt % KCD and 5.0–7.5 wt % photoinitiator, for example, DPI hexafluorophosphate based on the epoxy resin were added slowly with stirring. The photosensitive solution was coated on a glass plate with a doctor-blade (gap; 3–6 mil) and dried at 80–90°C for 2–10 min. Then 10 wt % poly(vinyl alcohol) (PVA) aqueous solution was spin coated on the photosensitive layer according to the occasion demands. This gave about a 1- μm thickness layer.

Preparation of Volume Type Transmission Holograms

The optical system is shown in Figure 1. The beam from a single-mode Ar⁺ laser, a Spectra Physics model-2020, is expanded using a microscope objective and a pinhole spatial filter. The laser was operating at either 488 or 514.5 nm.

The photosensitive plates, coated with a PVA film, were mounted on one side of a 90° corner reflector with a mirror on the opposite side to reflect the second interfering beam onto the plate. This configuration ensures that the two beams forming the holographic grating have equal intensities. The angle between two beams was 34°. Then the recording medium was exposed to the laser. After exposing, the photosensitive plate was heated at 65–85°C for 1–10 min (so-called postexposure baking; PEB). In addition, it was

cured with ultraviolet and visible light using the UV-printer (ORC, HMW-842-2UV) that produced about 2 J/cm² at the plate plane to fix the holographic images.

Preparation of Volume-Type Reflection Holograms

To form a reflection hologram, a photosensitive plate was placed on a mirror or a holographic master, made from a silver halide plate with the optical setup as shown in Figure 2(A), using an index matching fluid such as iso-octane as shown in Figure 2(B). The angle between object and reference beams was 135°. Holograms were recorded at one collimated beam from an Ar⁺ laser operating at 488 or 514.5 nm. After exposure, the procedure to fix the hologram was similar to that of the transmission holograms.

Evaluation

The diffraction efficiency of the transmission hologram was calculated as the ratio of the diffracted probe beams intensity (I_{diff}) to the preexposure undiffracted beam intensity (I_0) after passing through the holograms. The holographic characteristics of the reflection holograms, such as diffraction efficiency, wavelength reproducibility of reconstructed light, and spectral bandwidth was measured with a Shimadzu spectrophotometer UV-160A equipped with an absolute specular reflectance attachment to incident at an angle of 5° or a UV-2400PC equipped with an integrating

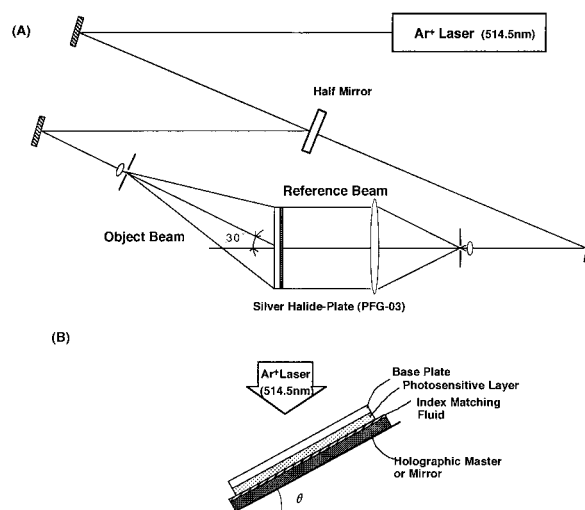
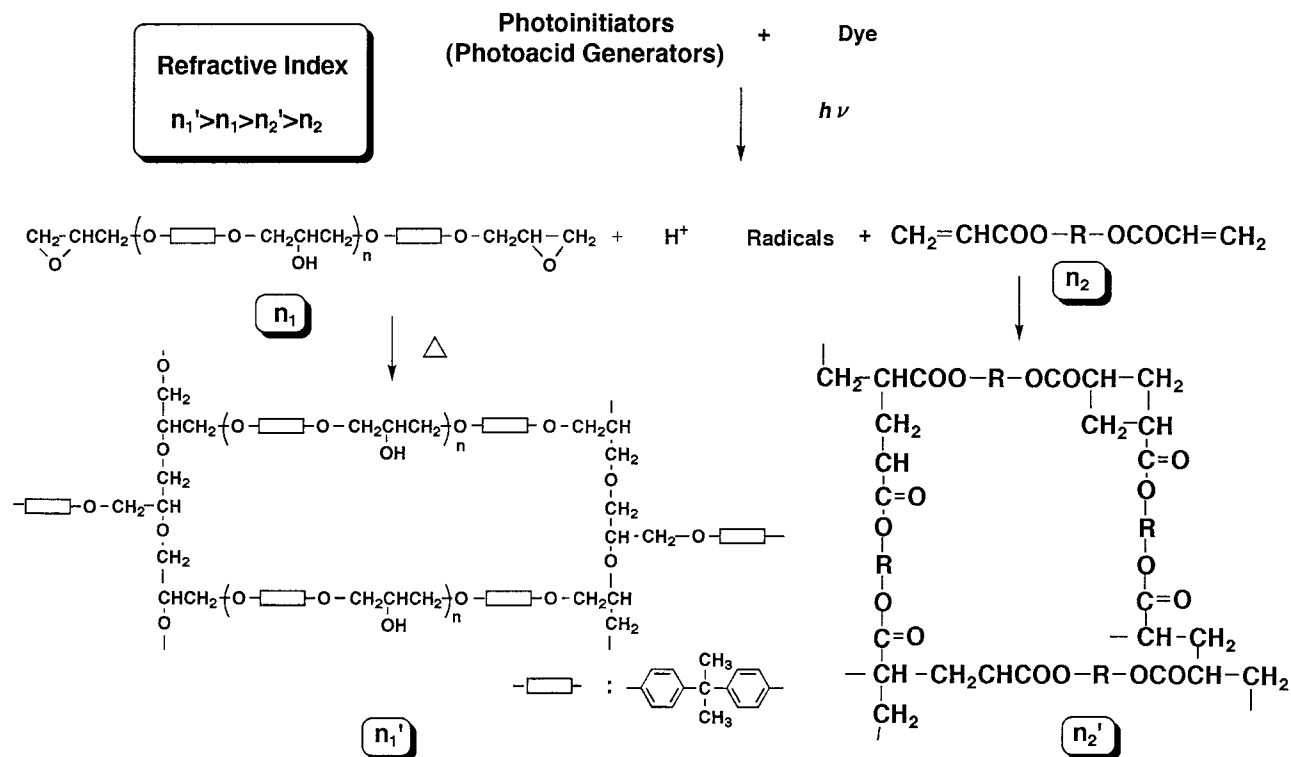


