Acrylate Oligomer-Based Photopolymers for Optical Storage Applications

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Photopolymers are attractive candidates for high-density holographic data storage because of their high sensitivity and refractive index contrast. We have incorporated several high-index organic monomers into high optical quality acrylate oligomer-based formulations. Using reactivity ratios, reaction kinetics, and component refractive indices as guidelines, a 6-fold increase in Δn has been achieved compared to an initial all-acrylate formulation. Samples prepared from these formulations have been used to write and read >200 high-quality holograms in a given volume of material. This is the first time a photopolymeric medium has successfully been used to multiplex this number of holograms. Using these resins, a protocol for the evaluation of photopolymers as holographic media has been developed.

Introduction

The development of new holographic recording techniques[1] has brought about a renewed interest in the use of photopolymerizable compositions (photopolymers) as recording media. Lithium niobate has been widely used as a recording medium to develop and evaluate storage techniques,[2] but due to its cost and the impermanence of holograms written therein, it is unlikely to be included in a commercial product. In addition, holograms recorded in this medium are erased on read out, making lithium niobate unsuitable for archival storage applications. Photopolymers are attractive alternatives because they are inexpensive and can be designed to exhibit high photosensitivity and to form permanent holograms. The ability to change sample shape, e.g., from a cube to a disk, and the inherent tunability of the physical properties for most polymer systems by changing component content and ratios are additional advantages which are especially important at the early stages of research and development.

Photopolymers have been considered for use as holographic recording media for several decades,[3] with research aimed at generating highly sensitive holographic film capable of storing single holograms with large diffraction efficiencies and high fidelity. In 1969, Close et al.[4] reported the first use of a photopolymer for holography based on a free-radical polymerizable metal acrylate monomer. In some later systems, photosensitive reaction components were guests in an inert host polymer or binder. For example, the commercial photopolymers designed for holographic recording by Dupont[1b,5] have been studied extensively and provide excellent material photosensitivity and refractive index contrast, Δn.[6] However, their application to data storage is severely limited due to their need for solvent processing, limited thickness (150 μm), and high polymerization-induced shrinkage (ca. 4−10%).[7] Small multifunctional acrylate monomers were used by Lougnot and coworkers in a solvent-free system.[8] Dye-sensitized photopolymerization reactions of vinyl monomers incorporated into a polymer matrix have been demonstrated by Polaroid for holographic recording.[9] In both of these systems, only thin (<45 μm) media can be prepared, which are unsuitable for high-density data storage. More recently, new Polaroid materials have been prepared in thicknesses of 150−200 μm.[10]

To be useful for data storage applications, a photopolymer must be designed with certain attributes that are lacking in currently available holographic films. To achieve commercially interesting storage densities (100 bits/μm^2), a holographic medium should be ≥200 μm

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(1) (a) Pu, A.; Psaltis, D. *Applied Optics* **1996**, *35*, 2389. (b) Curtis, K.; Psaltis, D. *Applied Optics* **1992**, *31*, 7425.

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(3) (a) Lessard, R. A.; Changkakoti, R.; Manivannan, G. *Processes in Photoreactive Polymers*; Krongauz, V. V., Trifunac, A. D., Eds.; Chapman and Hall: 1995; p 307. (b) *Selected Papers on Photopolymers: Physics, Chemistry, and Applications*; Lessard, R. A., Manivannan, G., Eds.; SPIE Optical Engineering Press: Bellingham, WA, 1995.

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(6) Harihan, P. *Optical Holography Principles Techniques and Applications*; Cambridge University Press: Cambridge, 1991; p 43. The refractive index, Δn, is a measure of the modulation in refractive index that is produced by holographic recording and is a measure of the optical response of a medium.

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thick because the thickness determines the number of holograms that can be overlapped (multiplexed) in a given volume of material. In addition, the extent of writing-induced dimensional change in currently available holographic materials is too large for data storage applications. Dimensional changes in the storage medium distort the holograms, degrade the fidelity with which data can be recovered and, ultimately, limit the storage density of a material.

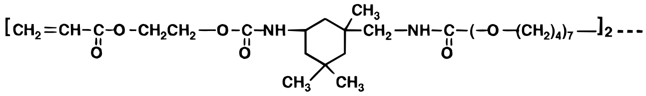
The storage medium must also have low absorption at the recording wavelength, to ensure uniform recording through the thickness of the material, and exhibit low levels of light scattering to minimize the noise in recorded images. There must also be sufficient (10−20%) mobile species for holographic writing and they must undergo rapid and complete photoinduced polymerization. The medium must have excellent long term thermal and chemical stability to maintain high-fidelity data recovery. The latter requirements suggest that cross-linked acrylate materials, similar to those used for UV-cured coating applications such as optical fiber coatings, may be well-suited to data storage applications. These solvent-free systems have high optical quality, are typically based on free-radical polymerizations, are designed to achieve fast, complete polymerization, and are environmentally robust.

Before photocuring, the typical acrylate resin is a viscous liquid which can be used to prepare thick samples, but in this state it is incapable of permanently fixing the fine compositional patterns that make up the holograms. However, acrylate oligomer-based resins can be partially polymerized to any level of cure by controlling the amount of exposure to light. By precuring the resin beyond a critical level to a gelled state before writing, the recorded holograms are stabilized. In addition, the number of mobile species in the polymer matrix can be optimized for both writing capacity and hologram stability. The precure level determines the achievable Δn of the storage medium and the extent of dimensional change that occurs during holographic recording.

