Monomer Functionality Effects in the Formation of Thiol−Ene Holographic Polymer Dispersed Liquid Crystals

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Received August 10, 2006; Revised Manuscript Received December 1, 2006

ABSTRACT: Holographic polymer dispersed liquid crystals (HPDLCs) are a polymer/liquid crystal (LC) composite with wavelength selective diffraction that can be switched in microseconds with electric field. As such, HPDLCs are widely applicable in optical and photonic devices. Recently, replacing acrylate polymer with thiol−ene polymer as host for HPDLCs has improved the stability and electrooptic performance of these materials. This work examines the electrooptic performance and morphology of thiol−ene-based HPDLC reflection gratings. To further understand the relationships between the formation and performance of thiol−ene HPDLCs, electrooptic performance was characterized as a function of polymerization rate, gel point conversion, and the presence of excess monomer (stoichiometry). To this end, HPDLC formulations were examined to isolate the contribution of ene monomer functionality, thiol monomer functionality, and thiol−ene stoichiometry. In all formulations, the performance of HPDLC reflection gratings is correlated to the generation of morphology typified by well-defined polymer/LC lamellae and small LC droplet size. Increasing the rate of polymerization through increasing laser intensity, increasing ene monomer functionality, or thiol−ene stoichiometry improves the diffraction efficiency (DE) of HPDLCs by reducing LC droplet size. Gel point conversion is also critical to producing well-performing HPDLC reflection gratings. HPDLCs based on thiol−ene polymer with gel points from 40 to 60% monomer conversion show optimal optical behavior. This increase in performance is related to the impact of gel point on morphology, as low gel point conversion leads to the formation of small droplets and poorly defined grating structures while high conversion gel points lead to the formation of large LC droplets. Therefore, optimal HPDLC materials are formed with moderate conversion gel points that allow both well-defined grating structure and small droplet formation.

Introduction

The development of dynamic diffraction gratings through the formation of holographic polymer dispersed liquid crystals (HPDLCs) has shown great promise in a variety of applications such as displays,[1] photonic components,[2] lasing,[3] electrooptic filters,[4] and pressure sensors.[5] Unfortunately, widespread use of acrylate-based HPDLC materials has been prevented by performance degradation[6] and suboptimal performance.[7] Recently, thiol−ene-based HPDLCs have been demonstrated that overcome many of these limitations as they exhibit stable performance for over 3 years,[8] improved switching voltage (SV), improved baseline transmission, and increased overall diffraction efficiency (DE).[9]

HPDLCs form through holographic illumination of a photosensitive mixture containing photoinitiator, monomer, and liquid crystal (LC). The periodic light intensity gradient resulting from holographic illumination induces mass transport of monomer into the light regions and LC into the dark regions. After vitrification, the morphology of HPDLCs consists of alternating lamellae of predominately polymer and predominately LC regions. The well-known dielectric nature of nematic LCs enables the apparent refractive index of the LC to be switched with application of an electric field. Typically, the ordinary refractive index of the LC is matched to that of the polymer, giving rise to HPDLCs as switchable diffraction gratings. The formation and performance of HPDLCs have been reviewed elsewhere in much greater detail.[10−13]

Numerous approaches have been taken to enhance HPDLC performance parameters such as DE and SV. Some factors known to influence the electrooptic performance of HPDLCs include LC droplet size, amount of LC phase separation, and refractive index mismatch of the polymer and LC.[10−12] Notably, improved performance in acrylate-based HPDLCs has been correlated to monomer functionality[14,15] and addition of *N*-vinylpyrrolidinone (NVP)[16,17] and octanoic acid.[18,19] The contribution of these additives to polymerization kinetics and LC phase separation in HPDLC formulations has been recently reported.[20,21] In acrylate systems, both NVP and octanoic acid serve to simultaneously increase the polymerization rate while delaying the onset of LC phase separation, subsequently resulting in reduced LC droplet size which ultimately corresponds to enhanced DE.

