

Photopolymers for holography

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ABSTRACT

Photosensitive films composed of dye, initiator, acrylic monomers, and polymeric film-forming binder, and their use in recording volume phase transmission and reflection holograms are described. Systematic variation of monomer-binder combinations reveals that the maximum attainable index modulation (hologram efficiency) increases with increasing difference between the refractive indices of monomer and binder. Addition of plasticizer is also useful for increasing index modulation. Thermal and wet chemical processing methods for altering hologram properties are described.

INTRODUCTION

Photopolymer films have been used for hologram recording since the late 1960's,¹⁻¹⁰ and over the ensuing years they have become increasingly important to the commercialization of holography. Mass production of surface relief holograms such as, for example, embossed rainbow transmission holograms and gratings, relies very heavily on photopolymers at the mastering/stamper-production stage, using photoresists, and in high volume wide-web embossing runs, using photopolymerizable resin coated on polyester. Appropriately formulated photopolymers also are ideally suited for recording volume phase transmission and reflection holograms, but, largely due to limited market size and (hence) unavailability of commercial films, mass production of volume phase holograms to date has primarily involved dichromated gelatin and fine grain silver halide emulsions. The *potential* market for volume phase holograms, however, is actually quite large as they have useful applications in fields ranging from optics, computing, and telecommunications to automotive/aerospace displays, graphic arts, and security devices. Recognizing this, several companies have developed and patented photopolymer technologies for recording volume phase holograms.¹¹⁻²¹ These technologies can be roughly divided into three general categories: (1) dry film compositions containing photoinitiator system, monomer, and a polymeric film-forming binder,¹¹⁻¹⁶ (2) liquid coatings containing photoinitiator and monomers,^{17,18} and (3) dry film compositions containing crosslinkable polymer and a photosensitizer or initiator.¹⁹⁻²¹ Only the first category has enjoyed any commercial success. Originally developed and used for hologram recording by Du Pont,¹¹ monomer-binder based photopolymers have a number of advantages, both for the manufacturer and for the user/holographer. For the manufacturer, monomer-binder compositions provide dimensionally stable polymerizable films that can be readily coated onto a variety of substrates and that can be easily reformulated to meet new markets and customer needs. When properly formulated, they offer the holographer a reproducible recording material with high resolution, high refractive index modulation, broad spectral sensitivity range, high photospeed, and excellent environmental stability before and after imaging. Du Pont's recent efforts to improve on its original compositions has led to new and better films,^{22,23} and has revealed some unexpected and interesting features about the formulation and use of photopolymers for holography. Our findings are summarized here and in the companion article that follows.

EXPERIMENTAL

Sample Preparation. The coating compositions used all have the following general formula:

- photosensitizing dye, 0.1-0.2%,
- initiator, 1-3%,
- chain transfer agent, 2-3%,
- plasticizer, 0-15%,
- acrylic monomer, 28-46%, and
- polymeric binder, 45-65%,

where percentages are with respect to the total composition weight. Except for dyes and initiators, all ingredients were obtained from regular commercial sources and were used as received. Coatings were cast from solvent, typically a mixture of dichloromethane and methanol, onto a clear film support of optical grade polyethylene terephthalate (Cronar® or D Mylar®)

using a conventional web coater equipped with a doctor knife, drier, and lamination station. A thin cover sheet of polypropylene or Mylar was laminated to the soft, slightly tacky coatings as they exited the drier, and the coated film was cut into short sections, put in black polyethylene bags, and stored at room temperature until used. Film samples for hologram recording and evaluation were mounted onto 4X5 inch glass plates by removing the cover sheet and hand laminating the tacky coating directly to the glass surface with a print roller. The Mylar support was left in place over the coating during subsequent imaging, processing, and analysis unless indicated otherwise.