In this paper, we describe the development of acrylate-based photopolymer systems sensitive to visible-light as holographic media. Kinetic studies by near-IR (NIR) spectroscopy are used to determine that the rates of monomer diffusivity and polymerization are sufficiently fast for optical recording, as well as to assess relative monomer reactivities and coreactivities as they relate to the refractive index contrast. Finally, the performance of several formulations is described along with the strategies to be used for optimizing the Δn in this class of materials.

Experimental Section

Materials. The monomers isobornyl acrylate (IBA), hexanediol diacrylate (HDODA), phenoxyethylacrylate (PEA), *N*-vinylcarbazole (NVC), *N*-vinylpyrrolidinone (NVP), vinyl benzoate (VBZ), and *tert*-butyl hydroperoxide (TBHP) were purchased from Aldrich Chemical Co. and used without further purification. Phenyl acrylate and β-naphthyl acrylate were purchased from Monomer-Polymer Corp. and used as received. The oligomer, ALU-351 (Echo Resins, Inc.), was used as received. It is a di(urethane−acrylate) oligomer ($M_n = 1700 \pm 10\%$) with a polytetramethylenepolyol backbone (structure 1).



Oligomer, ER 351 (n = 1.492)

The monomers, vinyl naphthoate (VNA) and vinyl dichlorobenzoate (VDCBZ), were synthesized as described below.

Synthesis of Vinyl 1-Naphthoate. A modification of the procedure of Hopf[11] was used. A mixture of 190 mL of vinyl acetate, 1.6 g of mercuric acetate, 0.25 mL of 20% oleum (i.e., fuming sulfuric acid; **Caution:** severely corrosive, causes burns to lungs and skin!), 25 mg of cupric 2-ethylhexanoate, and 31 g of 1-naphthoic acid (recrystallized from 200 mL of toluene with charcoal decolorization and hot filtration) was stirred and heated just below reflux for 8 h. Shorter heating times gave lower conversion, while longer heating times gave increased polymerization and colored impurities. After cooling to room temperature, the mixture was cautiously poured into excess dilute aqueous sodium bicarbonate, being careful of an induction period before the rapid reaction of the acidic components with the bicarbonate, accompanied by gas evolution. The organic layer was separated with the aid of ethyl acetate, further washed with aqueous sodium bicarbonate and deionized water, dried with magnesium sulfate in the presence of charcoal, and filtered.

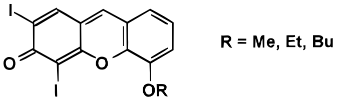
Concentration of the organic layer gave 60 g of crude product. Chromatography on 200 g of silica gel, eluting with hexane and (if necessary) methylene chloride in hexane gave 28 g (78%) of an off-white product. Complete decolorization could be accomplished with a second chromatography. ^{1}H NMR ($CDCl_3$): δ 4.73 (1H, d); 5.12 (1H, d); 7.45−7.7 (4H, m); 7.90 (1H, d); 8.04 (1H, d); 8.29 (1H, d); 8.94 (1H, d).

Synthesis of Vinyl 3,5-Dichlorobenzoate. The above procedure was followed, using 16 g of 3,5-dichlorobenzoic acid, 50−100 mL of vinyl acetate, 0.8 g of mercuric acetate, 0.1 mL of oleum, and 10 mg of cupric 2-ethylhexanoate. Chromatography was performed with methylene chloride elution. ^{1}H NMR ($CDCl_3$): δ 4.75 (1H, d); 5.13 (1H, d); 7.43 (1H, d of d); 7.57 (1H, s); 7.95 (2H, s).

Photoinitiators. A number of photoinitiators which absorb light in the visible region of the spectrum were screened to determine their utility for optical storage applications.

1. Hexaarylbiimidazole (HABI)-Dye Systems.[5] Several three-component photoinitiator systems comprised of HABI, 2-mercaptobenzooxazole (MBO), a chain transfer agent, and various sensitizer dyes were used. Typically HABI was 1−3 wt % and MBO was 2.5 wt % of the total composition. The dye used was 2,5-bis[[(4-diethylamino)phenyl]methylene]cyclopentanone (DEAW),[12] and the concentrations were varied from 0.01 to 0.05 wt %.

2. Spectra Group Limited Photoinitiator.[13] A three-component photoinitiator system was purchased from Spectra Group Limited and used according to the manufacturers instructions. The components consisted of (a) HNU470, a fluorone photoinitiator (structure 2);



(b) octyloxyphenyl phenyliodonium hexafluoroantimonate, OPPI, which facilitates electron transfer; and (c) *N*,*N*-dimethyl-2,6-diisopropylaniline, DIDMA, a coinitiator. They were mixed

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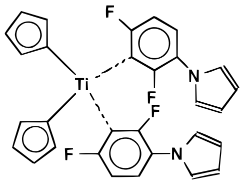
[11] Hopf, H.; Lussi, H. *Makromol. Chem.* **1956**, *18−19*, 227−238. Hopf reported the vinylation of naphthoic acids with acetylene to give vinyl naphthoates. The procedure described in this paper is based on Hopf's synthesis of vinyl *p*-nitrobenzoate, but with the reaction conditions and workup procedures substantially altered. Our procedure avoids the inconvenient use of acetylene under pressure.

[12] Wallach, O. *Chem. Zentralblatt* **1908**, *1*, 637.

