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# High dynamic range two-stage photopolymer materials through enhanced solubility high-refractive index writing monomers

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## ABSTRACT

Holographic photopolymers capable of high refractive index modulations ( $\Delta n$ ) on the order of  $10^{-2}$  are integral for the fabrication of functional holographic optical elements (HOEs) for use in a range of optical applications. A novel high refractive index liquid writing monomer suitable for two-stage photopolymer systems was designed and synthesized. This monomer exhibits facile synthetic procedure, low viscosity, high refractive index as well as excellent solubility in a low refractive index urethane matrix. The solubility limit, refractive index change and reaction kinetics/conversion were studied against a commercial reference high refractive index monomer, 2,4,6-tribromophenyl acrylate (TBPA). Superior performance in solubility to TBPA is shown with similar reaction kinetics and final conversion as confirmed by real-time Fourier transform infrared spectroscopy (FTIR) and real-time monitoring of diffraction grating growth. We demonstrate the ability to load substantial amounts of these writing monomers enabling a straightforward path to higher achievable  $\Delta n$  values (peak-to-mean  $\Delta n \sim 0.03$ ) without sacrificing optical properties (transparency, color or scatter) as validated through recording  $\sim 100\%$  efficiency volume transmission holograms in sub-15  $\mu\text{m}$  thick films.

**Keywords:** holography, photopolymer, writing monomer, refractive index modulation,  $\Delta n$ , HOEs, GRIN

## 1. INTRODUCTION

The maximum achievable refractive index modulation ( $\Delta n$ ) of holographic photopolymer recording materials is a key performance metric for use in interesting applications such as holographic optical elements (HOEs) or gradient refractive index (GRIN) lenses<sup>1,23</sup>. For HOEs, a greater  $\Delta n$  enables higher diffraction efficiency holograms and/or the ability to record multiple overlapping holograms (i.e. multiplexing) for a given media thickness. In the case of manufacturing GRIN lenses, greater focusing power can be achieved with a higher  $\Delta n$  material. However, in order to fully realize high performance HOEs and GRIN lenses with photopolymers,  $\Delta n$  on the order of  $10^{-2}$  are critical.

### 1.1 Two-stage photopolymer system

The two-stage photopolymer system is an ideal platform for designing holographic recording materials capable of generating a three-dimensional refractive index contrast ( $\Delta n$ ) between the bulk material and the recorded feature(s)<sup>4,5</sup>. Briefly, two-stage photopolymer comprise orthogonal chemistries that are typically independently reactive upon different stimuli (i.e. heat and light), presenting spatiotemporal control over material properties at different timescales<sup>6-9</sup>. In the case of holographic photopolymers, a patterned irradiation consumes the reactive writing monomer in the exposed regions setting up a concentration gradient for the diffusion of additional unreacted writing monomers in the unexposed regions to migrate to the exposed regions<sup>3,4,10-13</sup>. The final outcome is a recorded refractive index structure that ideally corresponds to the exposure pattern embedded within a thin, transparent polymeric film. In this work, we choose a prime

two-stage system that is used commercially for holography comprising a thermally cured stage 1 polyurethane matrix and stage 2 acrylate photopolymerization<sup>1,4,10,14</sup>.

## 1.2 Lorentz-Lorenz

The refractive index mixture rules derived from the Lorentz-Lorenz equation<sup>15</sup> can be rearranged to the following form:

$\Delta n = n_{12} - n_1 = \phi_2(n_2 - n_1)$  where  $n_{12}$  is the refractive index of the overall two-stage photopolymer,  $n_2$  is the refractive index of the stage 2 writing polymer,  $n_1$  is the refractive index of the stage 1 matrix and  $\phi_2$  is the volume fraction of the stage 2 writing polymer. Therefore, for a given urethane matrix, it is advantageous to design higher  $\Delta n$  two-stage holographic photopolymers by increasing the refractive index and/or increasing the volume fraction of the stage 2 writing polymer.