Transmission Holograms. Glass mounted coating samples were evaluated by recording a series of holographic gratings and determining diffraction efficiency as a function of exposure. The gratings were recorded at the intersection of two collimated beams from an argon ion laser operating at 488 nm, TEM₀₀, with the bisector of the angle between beams fixed perpendicular to the film plane and the beam incidence angle (in air) equal to 15°. This arrangement gives unslanted gratings with a spatial frequency of approximately 1061 lp/mm. The beam intensity ratio was maintained at about 1:1, unless noted otherwise, with absolute intensity ranging from 3-10 mW/cm² per beam. Grating formation was monitored in real time using a non-actinic 632.8 nm He:Ne laser probe beam passing through the center of the exposure area at the Bragg angle. The intensity of the He:Ne probe beam was monitored with a conventional power meter (Coherent model 212) attached to a stripchart recorder. Diffraction efficiency (η) was calculated as the ratio of the diffracted probe beam intensity (I_{diff}) to the pre-exposure undiffracted beam intensity (I_0) after passing through the sample:

$$\eta = \frac{I_{diff}}{I_0} \quad (1)$$

The maximum attainable η for each sample was determined from its exposure series. Grating thickness (d) was measured as the coating thickness with conventional instruments (Brown and Sharpe electronic comparator or Sloan DEKTAK 3030 surface profile monitoring system). Refractive index modulation (Δn) in the gratings was calculated from η and d using Kogelnik's coupled wave theory,²⁴ which for lossless unslanted gratings gives:

$$\Delta n = \frac{\lambda_a \cos \theta_m \sin^{-1} \sqrt{\eta}}{\pi d} \quad (2)$$

where λ_a is the probe wavelength in free space (air) and θ_m is the incidence angle inside the recording medium. For the 632.8 nm He:Ne probe, a value of $\theta_m = 12.93^\circ$ is calculated from the 488 nm recording beam's 15° incidence angle in air (θ_a) using a combination of Snell's law:

$$\sin \theta_m = \frac{\sin \theta_a}{n_m} \quad (3)$$

and Bragg's law:

$$\sin \theta_m = \frac{\lambda_a}{2n_m \Lambda} \quad (4)$$

where n_m is the average refractive index of the recording medium, for which we assumed a value of $n_m = 1.500$, and Λ is the grating spacing.

Reflection Holograms. Glass mounted film samples were clamped to a front surface mirror with a thin layer of index matching fluid (xylene) between and a series of reflection holograms were recorded by exposing to a collimated 514 nm argon ion laser beam oriented perpendicular to the film plane. Beam diameter and intensity were about 2.5 cm and 10 mW/cm², respectively, and the exposure was varied from about 0.1 to 200 mJ/cm² in each series using a timed shutter. After completing the exposure series, samples were overall exposed to ultraviolet light from a mercury-arc photopolymer lamp (Theimer Strahler #5027). The UV cured, but otherwise unprocessed reflection holograms generally were given thermal or wet chemical treatments prior to analysis, see below. Where no such treatment occurred, the results are designated as being from "unprocessed" holograms. Hologram reflection efficiency (η), peak reflection wavelength, and bandwidth were measured from transmission spectra obtained using a double beam spectrophotometer (Perkin Elmer Lambda-9) with the film plane of the hologram held at normal incidence to the sample beam. Index modulation, Δn , was calculated from η using coupled wave theory,²⁴ which for lossless unslanted reflection holograms at the Bragg condition and normal incidence gives:

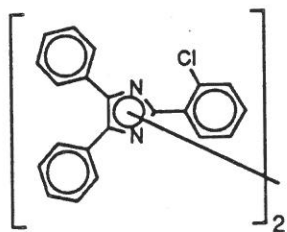
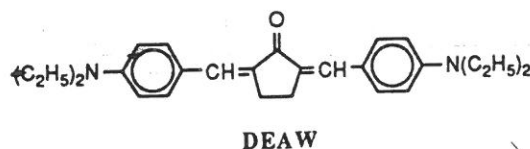
$$\Delta n = \frac{\lambda_a \tanh^{-1} \sqrt{\eta}}{\pi d} \quad (5)$$

where λ_a is the reflection wavelength at maximum η .