[13] Marino, T. L.; Martin; D.; Neckers, D. C. *Proc. Radtech* **1994**.

in a ratio of 1:3.6:7.67, respectively. The concentration of HNU was either 0.0159 or 0.03 wt % of the resin composition.

3. Ciba-Geigy Photoinitiator. A single-component photoinitiator, bis(η^5-2,4-cyclopentadien-1-yl)bis[2,6-difluoro-3-(1*H*-pyrrol1yl)phenyl]titanium (CG-784, structure 3), was purchased from Ciba Geigy as a 30% dispersion on Dicalite 4128, a mineral binder, and was isolated according to the manufacturer's directions, working under red light. The Dicalite suspension (50 g) was stirred with 200 mL of methyl ethyl ketone for at least 1 h to dissolve the photoinitiator. The slurry was then filtered through a Büchner funnel to remove most of the dicalite, followed by filtration through a medium- and fine-fritted glass funnel, successively. The filtrate was then concentrated on a rotary evaporator to remove the solvent and the orange solid was dried in vacuo ($P = 0.2$ mm) overnight. The photoinitiator was stored in a foil-wrapped bottle in a dark cabinet at room temperature until needed for formulation.



CGI-784

Resin Formulation. The resins were prepared by first weighing the neat monomers into a foil-wrapped brown bottle and stirring with a magnetic stir bar. The photoinitiator was added to the monomers and the stirring continued to dissolve the photoinitiator completely (~30 min). The viscous oligomer was then added to the mixture and the resulting formulation was blended overnight at room temperature on a jar mill (U.S. Stoneware # M93120DC)**.** TBHP was stirred into the mixture on the jar mill. The resin was then used for sample preparation at room temperature or stored in a refrigerator at 5 °C until needed. All formulations were prepared using this general procedure. The resins were filtered through 20 and 10 mm nylon filters, successively, in a Fisherbrand (# 09-753-25A) stainless steel filter apparatus, pressurized to 20−25 psi with nitrogen.

Sample Preparation. In general, samples were prepared by placing a portion of resin on a glass plate, typically a 75 × 50 × 1 mm microscope slide, surrounded by a Teflon spacer. A second glass plate was placed on top of the resin and the two plates were pressed together, by hand, to the thickness of the spacer. The spacers were typically 25 mm diameter Teflon rings, from 0.015 to 0.5 mm thick, purchased from Spectra Tech Inc.. (# 0018021, 2000-244, 2000357). Some thin samples were prepared without spacers by squeezing a weighed amount of resin between the two glass substrates. To prepare thicker samples, other materials such as polyethylene rings or rubber O-rings were used as spacers and thicker glass plates (3 mm) were used for improved optical quality. These plates were purchased from Edmund Scientific (# 32741) and had an antireflective (AR) coating on both sides of the glass. While the Teflon spacers roughly defined sample thickness, polymer resin did leak under and over the spacers, so sample thicknesses were not exactly equal to the spacer thickness.

Samples were precured to the desired level by exposure either to radiation from a 200 W high-pressure mercury lamp or to an Oriel Model 87436 Hg lamp, filtered with a Schott OG530 filter to provide approximately 10 mW/cm^2 on the 546 nm Hg line and block wavelengths <530 nm. The power was measured on a Newport Model 1830-C optical power meter with a Newport Model 818-SL detector. This particular visible light system provided uniform (± 5%) illumination over a 6 × 6 in. area, permitting several samples to be treated at the same time. The precure exposure was 40−70 s for most formulations. Samples prepared for holographic experiments were precured so that they exhibited a 0.9% change in thickness upon recording. After precure, samples were wrapped in foil and stored at room temperature until their use in holographic recording.

Both the degree of precure and the thickness of the samples were determined by near-IR (NIR) spectroscopy (LT Industries Quantum 1200 Plus spectrometer). NIR bands can be detected for thick samples through glass substrates, allowing direct evaluation of each holographic sample. The acrylate group has NIR peaks near 1600, 2100, and 2300 nm that disappear as the acrylates are polymerized. By using the second derivatives of these features as indicators of acrylate levels and by comparison to samples of known acrylate content, the extent of polymerization in a sample could be determined to ±2% accuracy. Sample thicknesses were established by comparison of second derivative peaks at ~2038 nm to those from samples of known thickness. This peak is an ether band of the oligomer polyether backbone and is sensitive to thickness but not precure level because these groups are not involved in the photoreaction. Sample thicknesses were determined to within approximately 5% in the range 50−1000 mm.

^{13}C NMR spectra were recorded at 100.5 MHz on a Varian Unity 400 spectrometer. Samples were placed in SiN rotors fitted with Vespel endcaps. Liquid formulations were examined without sample spinning; precured films were examined under conditions of magic-angle spinning (9.5 kHz). High-power proton decoupling was used with all samples. Spectra are referenced to an external sample of polyethylene.

Holographic Recording. The holographic performance of the formulations described above was characterized by recording multiple holograms in the materials. In these experiments, the output from a diode-pumped, frequency-doubled Nd:YAG laser (Coherent DPSS-532-400) was spatially filtered, using a microscope objective lens and a pinhole, and collimated to yield a plane-wave source of light at 532 nm. The light beam was then split between two arms of an interferometer as shown in Figure 1a and the two arms were spatially overlapped at the recording medium. The power of the light in each beam was 4 mW, the beam diameters were 4 mm, and the two arms intersected at an angle of 44° (measured in air).