## 1.3 Solubility of writing chemistry

The solubility of the initial writing monomer as well as of the final polymer in the stage 1 matrix are both critical considerations for the overall performance of a two-stage holographic photopolymer. It stands to reason that poor solubility of the writing monomer precludes use in recording however it is also possible that *initial* solubility is excellent but complications occur *after* recording<sup>16</sup>. This can be manifested in the form of macroscale phase separation whereby the resulting writing polymer is insoluble with its own monomer and/or the stage 1 matrix. Inhomogeneities during or after exposure limit the utility of the photopolymer as an optical material let alone as an optical element. To this end, we synthesize a high refractive index ( $n > 1.6$ ) writing monomer capable of increased solubility in a urethane matrix.

## 1.4 Refractive index groups

A typical drawback in designing molecules with high refractive index substituents such as heavy halogens or aromatic groups is the solubility<sup>17-19</sup>. A solution to overcome solubility limitation is to incorporate 'linker' groups that introduce flexibility to the overall molecule<sup>14</sup>. A standard method is to extend the high refractive index moiety with alkyl chains to suppress packing between polymer chains however this negatively contributes to the overall refractive index. Therefore, to achieve improved solubility without sacrificing refractive index our synthetic strategy (as shown in Figure 1) was to employ the thiol-epoxy ring opening reaction of epichlorohydrin with a thiol to introduce flexible thioether linkages to link the high refractive index unit (represented by the ball) with the polymerizable group<sup>17,19</sup>.

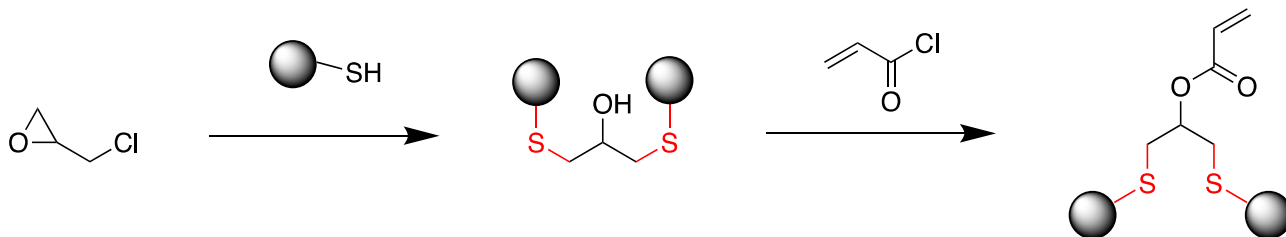


Figure 1. Synthetic scheme for high refractive index writing monomers exhibiting good solubility using a thiol-epoxy reaction of epichlorohydrin. The high refractive index moiety is represented by the shaded ball. The flexible thioether linkage units (in red) aid in the solubility properties of the monomer/polymer as well as contribute favorably in refractive index.

## 2. EXPERIMENTAL

### 2.1 Synthesis of writing monomer

A facile two-step synthetic scheme is employed involving a relatively high refractive index monothiol in excess ( $> 2$  equivalence) to epichlorohydrin under basic conditions to yield the symmetric intermediate alcohol. Subsequently, the acylation reaction of the isolated and purified alcohol produces the desired colorless, liquid acrylate. Detailed information on the synthetic procedure can be found in the literature<sup>20</sup>.



### 2.3 Refractive index

The refractive index of liquid chemicals was measured at the sodium-d line using an Abbe refractometer whilst the refractive index of polymeric films was measured with a Metricon 2010/M prism coupler at 633 nm. All measurements were taken at room temperature.