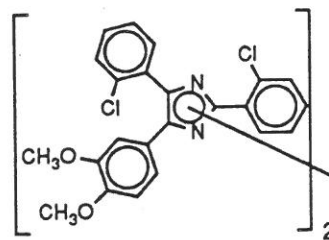
Hologram Processing. After imaging and UV cure, glass mounted reflection holograms covered by Mylar were placed between preheated glass plates in a conventional forced-air convection oven, generally at 100 °C. After the desired heating time elapsed, the holograms were removed and quickly cooled to room temperature by contacting them with a cold surface, typically a bench-top or running water. The holograms were then analyzed and/or subjected to further processing. Chemical (wet) processing was done starting either with unprocessed or thermally processed reflection holograms. The Mylar support covering the holograms was peeled off, and the holograms were immersed in aqueous processing solution for about ten minutes, removed from the solution, and air dried at room temperature. Transmission holograms were not thermally or chemically processed.

RESULTS AND DISCUSSION

Photoinitiator System. The photoinitiator system used in this work consists of three separate components: (1) a visible light absorbing dye, DEAW, (2) an ultraviolet light absorbing hexaarylbiimidazole (HABI) initiator, and (3) a chain transfer agent, 2-mercaptobenzoxazole (MBO).^{25,26} DEAW dye sensitizes the composition to blue-green light, *ca.* 400-560 nm, with λ_{max} at 480 nm.

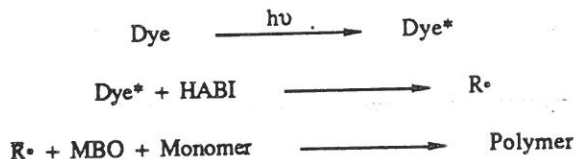


o-Cl HABI



TCTM HABI

During imaging, electronically excited dye forms and sensitizes decomposition of HABI to triarylimidazolyl radicals ($R\cdot$) that then oxidize the chain transfer agent to thiol radicals. Addition of thiol radicals to acrylic monomer initiates polymerization:



We find that the identity and level of the initiator components can be used to control nonholographic properties such as photospeed, spectral sensitivity range, background color, and shelf life, but in general they do not have a dominant influence on efficiency or index modulation, at least not to the extent that other film components do such as binder, monomer, and plasticizer. Dye level is an exception as it usually must be adjusted to obtain low to moderate optical density at the imaging wavelength, *e.g.*, $OD < 0.4$. Dye levels resulting in high optical densities can lead to inefficient holograms, particularly in cases where a recording beam must make two passes through the film, as for example with Lippmann or Denisyuk reflection holograms, because with photopolymers index modulation decreases as the beam ratio deviates from unity, see, for example, Figure 1.

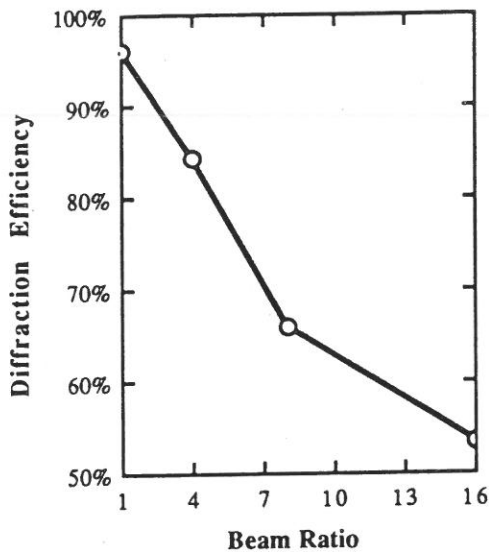


Figure 1. Effect of beam intensity ratio on hologram recording. Data from transmission gratings, 34 μ coating, 57% CAB, 35% POEA, 5% TDC, 1.9 % MBO, 1% o-Cl HABI, 1.9% MBO, 0.1% DEAW.

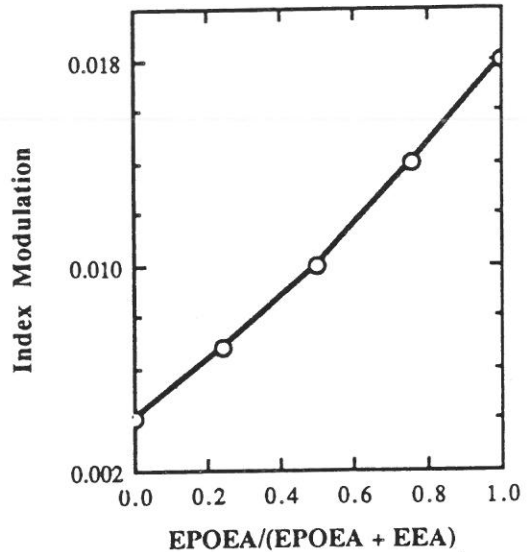


Figure 2. Change in index modulation with changing fractions of high index EPOEA and low index EEA monomers in low index PVAc binder. Data from reflection holograms recorded at 514 nm (playback $\lambda_{max} = 508$ nm).