Multiple holograms were written in a defined volume of each sample by rotating the sample with respect to the recording arms as shown in Figure 1a and recording holograms at different angular positions of the sample. In the majority of the samples, 25 holograms were recorded by rotating the sample in 2° increments. The recording times for each of the 25 holograms were optimized so that the holograms diffracted approximately equal amounts of light and so that the contrast of the material within the defined volume was fully developed. After the 25 holograms were recorded, the sample was allowed to sit in the dark for 10 min to allow any dark reactions to occur. It was then flood-cured using filtered visible light (450 nm < λ < 650 nm, Schott filters GG495 and BG 39) from a xenon arc lamp for 20−30 min. This postexposure flood-cure consumed any remaining photoactive species and rendered the recorded holograms permanent.

To measure the refractive index contrast of the samples, the diffraction efficiency of each of the recorded holograms was measured as the sample was rotated through each of the recording positions. The diffraction efficiency is the ratio of the intensity of the light diffracted from one of the beams used for recording to the intensity of light incident on the sample. The readout process is shown in Figure 1b. The total refractive index contrast of each formulation was measured from the diffraction efficiencies of all of the recorded holograms using standard models of volume holography[14] (Table 1).

Results and Discussion

Formulation of Acrylate-Based Resins. Typical UV-cured acrylate coating resins consist primarily of

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[14] Koegelnik, H. Coupled Wave Theory for Thick Hologram Gratings. *Bell System J.* **1969**, *48*, 2909.

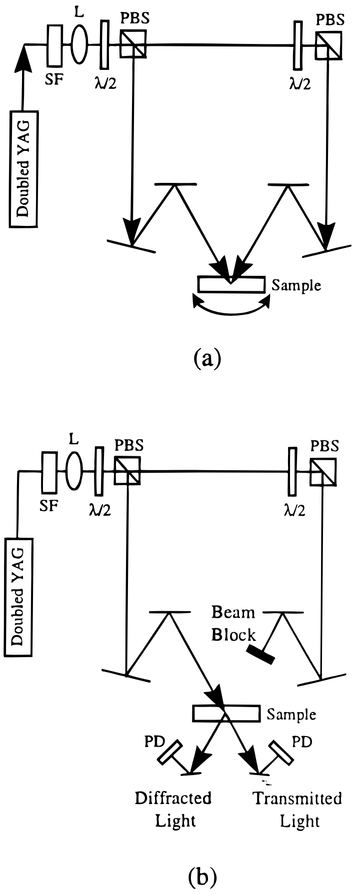

Figure 1. The experimental geometry used for angle multiplexing. A frequency-doubled diode-pumped Nd:YAG laser is spatially filtered (SF) and collimated by a lens (L) to yield a plane-wave source of light. The light is split between two arms of an interferometer by polarizing beam splitters (PBS) and half-wave plates ($\lambda/2$). The intensities of the diffracted and transmitted light are measured by silicon photodiodes (PD). The recording beams intersect at an angle of 44° external to the sample. The power of each beam is 2 mW and the spot diameter is 4 mm. After recording, the material is allowed to sit in the dark for 20 min and is then flood-cured with an xenon lamp filtered to transmit wavelengths longer than 530 nm.

di(urethane−acrylate) oligomers (e.g. structure 1) with a variety of different backbone moieties, e.g. polyesters or polyethers, in combination with one or more small monomeric species to achieve the desired physical and mechanical properties. The identity and ratio of the various components affect the handling of the resin during application, as well as the rate of cure and properties such as the cross-link density in the final polymer. Using these resins as a guideline, an acrylate-based formulation was developed for holographic recording.

Diffusion of unreacted species from the dark areas of a holographic grating into the light areas is a critical element in the formation of large and permanent holograms in photopolymers.[15] Typical grating spacings[14] for transmission holograms are 800 nm; to get diffusion times on the order of 100 s, the diffusion constant of the monomer must be on the order of 10^{-9} cm^2 s^{-1}.[15] Because the diffusion constants of monomers in glassy polymers below their T_g are typically at least 2 orders of magnitude lower than this value, it is unlikely that such systems would perform well as recording media; however, as the glass transition temperature is approached, either by heating, by reducing cross-link density, or by reformulating, diffusion becomes much more facile. The optimal material would strike a fine balance between the opposing material requirements of dimensional rigidity and fast diffusion time scales.

Table 1. Acrylate Oligomer-Based Formulations and Holographic Contrast

no.	abbrev	monomers (wt %)[a]	oligomers (wt %)	Δn^b (sensitivity, mJ/cm^2)
1	**VNVP**	IBA (25) VNA (10) NVP (5)	ER351 (60)	1.9×10^{-3} (3500)
2	**VNA**	IBA (30) VNA (10)	ER351 (60)	$1.4 \times 10^{-3\,c}$ (2000)
3	**VBZ**	IBA (30) VBZ (10)	ER351 (60)	$1.1 \times 10^{-3\,c}$ (3500)
4	**NVC**	IBA (30) NVC (10)	ER351 (60)	9.2×10^{-4} (1300)
5	**DCVBZ**	IBA (30) DCVBZ (10)	ER351 (60)	$3.6 \times 10^{-4\,d}$ (1000)
6	**IBA**	IBA (40)	ER351 (60)	3.4×10^{-4} (>3500)

[a] These formulations were prepared with 1 wt % photoinitiator and 0.17 wt % TBHP. [b] The values were extrapolated from measured values to 0.9% transverse shrinkage. [c] Single grating data points collected on the same formulations agreed within 20%. [d] Only a single grating data point was collected for these formulations.