### 2.4 Holographic testing

A two-beam interference setup (shown in **Figure 2B**) consisting of two mutually coherent s-polarized 405 nm beams (Ondax, 40 mW) was used to record unslanted, volume transmission holograms with a pitch spacing of approximately 1  $\mu\text{m}$ . Both recording beams were power matched with a  $1/e^2$  intensity diameter of 4.3 mm to give a total recording intensity of 16  $\text{mW}/\text{cm}^2$ . A low power 633 nm He-Ne laser (Thorlabs, < 1 mW) was aligned at approximately the Bragg angle to monitor the grating buildup and angular scan. Recording exposure times were controlled by a computer controlled electronic shutter (Uniblitz) and optical power measurements were recorded throughout the experiment using custom LabVIEW software. The diffraction efficiency ( $\eta$ ) of a hologram is calculated by taking the ratio of the 1<sup>st</sup> order diffracted power ( $P_D$ ) to the sum of the 0<sup>th</sup> order transmitted power and the 1<sup>st</sup> order diffracted power ( $P_T + P_D$ ).

## 3. WRITING MONOMER EVALUATION

### 3.1 Urethane matrix solubility

Matrix solubility of the writing monomer was evaluated by measuring the equilibrium weight increase of a pristine cylindrical urethane matrix film (i.e. only stage 1) submerged in a 20 wt% solution of writing monomer in heavy mineral oil. The solubility of BPTPA in the urethane matrix was assessed against a reference high refractive index acrylate, TBPA. Based on the initial and final weights measured, the theoretical maximum loading of writing monomer was calculated to be 45 and 63 wt% for TBPA and BPTPA respectively.

### 3.2 Bulk refractive index change

The refractive index of bulk two-stage photopolymer films was measured at their flood-cured stage 2 state at increasing increments of writing monomer as shown in **Figure 3A**. With the synthesized writing monomer, it is possible to achieve higher writing monomer loadings thus enabling a significantly larger dynamic range of refractive index contrast for patterned exposures. The marginally higher slope of the curve also indicates that BPTPA is more effective than TBPA in the refractive index increase per amount of writing monomer (i.e.  $\Delta n/[M]$ ) incorporated in the two-stage formulation.

### 3.3 Photopolymerization reactivity

The photopolymerization reactivity of two-stage photopolymer samples were assessed at 30 wt% writing monomer loading using real-time FTIR spectroscopy with a triggered incoherent 405 nm LED exposure as shown in **Figure 3B**. Quantitative conversions with effectively identical overlapping kinetic profiles were achieved with a short exposure of 2 seconds at a moderate light intensity of 16  $\text{mW}/\text{cm}^2$  for both two-stage formulations. Having said that, the extended capability of increasing writing monomer loading in two-stage formulations with BPTPA offers the additional design freedom of using less photoinitiator (to reduce absorption) whilst maintaining good photosensitivity.