Monomer and Binder. Transmission gratings were recorded in a series of compositions based on four binders and a variety of mono and multifunctional acrylic monomers. The binders tested were cellulose acetate butyrate (CAB), poly(methyl methacrylate) (PMMA), 75:25 poly(styrene-acrylonitrile) (PSAN), and 70:30 poly(styrene-methyl methacrylate) (PSMMA). These binders are conveniently categorized by chemical structure as being aliphatic, such as CAB, or aromatic, such as PSAN. The monomers tested are all liquids except one, 2-naphthyl acrylate, and like the binders can be categorized as being either aliphatic or predominantly aromatic. The solid 2-naphthyl acrylate was used in combination with a liquid monomer, 2-phenoxyethyl acrylate (POEA), to prevent crystallization in the film. Results are reported in Table 1.

Two related trends are clear from Table 1. First, for aliphatic binder compositions the refractive index modulation is much greater when aromatic monomers are used than when aliphatic monomers are used. Second, for aromatic binder compositions just the opposite holds true and it is the aliphatic monomers that give the greater modulation. The key physical property underlying these trends appears to be the relative refractive indices of the binder and monomer. Low refractive index (aliphatic) binders give higher Δn when used with high refractive index (aromatic) monomers, and, conversely, high refractive index binders give higher Δn when used with low refractive index monomers. Refractive indices of the binders and monomers are included in Table 1. Of course, in hologram recording the monomer is converted to polymer and it actually is the refractive index of this polymer that is contributing to Δn . Conversion of a monomer to its polymer generally increases refractive index by 2-4%, primarily due to increased density in the polymer. For example, the refractive index of poly(2-ethoxyethoxyethyl acrylate), 1.471, is 2.4% greater than that of its monomer, Table 1, and for styrene polymerization the index increases 2.9% from 1.547 to 1.592. The monomers in Table 1 should all give close to the same percent increase in refractive index upon polymerization, so the relative ordering of their polymers from low to high index is about the same as that shown for the monomers themselves.

The influence of monomer/binder refractive index on Δn in reflection hologram recording was examined using a series of compositions with various ratios of high and low index monomers in a single low index binder, poly(vinyl acetate) (PVAc), $n = 1.463$. The monomers, ethoxylated phenol acrylate (EPOEA), $n = 1.559$, and 2-ethoxyethoxyethyl acrylate (EEA), $n = 1.436$, were varied in level between 0% and 25% of the total composition while the sum of their levels was held constant at 25%. The other ingredients are 0.08% dye, 3% o-Cl HABI, 3% MBO, 3% ethoxylated bisphenol A diacrylate (EBPDA), and 66% PVAc. Coating thickness is 24-26 microns. Holographic mirrors recorded in the compositions were thermally processed, 100 $^{\circ}$ C, 90 minutes, and analyzed to obtain Δn . The results, Figure 2, show that Δn increases almost linearly with increasing level of high index monomer EPOEA.