This optimization could best be realized in these acrylate systems by tuning the cross-link density of the final polymer. One means of achieving this goal is to change the functionality of the reactive acrylates. A di(urethane−acrylate) aliphatic polyether, ER351, was used as the oligomer. IBA is commonly used as an acrylate monomer in coating resins due its relatively low volatility. Changing the ratio of monomer to oligomer in the formulation leads to a change in the cross-link density of the final polymer. Formulations were prepared with a number of different IBA/oligomer ratios ranging from 10:90 (w/w) to 90:10 (w/w), allowing the exploration of a range of cross-link densities.

Another significant effect of the IBA/oligomer ratio was on the overall viscosity of the prepolymer mixture. With only 10% oligomer added, the prepolymer mix was quite fluid and it was difficult to prepare high optical quality, thick films using the Teflon spacers. At the other extreme, with 90% oligomer, the viscosity of the solution was so high that adequate mixing could only be achieved by heating the prepolymer, which inevitably led to a shorter shelf life due to thermally initiated polymerization.

The use of difunctional monomer acrylates in combination with the monofunctional IBA was also explored as a means of tuning the cross-link density. A series of samples with varying hexanediol diacrylate (HDODA)/IBA ratios were studied, but those without HDODA showed the fastest and most efficient response to holographic exposure. This result suggests that the higher degree of cross-linking in the HDODA samples hindered monomer diffusion over the 800 nm length scales required for holographic recording. The reaction

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(15) Kagan, C. R.; Harris, T. D.; Harris, A. L.; Schilling, M. L. *J. Chem. Phys.* **1998**, *108*.

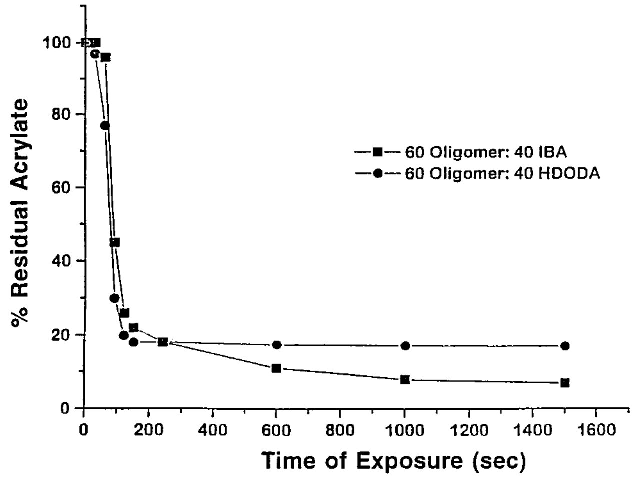

Figure 2. NIR kinetics of percent residual acrylate vs exposure time for 40:60 IBA or HDODA/oligomer mixtures.

kinetics as determined by NIR support this conclusion. Cure curves for two acrylate formulations with either 40 wt % of IBA or HDODA, respectively, in ER351 are shown in Figure 2. The long tail observed for both photopolymers is indicative of diffusion-controlled reactions in which the migration of radicals is the limiting factor. For the IBA resin, diffusion is adequate to carry the reaction to completion. However, in the HDODA formulation, the polymer does not reach full cure, even after 3000 mJ/cm^2 exposure. Apparently, the higher cross-link density of the polymer decreases the diffusion rate and effectively stops the reaction.

Visible-Light Absorbing Photoinitiators. A key element of any photopolymer system is the photoinitiator used. It is advantageous to have high concentrations (~5%) of initiator to increase the rate of the free radical reactions and ensure complete cure. However, in thick samples, absorption of light through the entire depth of the polymer is also necessary for uniform cure. Lower photoinitiator concentrations, while slowing the overall polymerization kinetics, result in better controlled and efficient recording properties. Low photoinitiator levels also have the added advantage of suppressing extraneous holographic signals from the diffusion of photoinitiator alone. Any small molecule present in the photopolymer mixture, such as the photoinitiator or its byproducts, will respond to holographic recording and form its own concentration gradients independent of the photopolymerization process. The formation of dual holographic gratings leads to unusual and sometimes impaired recording properties. For samples up to 500 μm thickness, 1 wt % of photoinitiator was used; for thicker samples 0.5 wt % of photoinitiator provided uniform cure through the sample thickness.

The recent commercial offering of compact diode pumped Nd:YAG lasers operating at 532 nm provided strong incentive for the use of visible-light photoinitiators. There are numerous examples of visible-light photoinitiators used in free-radical polymerizations.[3a] Initial experiments in our acrylate materials used a three-component initiator marketed by Spectra Group Limited.[13] An amine (coinitiator) is oxidized by a photoexcited fluorone dye (structure 2) to a radical cation. The loss of a proton from the radical cation forms a neutral radical which initiates polymerization. The inclusion of an onium salt improves the bleaching efficiency and contributes to a more complete cure. The use of this photoinitiator system with our acrylate formulation gave fast initial reaction rates, but full cure was not readily achieved. This result is not surprising because it has been reported[13] that, at the low concentrations required for thick films, this photoinitiator system does not completely cure acrylates. It is possible that the recommended ratio of the three components was not optimal for this formulation or that one or more components underwent side reactions that reduced the overall efficiency. Alternatively, diffusion in the somewhat glassy matrix could be hindered enough that the probability of three components finding each other before quenching was low at the high level of cure. An additional multicomponent photoinitiator, the HABI dye system,[5] also showed low cure efficiency, suggesting that the problems in multicomponent photoinitiators may be general.