Using highly cross-linked acrylate polymer as host for HPDLCs, however, has a number of disadvantages. In particular, shrinkage in cross-linked acrylate polymerization is notoriously inhomogeneous, imparting blue shift, chirp, and nonsymmetric optical behavior to HPDLC diffraction gratings.[7,9] Much of the performance enhancement observed in thiol−ene-based HPDLCs is the result of distinct differences between acrylate and

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10.1021/ma061829m CCC: $37.00

thiol−ene polymerization mechanisms, particularly gel point. Acrylates polymerize through a free radical chain mechanism, typified by a rapid increase in molecular weight, low double bond conversion, significant microgel formation, and polymer macrogelation at conversions as low as 2%.[22] On the other hand, the molecular weight of thiol−ene polymer increases slowly throughout the polymerization until high conversion is reached, unlike acrylates. Based on this step-growth mechanism, the gel point of thiol−ene polymers in stoichiometric mixtures can be as high as 71% in cross-linked systems. Using thiol−ene polymer overcomes the deleterious influence of shrinkage and performance degradation evident in acrylate-based HPDLCs. The thiol−ene polymerization mechanism is detailed in the complementary examination of thiol−ene PDLCs.[23] Thiol−ene polymerization has been well-reviewed by Jacobine[24] and Hoyle.[25]

The original report of thiol−ene-based HPDLCs utilized the commercial thiol−ene mixture NOA65 (Norland Products).[9] The composition of NOA65 is reportedly a mixture of trimethylolpropane tris(3-mercaptopropionate) and a tetrafunctional urethane allyl ether.[26] NOA65 has a refractive index of 1.524,[27] similar to the ordinary refractive index of common cyanobiphenyl liquid crystals. Though most reports of thiol−ene polymer/LC composites have utilized NOA65, a number of commercially available thiol and ene monomers are readily available that can be used to form polymer matrices with unique composition over a wide range of gel points.

Recent examination of polymerization kinetics and LC phase separation in thiol−ene-based PDLCs can provide a foundation for further understanding the formation of HPDLCs.[23] Specifically, the role that polymer gel point and polymerization kinetics play on determining PDLC morphology was explicitly examined as a function of light intensity, monomer functionality (both thiol and ene), and ene monomer electron density. In general, reducing the gel point conversion of thiol−ene polymer decreases LC droplet size, which may be beneficial to HPDLC optical performance. Increasing polymerization kinetics, through light intensity, ene monomer functionality, or ene monomer electron density serves to further reduce LC droplet size.

The application of HPDLCs for many technologies still requires significant improvement in baseline transmission and overall diffraction efficiency. This report investigates the correlation between polymerization kinetics, LC phase separation, and polymer gel point in examining thiol−ene HPDLC formulations to enable more complete understanding of the formation of thiol−ene HPDLCs. In particular, this work examines the influence of laser intensity (polymerization kinetics), ene monomer functionality, thiol monomer functionality, and thiol−ene stoichiometry on the DE and SV of thiol−ene HPDLCs. The influence of monomer functionality on HPDLC performance is complemented with examination of polymer/LC morphology with transmission electron microscopy (TEM). Such understanding may allow further optimization of the performance of thiol−ene-based HPDLC devices.

Experimental Section

In these studies, HPDLC formulations contain 2 wt % of the ultraviolet (UV) absorbing photoinitiator mixture Darocur 4265 (DC-4265, Ciba) and 27 wt % of the LC BL037 (EMD Chemical). BL037 is a eutectic mixture of cyano-*n*-phenyl compounds with a nematic−isotropic transition at 109 °C, positive dielectric anisotropy, an ordinary refractive index of 1.5280, and an optical anisotropy (Δn) of 0.2820.[28] Unless otherwise noted, formulations incorporate equal moles of thiol and "ene" groups. The effect of ene monomer functionality was examined by polymerizing a series of allyl ether monomers (ene) of functionality two, three, and four with the thiol monomer trimethylolpropane tris(3-mercaptopropionate) (trithiol, Aldrich). Ene monomers used in this work are trimethylolpropane diallyl ether (diene, Aldrich), pentaerythritol allyl ether (triene, Aldrich), and glyoxal bis(diallyl acetal) (tetraene, Aldrich). Similarly, increasing thiol monomer functionality was studied by polymerizing a series of mercaptopropionate thiol monomers of functionality two, three, and four with tetraene. The trithiol system was compared with polymerization of formulations containing glycol dimercaptopropionate (dithiol, Evans Chemetics) and pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol, Aldrich). Chemical structures of the thiol and ene monomers used in this examination are shown in Figure 1.