Table 1. Influence of Monomer and Binder on Transmission Hologram Recording.^a

Monomers	Monomer Ref. Index ^c	Index Modulation, Δn^b			
		Aliphatic Binders		Aromatic Binders	
		CAB ^d	PMMA ^e	PSAN ^f	PSMMA ^g
Aliphatic Monomers					
2-[2-(Ethoxy)ethoxy]ethyl acrylate (EEA)	1.4361	0.0013	-	0.013	-
Diethylene glycol diacrylate	1.4580	0.0030	-	0.0093	0.0086
Decanediol diacrylate	1.4589	0.0018	-	0.011	0.0090
Triethylene glycol dimethacrylate	1.4590	0.0027	0.0017	0.0062	0.0067
Triethylene glycol diacrylate (TDA)	1.4594	0.0028	0.0017	0.011	0.0090
Isobornyl acrylate	1.4732	0.0020	0.0007	-	0.0065
Trimethylol propane triacrylate	1.4742	0.0024	-	0.0017	-
Aromatic Monomers					
2-Phenylethyl acrylate	1.5084	0.0055	-	-	0.0028
2-Phenoxyethyl methacrylate	1.5121	-	-	-	-
2-Phenoxyethyl acrylate (POEA)	1.5143	0.010	0.0081	0.0031	0.0022
Phenyl acrylate	1.5170	0.0096	0.0061	-	-
<i>p</i> -Chlorophenoxyethyl acrylate	1.5273	0.011	-	-	-
1:4 2-Naphthyl acrylate:POEA	1.5320	0.014	0.010	-	-
<i>p</i> -Chlorophenyl acrylate	1.5323	0.011	-	-	-

^a Formulation: 50.4% binder, 46.4% monomers, 1.2% o-Cl HABI, 1.8% MBO, 0.07-0.28% DEAW (depending on thickness). Coating thickness range ca. 18-64 microns. ^b From gratings recorded at 488 nm, analyzed at 633 nm. ^c At room temperature, Abbe refractometer. ^d refractive index $n = 1.475$. ^e $n = 1.489$. ^f $n = 1.57$. ^g $n = 1.56$.

Plasticizer. We find that Δn can increase by as much as two to three fold when nonvolatile plasticizer is added to the formulation. Results from holographic gratings recorded in compositions containing varying amounts of triethylene glycol diacrylate (TDC) plasticizer, CAB binder, TCTM HABI initiator system, and either POEA or triethylene glycol diacrylate (TDA) monomer are shown in Figure 3. The sum total of monomer and plasticizer levels in these compositions was held constant at ca. 45%.

Prior to actinic exposure, photopolymers actually are highly plasticized polymeric binder compositions in which monomer and other low molecular weight components act as plasticizing agents. Because of this, the initiator, chain transfer agent, and monomer diffuse freely through the composition during the early stages of photopolymerization. However, as photopolymerization proceeds and monomer is consumed, the composition soon begins to gel or vitrify, diffusion becomes more difficult, and, finally, polymerization stops as the remaining monomers are unable to reach reactive (polymer) radical centers.^{27,28} The rate and extent of vitrification is strongly dependent of the type of monomers used and generally is most rapid with multifunctional monomers like TDA due to their tendency to form highly crosslinked polymer networks.²⁸ Addition of "inert" plasticizers, typically phthalate, alkyl diacid, or polyethylene glycol esters, is commonly used to reduce the extent of vitrification in photopolymers and thereby increase flexibility in the cured film. The presence of plasticizers allows more efficient diffusion to occur at the later stages of polymerization and we believe this is the principal reason they increase Δn .

Thermal Processing. When imaging photopolymer film, the hologram forms and intensifies in real time while monomer is being converted to polymer. Once the film vitrifies and polymerization stops, the hologram is stable toward further exposure. In our work we typically give the resulting hologram an overall non-imagewise ultraviolet exposure to ensure complete cure in imaged and non-imaged areas. Surprisingly, after UV curing we find that index modulation can be significantly enhanced with little change in playback wavelength by simply heating the hologram in a conventional oven while sealed between glass and/or Mylar.

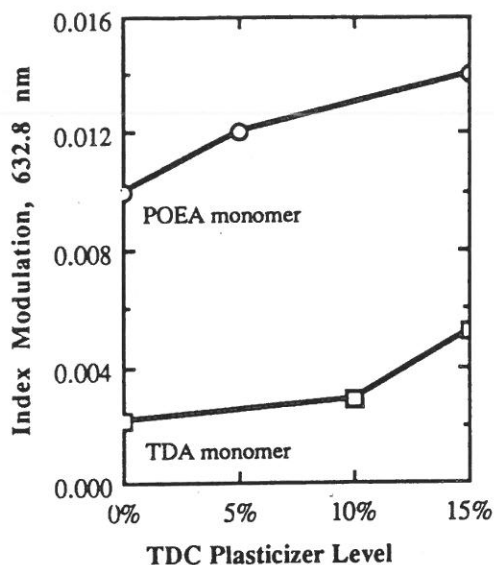


Figure 3. Effect of plasticizer level on Δn . Data from holographic transmission gratings recorded at 488 nm. Binder is CAB.