The single-component photoinitiator recently developed by Ciba-Geigy (CGI-784, structure 3) was found to be more effective. Complete cure in typical acrylate formulations was achieved in 5 min at 10 mW/cm^2 ($\lambda >$ 530 nm). For thick samples, the relatively weak extinction coefficient at 532 nm ($\epsilon = 60$ M^{-1} cm^{-1}) is an advantage in comparison with dye-based systems where ϵ may be $>10^4$. At concentrations of 1 wt %, the photoinitiator absorbance is less than 0.2 in a 1 mm sample and uniform curing can be achieved throughout the polymer volume.

An undesirable feature of early experiments with the Ciba-Geigy photoinitiator was the formation of a deep purple color in the sample upon extended irradiation. The color was believed to arise from the formation of Ti^{3+}, possibly formed by reaction of the photoinitiator with the inhibitors found in the acrylate components. To confirm this interaction, the standard sample was compared to samples which either had the inhibitor removed from the monomer or were saturated with O$_2$ before precure. In both cases, the purple color was less intense than in the standard sample. Also, the color was eliminated by exposing the samples to oxygen after cure. These results suggest that either the addition of an oxidizing agent or the removal of all inhibitors would eliminate the formation of the purple color. Because the removal of inhibitors from the acrylate components would shorten the shelf life of the formulations, the use of oxidizing agents was explored. It was determined that addition of *tert*-butylhydroperoxide (TBHP, 0.17 wt %) to the formulation was sufficient to eliminate the purple color from the irradiated samples. Although the initiation step of the photopolymerization was somewhat slower in the presence of TBHP, no adverse effects on recording performance were observed.

On the basis of these preliminary evaluations of cross-link density and photoinitiator, a resin of IBA/ER351 (40:60) with 1 wt % CG-784 photoinitiator and 0.17 wt % TBHP was established as the benchmark formulation (**IBA**) with a diffraction efficiency of 23% (Figure 3A). All other formulations were compared to this standard (Table 1).

Monomer Tuning. One important parameter of a holographic medium is its ultimate refractive index contrast, Δn, or dynamic range. Most of the Δn in our

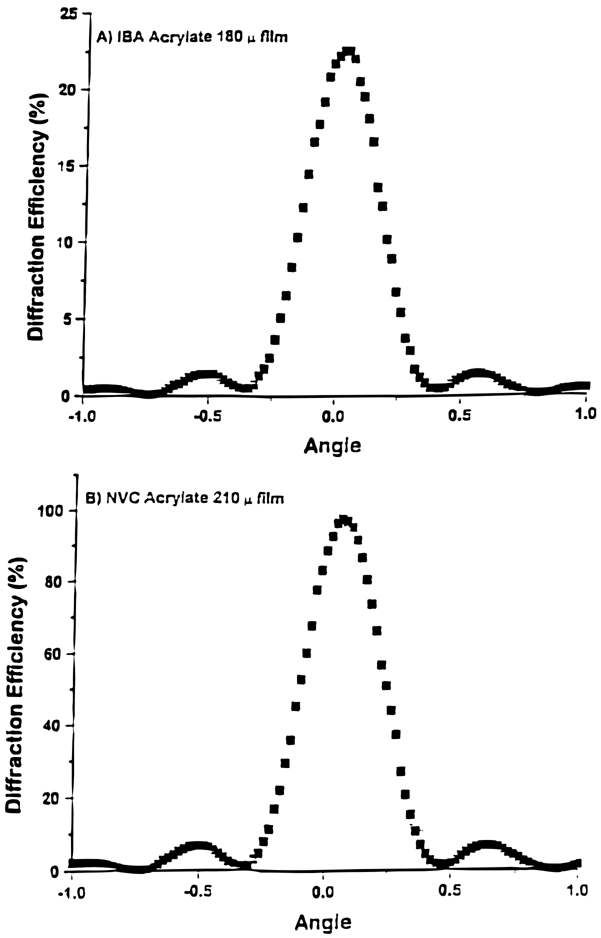

Figure 3. (a) The angle response of a plane-wave hologram in a 180 μm 85% prepolymerized IBA sample. The peak diffraction efficiency of 23% corresponds to a grating contrast (Δn) of 0.00052 under these writing conditions ($q_{\text{ext}} = 15.6°$, $d_{\text{spac}} = 986$ nm). (b) The angle response of a plane-wave hologram in a 210 μm thick, 82% prepolymerized NVC sample. The large diffraction efficiency seen in this material ($\Delta n = 0.0012$) results from the enhanced grating contrast between the aromatic/aliphatic matrix and the mobile IBA.

samples arises from a compositional variation induced by polymerization and subsequent diffusion of additional monomer into the polymerized (irradiated) areas of the sample. Because the refractive indices of the polymer matrix and the monomer are similar in the benchmark formulation, the monomer concentration variation results in a low Δn. A better solution would be to enhance the contrast between the irradiated and unirradiated regions by changing the monomer components to increase the Δn per unit of diffusing monomer. Aromatic components typically have a higher n than the IBA monomer and the Echo oligomer and have been used in other systems to increase Δn.[16] Phenyl acrylate ($n = 1.5170$) was included in several formulations but was not miscible with the polymerized resin and formed a separate phase during the precure step. β-Naphthylacrylate is a solid and had low solubility in the IBA/ER351 resin. In general, the simple aromatic acrylates have poor compatibility with the aliphatic acrylate components. Aromatic ether acrylates, such as phenoxyethyl acrylate (PEA) ($n = 1.5143$), give a compromise between high n and miscibility. Assuming that hologram formation occurs primarily due to diffusion of the monomeric species, inclusion of PEA (10 wt %) in the formulation would be expected to increase Δn. In fact, diffraction efficiencies only comparable to the benchmark formulation ($\Delta n \sim 3 \times 10^{-4}$) were observed for the PEA samples, suggesting that the matrix formed during the precure incorporated a substantial amount of the high n component, making the observed Δn fairly small.