Figure 2 Optical setup for (A) the holographic master, and (B) reflection holograms (the contact copying method).



Scheme 1 The concept of the photopolymer system for volume phase holograms with a dry process.

sphere assembly. In this measurement a standard white plate made of BaSO_4 is used as the reference. The values of Δn are calculated by means of Kogelnik's formula³ with the peak values of the obtained diffraction efficiency and the film thickness of the hologram layer.

Differential Photocalorimetry Analyses

The differential photocalorimetry (DPC) of photopolymerization of monomers to obtain the heat of polymerization (enthalpy) was run by a Du Pont Instruments Model-192 Differential Scanning Calorimeter. To a solution of epoxy or acrylic, the monomer in MEK was doped with KCD and a photoinitiator. A drop of the solution was placed on an aluminum sample pan and dried at 80°C for 5 min. This sample was exposed to a light that was obtained from a super pressure Hg lamp or an Xe lamp that had a glass filter (Toshiba UV-31, UV-39, L-42) that, according to the occasion demands, is in an isothermal mode at 25°C .

RESULTS AND DISCUSSION

The concept of the photopolymer system we proposed is summarized in Scheme 1. A radically

polymerizable monomer, for example, a bifunctional acrylic monomer, and a cationically polymerizable binder, for example, a bisphenol A-type epoxy resin of different refractive indices are combined in photopolymer compositions. That is to say, we guess that the epoxy resin serving as the polymeric binder turns out to have a crosslinked structure attributable to the cationic polymerization, so that the thermostability of the resulting volume-type hologram can be improved, and additionally, the Δn of this hologram is higher.

The Δn in the recorded holograms is calculated from the measured diffraction efficiency and film thickness using Kogelnik's coupled wave theory,³ which, for the unslanted transmission hologram gives:

$$\eta = \sin^2\Theta \quad (1)$$

which for the unslanted reflection hologram gives:

$$\eta = \tan^2 h^2\Theta \quad (2)$$

$$\Theta = n\pi\Delta nT/[\lambda(n^2 - \sin^2\theta)^{1/2}] \quad (3)$$

where η is the maximum diffraction efficiency, n is average refractive index of the recording me-

dium, θ is an angle within the recording medium between the probe radiation and a line perpendicular to the plane of the medium, T is the film thickness, and λ is the recording wavelength. Therefore, Δn has to increase to obtain a higher diffraction efficiency without changing the film thickness. If the refractive index difference between the binder and monomer is larger, it is possible for Δn to become larger. For this reason, the acrylic monomer was selected from the aliphatic compounds because of the bisphenol-type epoxy binder used here. On the other hand, the photoinitiator needs to generate not only radical species but also cations, and it is necessary to sensitize itself by a sensitizer in the visible region.