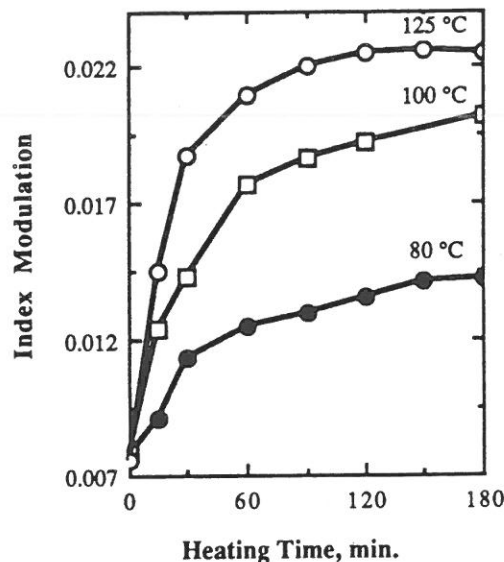


Figure 4. Effect of temperature and time on Δn . Data from holographic mirrors recorded at 514 nm, playback $\lambda_{\max} = 506 \pm 2$ nm before and after heating.

Thermal processing results are presented in Figure 4 from holographic mirrors recorded at 514 nm in a 26 micron coating composed of 66% PVAc, 25% EPOEA, 3% EBPDA, 3% o-Cl HABI, 3% MBO, and 0.08% dye. The coating was imaged and thermally processed while mounted between glass and Mylar. Upon heating, Δn increases rapidly at first and then gradually approaches a constant maximum value. As shown in Figure 4, the rate of change and the maximum attainable Δn increases with increasing temperature. The peak reflection wavelength, λ_{\max} , changes very little during heat processing, 0-3 nm toward shorter wavelengths is typical, provided that the hologram is sealed between glass and/or Mylar. When heated unsealed and open to air, λ_{\max} blue shifts 10-20 nm or more, probably as a result of (trace) volatile components evaporating from the hologram, but Δn still increases much the same as shown in Figure 4 for sealed holograms.

Wet Chemical Processing. Photopolymer holograms also can be altered by immersing them in organic liquids that swell or dissolve the coating. Examples of such liquids are ketones, esters, glycol ethers, chlorocarbons, xylenes and related aromatics, and low molecular weight acrylic, methacrylic, and vinylic monomers. Typically, upon immersion the hologram playback wavelength shifts to longer wavelength and the bandwidth increases so that the hologram appears brighter to the eye. With some swelling solvents the hologram may actually seem to disappear as it shifts out of the visible spectrum to the near infrared. Strong solvents such as acetone, pyridine, and dichloromethane rapidly attack and destroy the coating and hologram, and these must be diluted with low or non-swelling liquids like isopropanol or water, or they must be lightly applied as a spray or thin wipe. For most swelling solvents, particularly volatile ones, the effects of processing are not entirely permanent. Once removed from the processing bath, the hologram's playback wavelength slowly shifts back to about its original value as solvent evaporates and the hologram dries out.

Results from holographic mirrors processed in 10% aqueous acetone and pyridine solutions are given in Table 2. Interestingly, changing from a low refractive index processing solvent like acetone ($n = 1.359$) to a high index solvent like pyridine ($n = 1.510$) does not result in substantially different reflection efficiency values, η , and neither solvent causes marked lowering of η relative to unprocessed holograms. This suggests that microscopic pores, cracks, or voids do not play a significant role in forming the hologram as these would have filled with liquid and η would have decreased dramatically due to index matching of the (filled) voids to the surrounding photopolymer matrix.^{29,30}

The effects of chemical processing can be made permanent by using reactive swelling solvents that become entrapped in the photopolymer hologram. Monomers are particularly useful for this as they can be polymerized in place simply by exposing the processed hologram to ultraviolet light.³¹