To avoid reduction of final refractive index differences due to the coreaction of high and low index monomers during the precure step, the components must also have very different reactivities. *N*-Vinylcarbazole (NVC) has been included in many previous formulations used for holographic studies.[16] It has a very high refractive index (1.68) and has been used as a "low reactivity monomer" in these formulations. In the current study, NVC was formulated with IBA and ER351 (NVC/IBA/ER351, 1/3/6, **NVC**) and the holographic behavior compared to that of **IBA**. Samples of **NVC**, precured to 80%, gave a Δn of approximately 9.2×10^{-4} (Figure 3b). Although the diffraction efficiency was improved, the degree of improvement was less than expected on the basis of the high refractive index and the assumed low reactivity of NVC during the precure step, suggesting that NVC is being incorporated into the matrix to some degree during the precure, rather than being involved in the grating writing. NIR showed that a portion of the NVC was reacting during the precure step, but due to overlapping peaks, the exact concentrations of unreacted monomers present at any given time could not be determined.

Using solid-state ^{13}C NMR, the relative amounts of reacted and unreacted species in **NVC** samples could be determined by examining unique resonances for the various components. A comparison of the spectra observed before and after a 40 s precure (Figure 4) shows that all of the NVC was incorporated into the matrix during the early stages of the precure. There is no NVC olefinic methylene resonance at 103 ppm after precure. In addition, the portion of the acrylates remaining is represented by the carbonyl signal at 166 ppm. The ratio of this peak area to that of the carbonyl from the polymerized acrylates (175 ppm) indicates that 90% of the total initial acrylate groups have reacted during precure. In this formulation, the high n component, NVC, is diluted by reaction with lower index acrylates during precure to give a copolymer matrix with an averaged n. The hologram is then written by polymerization of the remaining low index acrylates and results from concentration of these low n species in the irradiated areas. However, the polymerization reaction increases n by 2−4%, due to densification.[5a] Because the effect on n of acrylate accumulation and increased polymerization in a particular region of the matrix are opposite in sign, the total Δn is less than expected from diffusion alone. To maximize the refractive index contrast, the ideal formulation would have low n components reacting first, leaving high n components to write the holograms. In this case, monomer accumulation and polymerization contribute constructively to Δn.

A second potentially slow-reacting, high-index monomer is vinyl benzoate (VBZ). Figure 5 shows a theoreti-

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(16) Tomlinson, W. J.; Chandross, E. A.; Weber, H. P.; Aumiller, G. D. *Appl. Opt.* **1976**, *15*, 534.

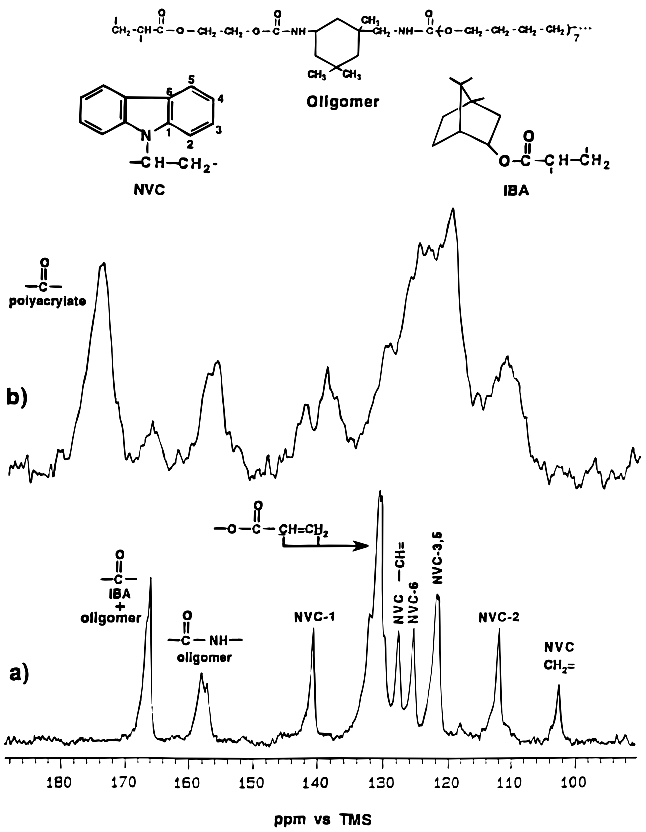

Figure 4. ^{13}C NMR spectra of the NVC formulation (a) before and (b) after a 40 s precure.