Photoinitiation System

As described above, it is necessary for the formation of the volume hologram with a high diffraction efficiency that a photoinitiator must concurrently generate radical species and acids by irradiation with a laser light. Consequently, the selection of a pertinent photoinitiator is very important in this system. Onium salts, triazines, and an iron-arene complex were well known to generate some radical species as well as a strong acid on the photodecomposition. The effect of the photoinitiator was studied by use of several compounds including DPI, TCT, and IAC. On the other hand, BTTB, known as the radical initiator, was used to compare the behavior of photopolymerization by means of DPC and the characteristics of the forming hologram. A lower molecular weight of the epoxy resin was used than that of the actual holographic recording material by considering the diffusion of the monomer in a polymeric matrix. The results of the DPC analyses are shown in Table II. The enthalpy obtained by DPC refers to the calorific value of the polymerization, that is, it shows to be apt to proceed the polymerization by photoinitiator. Large enthalpy in these additional acrylic monomer systems show more reactivity in the radical polymerization. These initiators do not absorb and undergo photolysis to any measurable extent in the presence of visible light. In particular, iodonium salts dye-sensitized photolysis studies have been carried out.¹³ Various dyes have been evaluated already, for example, acridine orange, benzoflavin,¹⁴ dimethylaminobenzilidene derivatives,¹⁵ and so on. 3-Ketocoumarin (KCD) was adopted in this studies because the high sensitivity (sensitized efficiency) was ad-

vantageous to the holographic exposure. Moreover, other initiators were well known to sensitize with KCD in the visible region. The order of reactivity of photoinitiators in the radical polymerization of the acrylic monomer is therefore BTTB > TCT > DPI \gg IAC. However, the reason for IAC being less reactive in the radical polymerization is not presently known. On the contrary, the enthalpy in only the epoxy resin system shows that cationic polymerization is apt to proceed. But it is impossible for the epoxy resin having a molecular weight of about 900 to polymerize in this light source or when exposed to energy at room temperature. Then CEP was used instead of the epoxy resin to evaluate the activity against the cationic polymerization of the resin. The enthalpy value obtained by the cationic polymerization including DPI was 19.8 J/g. It is predicted that only DPI served effectively as an initiator for the polymerization. Among these initiators, DPI furnishes excellent holographic characteristics by way of exposure to laser light followed by heat treatment (PEB), as shown in Table II, while the performance was most strongly affected by reversing the order of irradiation and PEB. This supports the importance of ring opening polymerization of the binder.

A number of iodonium salts were prepared employing a known literature technique.¹³ Table III shows the data collected in a study of the effect of variations in cation structure on their relative holographic characteristics by considering their mutagenes. Holographic characteristics using all substituted iodonium salts were similar to that using unsubstituent DPI. Moreover, the counter anions of iodonium salts were evaluated to the effect of the holographic characteristics.

Table IV shows holographic characteristics for the use of BF_4^- , PF_6^- , and SbF_6^- salt of bis(*tert*-butylphenyl)iodonium (BBI), respectively. The order of the diffraction efficiency of forming the holograms by use of iodonium salts is, therefore, $\text{PF}_6^- > \text{SbF}_6^- > \text{BF}_4^-$ salt.

In Figure 3 are shown data from the reactivity of the radical polymerization of acrylic monomer by means of dye-sensitized photodecomposition using three counter anions of iodonium salts. These curves show similar results of the holographic characteristics. In addition, PF_6^- salt results in a higher reactivity of the cationic polymerization of CEP instead of the binder of the SbF_6^- salt, although this result is not in agreement with other results found in the literature,¹⁶ in which the general order of reactivity of the

Table II Effect of the Photoinitiators on Photopolymerization and Holographic Characteristics

	Enthalpy (J/g) on DPC ^a	Diffraction Efficiency (%) [Reconstructed Wavelength (nm)]
Binder	$\text{CH}_2-\text{CH}-\text{CH}_2-\left(\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{CH}(\text{OH})-\text{CH}_2\right)_n$ $-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{CH}(\text{O}^-)-\text{CH}_2$ (E1) ^d	$\text{CH}_2-\text{CH}-\text{CH}_2-\left(\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2\text{CH}(\text{OH})-\text{CH}_2\right)_n$ $-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{CH}(\text{O}^-)-\text{CH}_2$ (E3) ^d
Monomer	$\text{O}=\text{C}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n$ (CEP)	Acrylic monomer
DPI	15.5	58.1 ^[505]
TCT	21.3	34.3 ^[507]
IAC	4.4	—
BTTB	23.4	63.4 ^[507]
		UV curing ^c before heating
		Heat 30 min at 80°C
		Holographic exposure ^b
	19.8	76.0 ^[511]
	4.5	49.2 ^[512]
	5.1	—
	4.8	83.5 ^[511]

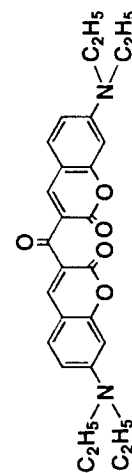
^a Irradiation with a Xe arc lamp for 5 min through a UV cut filter.^b Exposure energy; 100 mJ/cm² (514.5 nm).^c Exposure energy; 100 mJ/cm².^d See Table V.^e All experimentals were used for 3-ketocoumarin^f as a sensitizer.