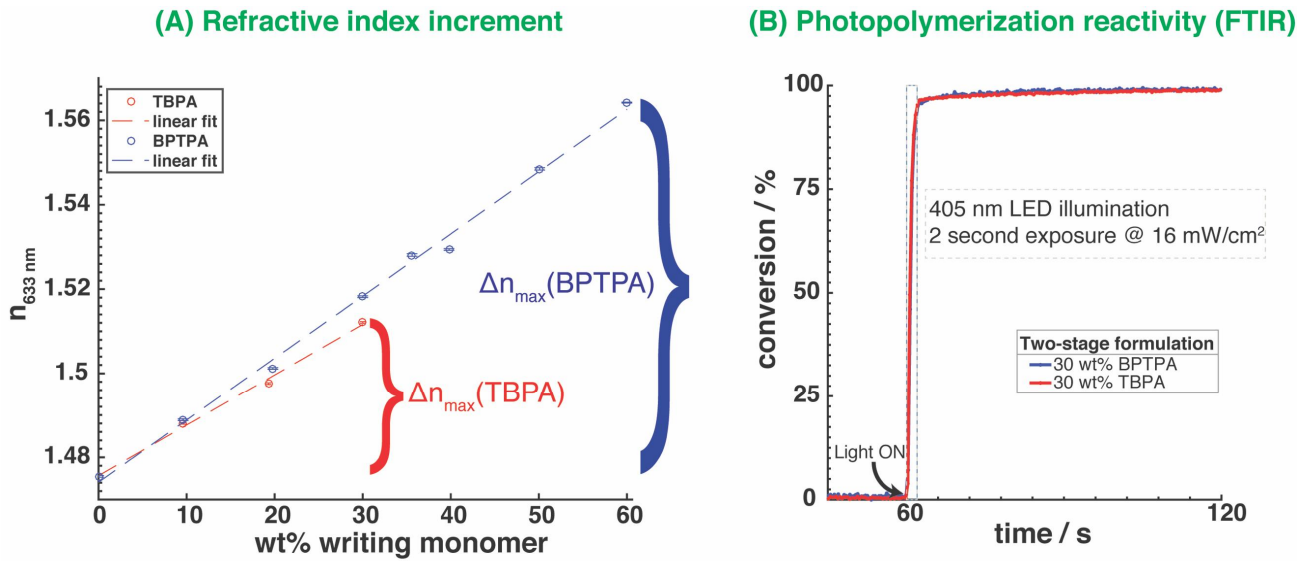


Figure 3. (A) Prism coupler measurements of two-stage photopolymer film formulations containing increasing amounts of writing monomer (TBPA – red; BPTPA – blue). Measurements were taken at room temperature using a 633 nm HeNe laser. The curled brackets indicate the maximum  $\Delta n$  range achievable for two-stage formulations containing the respective writing monomers at their highest loading content. (B) Real-time conversion of 30 wt% acrylate writing monomers (TBPA – red; BPTPA – blue) in a two-stage formulation upon a 2 second irradiation (at the 60 s mark) of an incoherent 405 nm LED source at 16 mW/cm<sup>2</sup>.

## 4. HOLOGRAPHIC RESULTS

### 4.1 Volume transmission holography

Single, strong transmission holograms were recorded into relatively thin photopolymer materials (<15  $\mu\text{m}$ ) to avoid over-modulation. The thickness and peak-to-mean  $\Delta n$  were obtained by fitting to Kogelnik Coupled Wave Theory for thick, transmission volume gratings<sup>21</sup>. Representative grating development curves (left) and their corresponding angular scans (right) are shown for 40, 50 and 60 wt% BPTPA in **Figure 4**. As evidenced by the angle scans, well-defined characteristic sinc-squared profiles were obtained allowing for reliable fits for determining  $\Delta n$ . Rapid refractive index formation is evident in each grating development curve from only a 1 second exposure (represented by the miniscule rectangle at the 10s mark) at a total  $1/e^2$  recording intensity of 16 mW/cm<sup>2</sup>. In the case of the 60 wt% BPTPA sample, diffraction efficiencies approaching 100% are readily achieved with a rapid step function-like response corresponding to a  $\Delta n$  of 0.0296.