Table 2. Effect of Wet Chemical Processing on Reflection Holograms.^a

Post-soak Drying Time, hrs	Unprocessed holographic mirror soaked in 10% aqueous acetone			Heat processed holographic mirror soaked in 10% aqueous acetone			Heat processed holographic mirror soaked in 10% aqueous pyridine		
	λ_{max} , nm	Bandwidth ^b	%Eff., η	λ_{max} , nm	Bandwidth ^b	%Eff., η	λ_{max} , nm	Bandwidth ^b	%Eff., η
(presoak)	508	5	76	508	10	99	507	10	99
0.00	528	7	55	534	15	97	581	19	88
0.25	521	6	62	528	17	93	556	20	88
0.50	519	7	56	524	26	95	547	21	87
1.50	515	7	56	519	26	94	533	33	83
86	503	7	65	501	13	98	500	14	97

^a Formulation: 66% PVAc, 25% EPOEA, 3%EBPDA, 3% o-CI HABI, 3% MBO and 0.08% dye; coating thickness before and after processing is 25 ± 1 micron; mirrors recorded at 514 nm. ^b Full width at half maximum, nm.

Hologram Structure. Electron micrographs from cross-sections of a holographic transmission grating recorded in photopolymer are shown in Figure 5. The sections were prepared in two ways: diamond knife microtome and freeze fracture at liquid nitrogen temperature. The microtomed section faintly shows the hologram fringe planes, but is otherwise almost featureless. The freeze fractured section shows the fringe planes more clearly and also reveals evidence of submicron structural features along the plane of the fracture. These submicron features may be related to compositional inhomogeneities that commonly exist in monomer-binder compositions.²⁷ Previously discussed chemical processing results, above, suggest the submicron features are not microscopic pores, cracks, or voids, though such structures have been found in other monomer-binder photopolymers (after wet processing).^{29,30,32} Another significant feature of the cross-sections is that they show no structural relief at the film surface, *i.e.*, the hologram is entirely of the volume phase type.

Recording Mechanism. Diffusion mechanisms for hologram recording have been discussed in previous reports on Du Pont's original compositions,^{4,5,7} and in reports on other photopolymer systems.^{8,33} Some aspects of the proposed mechanisms are open to argument.^{5,7} In particular, we find no evidence in our work that would support Colburn and Haines' hypothesis⁴ that refractive index initially decreases in the bright (constructive) interference regions during image wise exposure. Also, the view that binder is an inert component that contributes only to the holograms average refractive index and not to its index modulation is inconsistent with our finding that the magnitude of Δn is dependent on the difference in refractive index between monomer and binder.

Though some details remain speculative, a diffusion based mechanism still gives the best account of all experimental observations. In general, during hologram recording it appears that monomer polymerization starts and proceeds rapidly in regions exposed to bright interference fringes. As the monomer level is depleted by polymerization, fresh monomer diffuses in from neighboring dark regions, thus setting up chemical concentration and density gradients that result in refractive index modulation. The shrinkage or decrease in molecular volume associated with converting monomer to polymer, typically 10-20% for acrylates, is probably a major factor in drawing additional unreacted monomer into the polymerizing region. As exposure and polymerization proceed, the initial highly viscous composition gels and hardens, diffusion is suppressed, and further hologram recording stops. The hologram is then fully formed and stable toward further exposure.

CONCLUSIONS

Photosensitive films based on mixtures of sensitizer, initiator, monomer, and polymeric binder are capable of recording highly efficient volume phase holograms by a monomer diffusion mechanism in "real time" without the need for any processing step other than imaging itself. The recorded hologram (fringe) structure is free of voids or pores and consists of (i) photopolymer-rich regions formed by monomer polymerization in areas of constructive interference and (ii) binder-rich regions formed by monomer diffusion out of areas of destructive interference. The difference in refractive index between monomer and binder controls the refractive index difference between the photopolymer-rich and binder-rich regions, and hence controls the hologram's index modulation value, Δn . Plasticizers can be used to increase monomer diffusion and obtain higher Δn . Thermal treatment of the recorded hologram also increases Δn , presumably due to further diffusion and reaction of film components at elevated temperatures.