Table III The Effect of the Cation's Structure on Their Relative Holographic Characteristics and Their Mustagenes

$(R - \phi)_2I^+ PF_6^-$	Results of Ames Test ^a	Diffraction Efficiency (%) ^b Exposure Energy at 514.5 nm (mJ/cm ²)			
		110	120	130	140
H—	TA1573 + S9●, TA1573●	72.3	66.2	47.6	42.2
CH ₃ —	TA1573●, TA1573 + S9●	51.3	75.6	69.3	69.0
(CH ₃) ₂ CH—	TA1573 + S9 ●	55.8	67.4	72.9	82.6
(CH ₃) ₃ C—	○	38.5	59.4	78.8	76.1

^a ●; negative, ○; positive.

^b Epoxy : monomer : initiator : KCD = 100 : 50 : 5 : 0.25, the contact copying method (mirror; $\theta = 0$).

cationic polymerization in the iodonium salt was found to be $SbF_6^- > AsF_6^- > PF_6^- > BF_4^-$, this reason for this is not known at present.

Polymeric Binder

Transmission and reflection holograms were recorded in a series of compositions based on four bisphenol A-type epoxy resin having various molecular weights as a polymeric binder. The binders tested are shown in Table V.

Results of holographic characteristics on transmission and reflection types are reported in Figure 4 and Table V, respectively. Several related trends are clear from these results. First, for transmission type, the diffraction efficiency was higher when the binders of lower epoxy equivalent weight, such as E1 and E2, were used. On the other hand, for reflection type, the diffraction efficiency was low with similar binders. Second, for the holograms of both types, the sensitivity was higher with the binders of E1 and E2. Moreover, the sensitivity of exposure for 488 nm was higher than for 514.5 nm in the transmission type, but the holograms made for both recording wavelengths almost reached the same maximum dif-

fraction efficiency. However, the diffraction efficiency of reflection type was relatively high only with the binder of a higher molecular weight such as E3 and E4.

Recording of a Volume-Phase Hologram

To obtain a reflection hologram having higher spatial frequency, the composition of the photopolymer consists of the epoxy resin E4, which has given a good result as noted above and radically polymerizable aliphatic monomers such as tetraethylene glycol diacrylate and tripropylene glycol diacrylate, along with DPI and KCD. The solution of these recording materials for a reflection hologram in MEK was applied on substrates such as a glass plate to yield a 15–27- μ m film thickness having dye absorption peak at about 460 nm. This photosensitive layer was shielded from oxygen, which inhibits radical polymerization of monomers by coating PVA on it. Holograms have been produced in the photopolymeric layer by the contact copying method, employing a mirror to test the ability of this recording medium under similar conditions to that of mass production. The photopolymer possessing the mirror was

Table IV The Effect of a Counter Anion on Its Relative Holographic Characteristics

$[(CH_3)_3C - \phi]_2I^+ X^-$	Diffraction Efficiency (%) ^b Exposure Energy at 514.5 nm (mJ/cm ²)					
	75	100	125	150	175	200
BF_4^-	++ ^a	++	9.3	13.5	21.6	42.3
PF_6^-	77.0	83.7	85.8	87.9	68.5	68.0
SbF_6^-	23.7	57.4	72.3	82.7	63.8	53.9

^a ++; Hologram not producible.

^b Epoxy : monomer : initiator : KCD = 100 : 50 : 5 : 0.25, the contact copying method (mirror; $\theta = 0$).