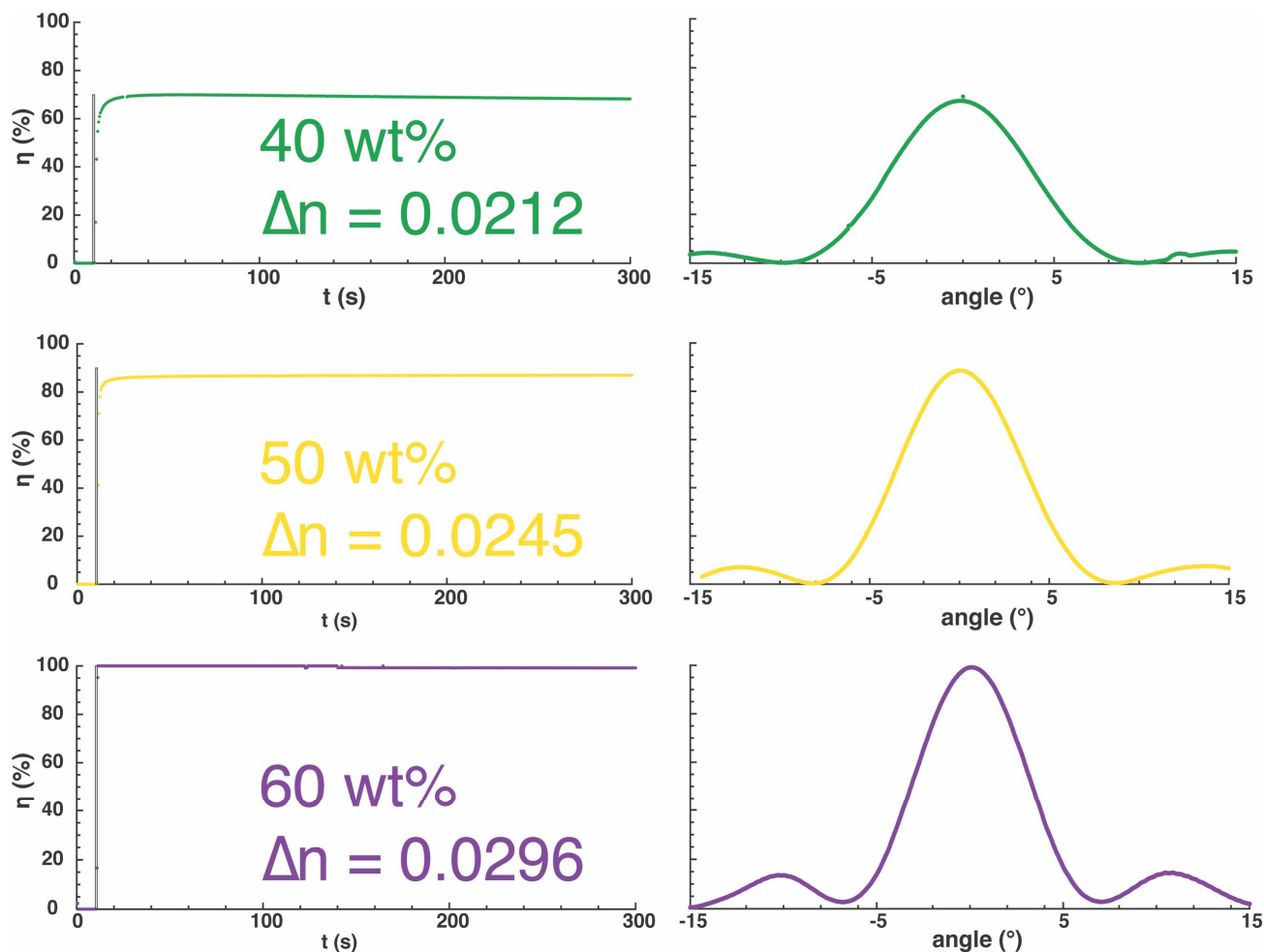


Figure 4. Representative grating development curves (left) and corresponding angular scans (right) for 40, 50 and 60 wt% of the synthesized writing monomer, BPTPA. The sample is exposed for 1 second at a total  $I/e^2$  recording intensity of approximately  $16 \text{ mW/cm}^2$  at the 10s mark (represented by the narrow rectangle). In the case of the 60 wt% BPTPA loading (bottom) diffraction efficiencies approaching 100% are readily achieved.

## 5. CONCLUSION

We demonstrate two-stage holographic photopolymers with  $\Delta n \sim 0.03$  for volume transmission holograms with a pitch spacing of  $1 \mu\text{m}$ . This is achieved via the facile synthesis and implementation of a novel liquid acrylate writing monomer, BPTPA, that is both high in refractive index ( $n_D = 1.60$ ) and exhibits excellent solubility in the stage 1 matrix. BPTPA was employed in two-stage formulations and compared against a reference, widely used high refractive index monomer, TBPA. In terms of refractive index increment and the ability to load up to 60 wt% of writing monomer, BPTPA was visibly superior to TBPA. This writing monomer can be used in a range of two-stage photopolymer materials for the fabrication of a variety of embedded refractive index structures such as HOEs and GRIN lenses.

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