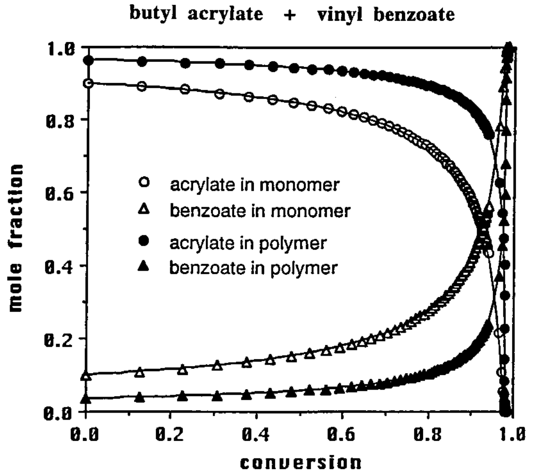

Figure 5. Reactivity profile of VBZ with butyl acrylate. The reactivity profile was calculated using the Alfrey–Price equation[17] with parameters reported by Greenley.[18] The y-axis represents the mole fraction of a component either in the remaining monomer or in the polymer being produced at the instant when a particular degree of conversion, represented by the x-axis, is reached.

cal reactivity profile for the copolymerization of VBZ with butyl acrylate, calculated using the Alfrey–Price equation[17] with parameters obtained by Greenley.[18] The y-axis represents the mole fraction of any monomer component either in the mixture of unreacted monomers or in monomers being converted to polymer at the instant when a particular degree of conversion (x-axis) is reached. The VBZ concentration, which starts at $\sim$0.1 mole fraction on the plot remains relatively constant up to 80% conversion, where writing typically begins, suggesting that there would be a slow incorporation of VBZ into the matrix up to this point. The writing species would therefore be enriched in VBZ, the high index component. The **VBZ** formulation (VBZ/IBA/ER351, 1/3/6) does in fact show improvement in Δn over **NVC** (Table 1) even though the n of VBZ (1.53) is considerably lower than that of NVC (1.68).

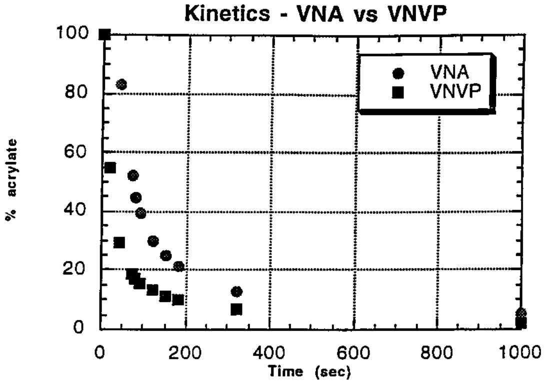

Figure 6. Comparison of the reaction kinetics between the **VNA** and **VNVP** formulations show that the addition of NVP affects the initial reaction rates, resulting in more index contrast during holographic recording.

Reactivity considerations, shown graphically in Figure 5, are useful as guidelines for choosing components but, in fact, do not reflect the exact reactivities in the formulations containing more than two components. In addition, the x-axis shows degree of conversion but does not include any time factor. For example, **VBZ** has a better index contrast, but at the same time a lower sensitivity than **NVC**; for **VBZ** the sensitivity is 3500 mJ/cm^2 as compared to 1300 mJ/cm^2 for **NVC** (Table 1). Because the mobile species remaining after precure of **VBZ** are mostly vinyl ester monomers, the polymerization during writing is primarily a homopolymerization reaction and is slower for this formulation than for **NVC**. This characteristic is not portrayed by the reactivity profile. In the optimization process, sensitivity as well as Δn must be considered.

Two additional high index vinyl esters were synthesized and included in formulations as substitutes for VBZ. Assuming a similar reactivity profile, the higher n should translate directly into higher contrast during recording. The **VNA** formulation does show the expected increase in Δn over **VBZ** at essentially the same sensitivity level (Table 1). Substitution of vinyl-3,5-dichlorobenzoate, DCVBZ, however, gave a lower contrast (Table 1). Apparently, the chloro substituents alter the reactivity enough to cancel the index increase relative to **VBZ**.

The Δn values that are obtained for **VBZ** and **VNA** are higher than that of **NVC**, but the partial incorporation of the high-index components during precure has reduced the contrast expected on the basis of the refractive indices alone. By taking further advantage of differential reactivities, additional improvement in Δn could be achieved. It is known that N-vinylpyrrolidinone (NVP) is incorporated very rapidly into an acrylate matrix. By inclusion of both NVP and VNA in the same formulation (**VNVP**), an additional 30%

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(17) Alfrey, T.; Price, C. C. *J. Polym. Sci.* **1947**, *2*, 101.

(18) Greenley, R. Z. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989; pp II 267–II 274.

increase in Δn was observed (Table 1). Figure 6 compares the kinetics of the **VNA** and **VNVP** formulations, showing the faster reaction during the early stages of precure for the **VNVP**. The NVP reacts preferentially with the acrylates over VNA during precure, leaving an increased concentration of the high index VNA to be reacted during grating writing and accounting for the increased contrast. The sensitivity of the **VNVP** formulation is comparable to that of **VNA**, because the principal writing reaction is the homopolymerization of VNA. The contrast obtained for the **VNVP** formulation is the highest observed for the acrylate-based systems that we studied.

Conclusions

We have demonstrated that acrylate oligomer-based photopolymers have potential for use as holographic recording media. On the basis of the evaluation and optimization of material properties, several formulations have been developed, with successive improvements realized through consideration of refractive indices and relative reactivities. Work is currently in progress to prepare new formulations with further improved performance (Δn) and lower shrinkage on writing. In addition, a protocol has been established for evaluating new photopolymer formulations for holography which will be essential in future materials development of optical recording media.

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