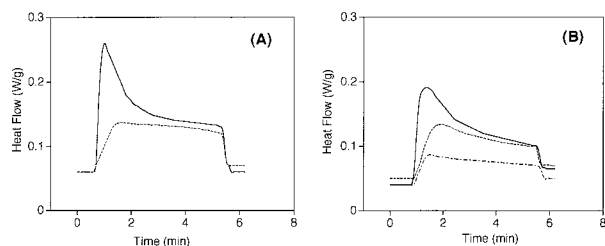


Figure 3 DPC curves for the mixture of monomers and photoinitiation system where the content of BBI and KCD are 5.0 wt % and 0.25 wt % against the epoxide, respectively, with an Xe arc lamp at 25°C: the counter anions of BBI (A) containing acrylic monomer in epoxy resin (E1) and (B) alicyclic epoxide (CEP): ---;BF₄⁻, —;PF₆⁻, ···;SbF₆⁻.

horizontally set and exposed to a 514.5-nm Ar⁺ laser light of 80 mJ/cm². Subsequently, the medium was baked at 80°C for 10 min and exposed to a UV light of about 2 J/cm². Figure 5 shows the performance of a reflection hologram produced by this method. These recording materials gave sufficient holographic characteristics with a high diffraction efficiency of over 90% and appropriate wavelength selective of approximately 510 nm. On the other hand, the curve in this figure describes the values calculated from Kogelnik's theory. Δn was 0.022, and the experimental results agreed well with the theoretical values. Moreover, this holographic characteristics scarcely changed when the hologram was heated at 150°C for 30 min, as shown in Figure 6.

Recording Mechanism

It has generally been assumed that diffusion of the photopolymerizable monomer plays an impor-

tant role in the formation of a volume-type hologram used a photopolymer system. Besides this diffusion phenomenon, the cationic polymerization of glycidyl groups is significant in our recording material. That is to say, it is considered that the mechanism for the holographic image by use of this photopolymer contains two steps, as shown Scheme 2.

When holograms are recorded in this system, laser irradiation is applied in accordance with the desired images. More specifically, in the photosensitive layer, the radical polymerizable monomers and the cationic polymerizable epoxy resin are uniformly distributed. In the hologram recording, upon exposure of this photosensitive layer to laser light (i.e., light of a dual light flux optical system), the initiator-sensitized KCD simultaneously generates radical species and acids at portions undergoing a strong light interference action among laser-irradiated portions. The radical species generated here cause the monomers to undergo polymerization. As the monomer is polymerized, the recording material causes differences in density in the photosensitive layer, so that the monomers move from the expose to weaker irradiated portions to the terminal gel points. That is, the density of the monomers becomes higher at the portions undergoing a strong light irradiation, and density becomes lower at the portions of a weak light. Thus, differences in the refractive index are produced between both the portions to a effect hologram recording. After the exposure to the laser interference light, a heat treatment, a so-called PEB, is further applied, whereupon acids simultaneously generated during the laser light intensity distribution, so that

Table V Results from Reflection Holograms^b Made from Various Epoxy Resins

Epoxy Resin [Epoxy Equivalent Weight (g/Eq)]	Recording Wavelength (nm)	Diffraction Efficiency (%), Reconstructed Wavelength (nm), Film Thickness (μm) Exposure Energy at 514.5 nm (mJ/cm ²)				
		20	40	60	80	100
E1	488	31.7, 487, 31.5	++ ^a , ++, 31.9	++, ++, 32.3	++, ++, 31.5	++, ++, 31.2
[450–500]	514.5	++, ++, 31.8	43.7, 516, 32.1	30.0, 512, 28.3	21.1, 510, 32.4	++, ++, 32.3
E2	488	33.9, 488, 26.6	++, ++, 26.4	++, ++, 26.6	++, ++, 27.8	++, ++, 28.1
[875–975]	514.5	++, ++, 27.4	70.7, 519, 27.6	67.0, 512, 28.3	43.4, 512, 27.9	33.2, 513, 26.9
E3	488	62.3, 483, 26.6	62.9, 488, 24.0	44.7, 489, 23.6	43.8, 489, 24.1	34.7, 489, 23.6
[1750–2200]	514.5	++, ++, 23.4	51.8, 527, 23.5	81.8, 525, 23.6	78.3, 521, 24.2	62.4, 519, 23.8
E4	488	73.0, 487, 22.9	74.6, 489, 23.5	78.9, 488, 23.8	69.9, 487, 24.0	37.9, 489, 22.8
[3000–5000]	514.5	++, ++, 22.4	52.7, 521, 23.1	73.6, 518, 21.0	85.4, 515, 22.3	72.0, 518, 22.5

^a ++; Hologram not producible.

^b Epoxy : monomer : BBI : KCD = 100 : 50 : 7.5 : 0.25, the contact copying method (mirror; $\theta = 0$).