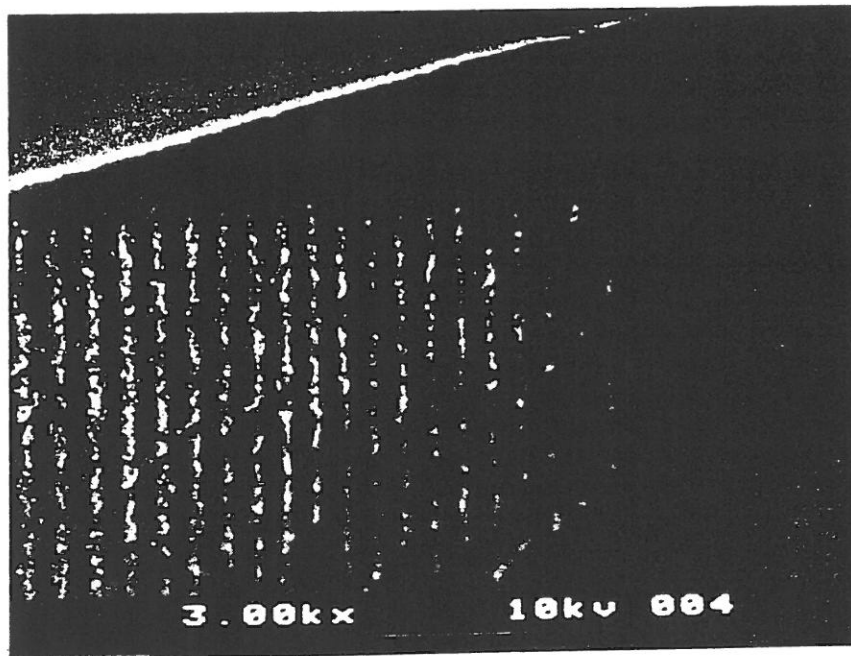
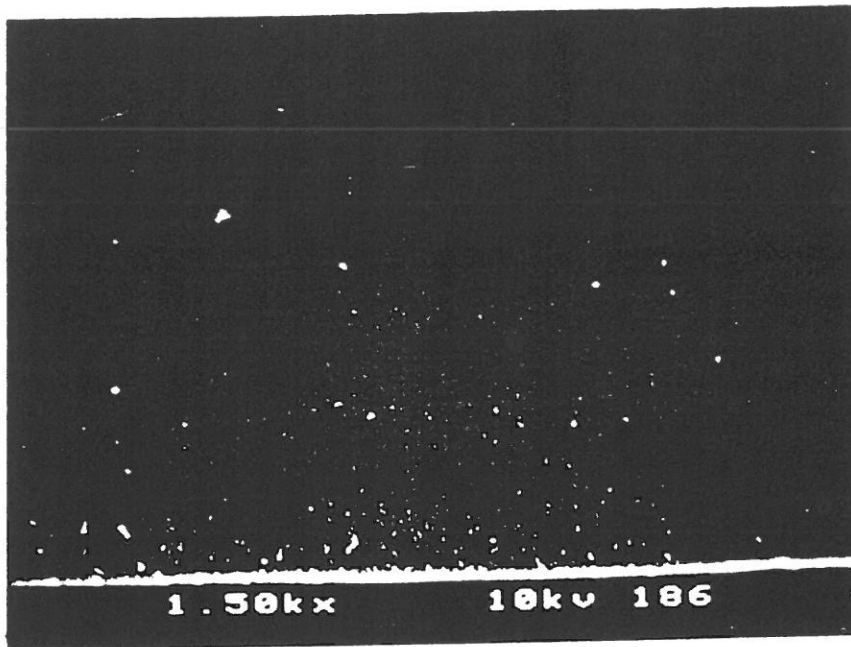


Figure 5. Electron micrographs of a holographic grating recorded in photopolymer (CAB binder, TDA monomer) and cross-sectioned perpendicular to fringe planes. Grating recorded as described in the Experimental section, except using 514 nm write beams. Calculated fringe spacing (eqs 3, 4) is 0.99μ . **Top Micrograph:** diamond knife cut; grating/coating surface is in upper 1/3 of micrograph; lower faint horizontal lines are artifacts of the knife cut. Scale (broken line) is 10 microns. Measured fringe spacing is 0.96μ . **Bottom Micrograph:** Freeze fractured sample; coating surface in upper left corner. Scale (broken line) is 10 microns. Measured fringe spacing is 1.16μ .

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