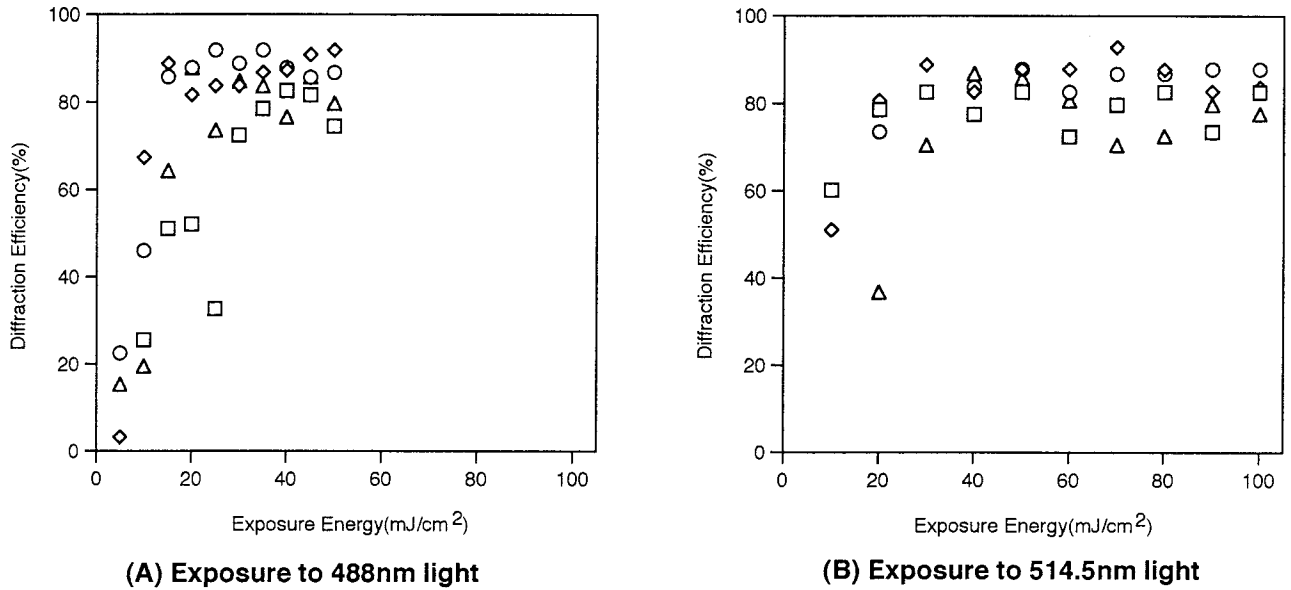


Figure 4 Diffraction efficiency of transmission holograms with a spatial frequency of 1400 lines/mm, made from epoxy resins having various molecular weights: □;E1, ◇;E2, ○;E3, △;E4.

presumably a structure with different crosslink density is formed, and hence, this contributes to an increase in the difference in the refractive index between the portions undergoing a strong and a weak light interference action, thus making

it possible to obtain a volume-type hologram having a high diffraction efficiency.

Based on the above, the phenomena described below have been observed, that is, the change of diffraction efficiency in forming holograms was

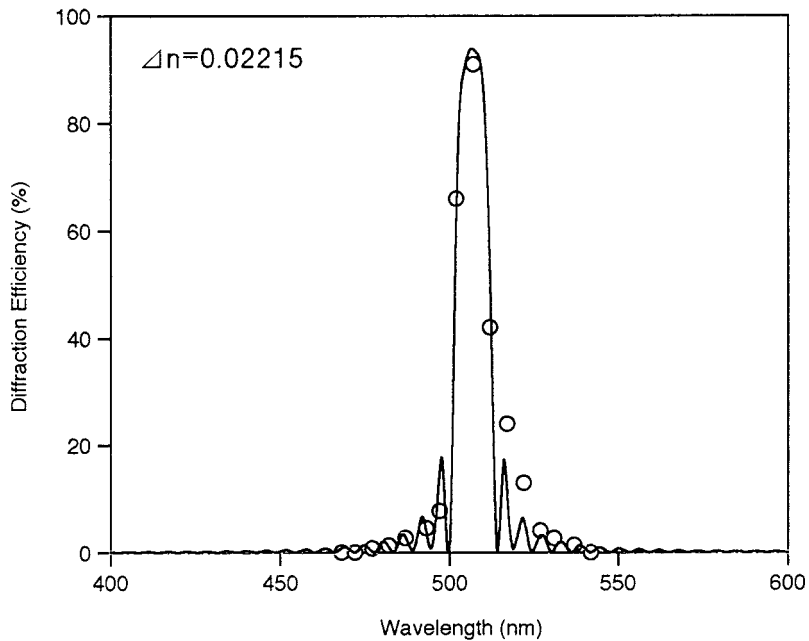


Figure 5 The holographic characteristics of a reflection hologram produced by the contact copying method: ○; experimental values, —; calculated values from Kogelnik's theory.

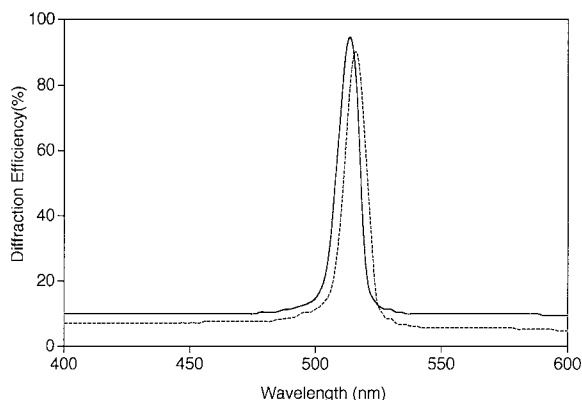


Figure 6 Diffraction efficiencies of a reflection hologram made from this photopolymer system by the contact copying method before (dotted line) and after (solid line) heat treatment at 150°C for 30 min.

observed before and after PEB on iodonium salt and the KCD system, which could generate the cations, and when the exposure to UV irradiation was carried out before PEB, the cationic polymerization of epoxy brought about no improvement in diffraction efficiency, as shown in Table II.

On the other hand, the cationic polymerization of CEP was confirmed by DPC analyses the different behavior of the reaction with an irradiation of the light source, that is, the CEP was scarcely polymerized with the unsensitized system upon exposure to an Xe arc lamp emitting only visible light, but was easy to polymerize with the same system upon exposure to an Hg lamp emitting UV-visible light, as shown in Table VI.

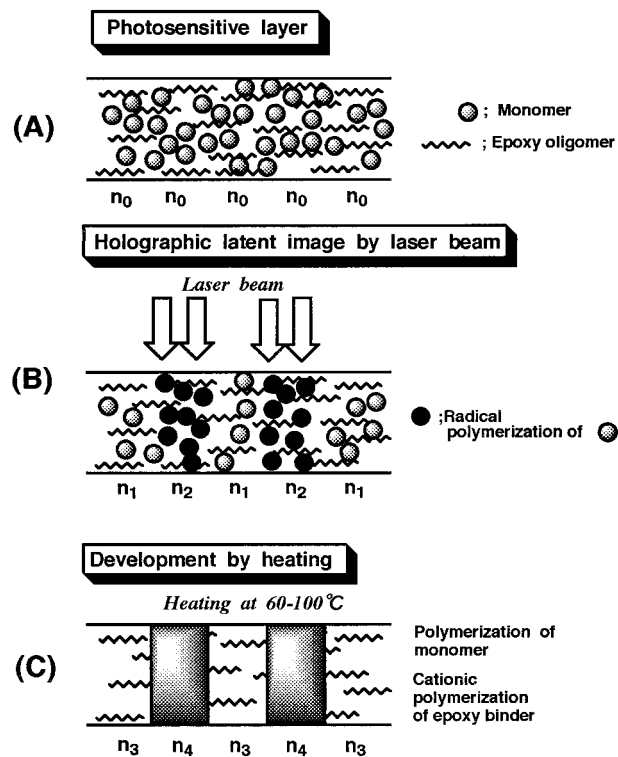
However, it is impossible to compare the enthalpy between the two light sources because of the difference in the light intensity. The cationic polymerization of the epoxide scarcely proceeded in the unsensitized system with irradiation of the visible light. Similar experiments were carried out by the use of epoxides of bisphenol A-type, which were less reactive than the alicyclic type. As a result, the cationic polymerization of this epoxide proceeded by sensitizing with KCD upon only the Hg lamp emitting the UV light.

In Table VII are shown the comparison of behavior between BTTB as the only radical generator and iodonium salt in the forming process of the reflection hologram. The diffraction efficiency was reached about 70% after holographic exposure in the BTTB system, but it was lowered after PEB. On the other hand, the efficiency was improved after PEB in the iodonium salt system, although it was very low after holographic expo-

sure. From the results of DPC analyses mentioned above, it was difficult to proceed with the cationic polymerization at about 80 mJ/cm² of holographic exposure.

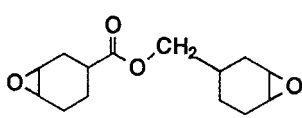
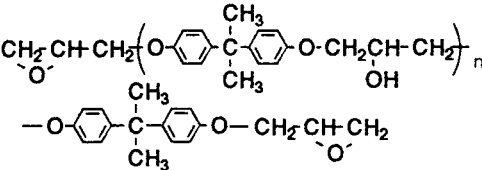
Thus, it is considered that changes of diffraction efficiency before and after PEB were attributable to the diffusion transfer of the radical polymerizable monomers while heating. Because BTTB having a peroxide group decomposes easily upon heating and the generated radicals were uniformly distributed, the monomers become polymerized at the portions exposed to a weak light. On the other hand, because the radical polymerizable activity was not relatively as high as other initiators, the monomers became polymerized at the portions undergoing a strong light. Moreover, the fringe patterns were formed according to the movement of unpolymerized monomers from the neighborhood to the gelification points. Thus, with these phenomena, the recording mechanism of the hologram in this system can be developed.

Now, as shown in Scheme 3, radical polymerization of the monomers is initiated with holographic exposure (B). The heating (PEB) promotes diffuse transfer of the monomers subse-



Scheme 2 Mechanism to form holograms in this photopolymer system.

Table VI DPC Analyses of Cationic Polymerizable Compounds

Compound	Light Source ^a	Sensitizer ^b	Enthalpy (J/g) ^c
 (CEP)	Xe	KCD	25.4
	Xe	none	5.0
	Hg	KCD	124.3
	Hg	none	90.3
 (E4)	Xe	KCD	1.1
	Hg	KCD	65.0

^a Xe arc; 150 W, Hg; 200 W.

^b Epoxy : BBI (: KCD) = 10 : 1 (: 0.5).

^c Exposure time; 2 min.

quently, but cationic polymerization of the binder cannot be initiated with this exposure energy. Therefore, differences in the refractive index are produced between differences in the light intensities, that is, differences in the distribution of the monomer concentration. After PEB, radical species and cations simultaneously generated at the exposure area causes the epoxy binder to proceed with the cationic polymerization and the remaining monomers to undergo the radical polymerization by means of irradiation with a UV light. Thus, it is possible to obtain a volume-type hologram having a high diffraction efficiency and thermostability.

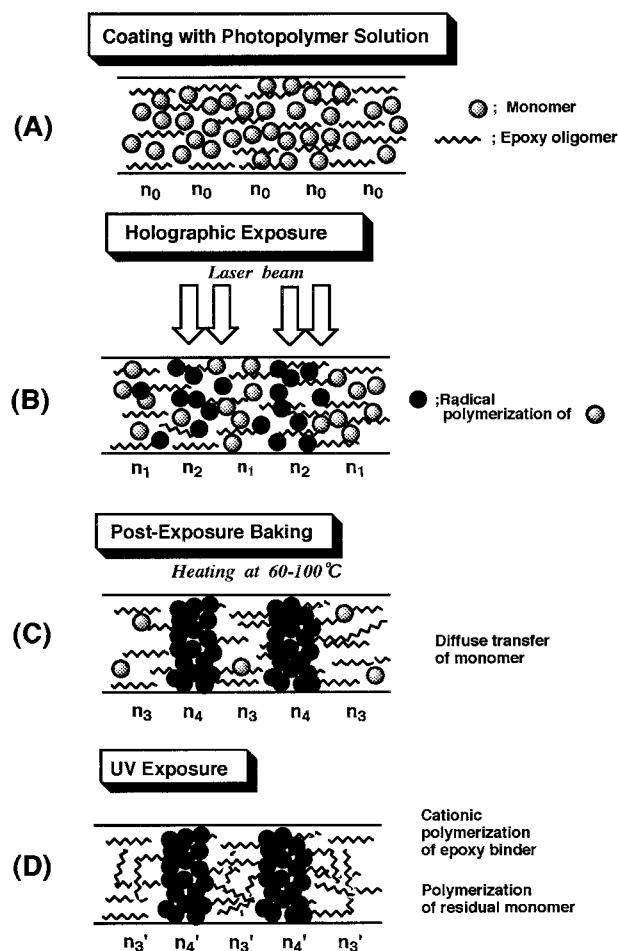
In conclusion, the photopolymer consists of a bisphenol A-type epoxy resin as a polymeric

Table VII Different Behavior by Initiator System on Before and After PEB

Initiator ^a	Diffraction Efficiency (%), Reconstructed Wavelength (nm) ^b Before PEB/After PEB
BTTB	69.0, 546/46.2, 558
BBI	35.3, 541/77.6, 549
TCT	19.5, 553/66.7, 548

^a E4 : monomer : initiator : KCD = 100 : 60 : 7.5 : 0.25.

^b Holographic exposure; 514.5 nm, 80 mJ/cm², the contact-copying method (holographic master of the angle between two beams is 135°).


Scheme 3 Corrected mechanism to form holograms.

binder, acrylic monomer, diaryliodonium salt as a photoinitiator, and ketocoumarin as a sensitizing dye. Exposure of these photopolymer films to an Ar⁺ laser beam emitting 488 nm light for the transmission holograms at 20–60 mJ/cm² and 514.5 nm light for the reflection holograms at 60–150 mJ/cm² and subsequent heat treatment resulted in refractive index alteration according to the light intensity. High diffraction efficiency and heat-stable holograms can be formed without the wet process.

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