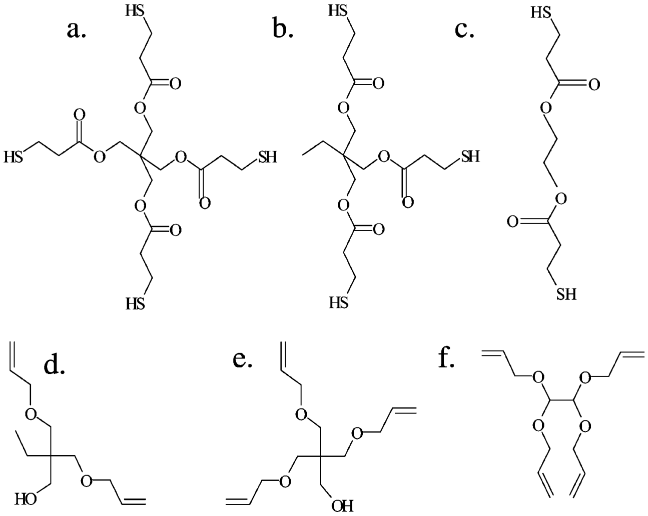

Figure 1. Chemical structures of monomers used in this study: (a) pentaerythritol tetrakis(3-mercaptopropionate) (tetrathiol), (b) trimethylolpropane tris(3-mercaptopropionate) (trithiol), (c) glycol dimercaptopropionate (dithiol), (d) trimethylolpropane diallyl ether (diene), (e) pentaerythritol allyl ether (triene), and (f) glyoxal bis(diallyl acetal) (tetraene).

HPDLCs were written in a one beam setup using the 363.8 nm line of a argon ion laser (Coherent, model 308C) and an isosceles 90° glass prism, as previously reported.[9] HPDLCs reflection gratings were fabricated to produce diffraction from 540 to 555 nm based on writing geometry. Samples were sandwiched between uncoated glass slides (diffraction efficiency studies) or indium−tin oxide (ITO)-coated glass slides (switching voltage studies) with 10 μm glass spacers and holographically exposed for 1 min. The electrooptical behavior of HPDLC reflection gratings was characterized with a white light source, a fiber-optic spectrometer (Ocean Optics), an oscilloscope, and an amplifier.[9] The diffraction efficiency (DE) was experimentally determined from the transmission spectra of the HPDLC reflection grating. The baseline of the spectra was fitted with a four-parameter differential equation which was compared directly with the actual transmission spectra. The DE reported here is the difference in transmission at the center of the reflection notch from the baseline fit to the peak of the reflection notch. The switching characteristics of HPDLC reflection gratings were studied by examining the optical behavior of the grating as voltage was increased. Voltage was increased stepwise with an oscilloscope (square wave, 1 kHz, 5 V rms) until DE approached 0%.

The influence of monomer functionality on the polymer/LC morphology of thiol−ene HPDLCs was characterized with transmission electron microscopy (TEM). Sample films were embedded in flat molds with Epo-fix, a low-viscosity TEM resin. The fixing resin was then polymerized at 60 °C in a vacuum oven overnight. The blocks were then trimmed and ultramicrotomed (RMC PowerTome XL) using a 35° diamond knife (Diatome). Sections were cut at a thickness of 60 nm. Thin sections were vapor stained with RuO_4 for 1 h to give improved contrast and stability under the electron beam. The sections were imaged with a transmission electron microscope (FEI CM200) at 200 kV.

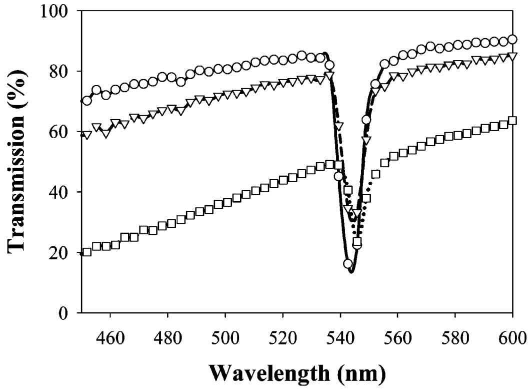

Figure 2. Transmission spectra of HPDLC reflection gratings based on a trithiol/tetraene formulation polymerized at 51 (□), 95 (▽), and 388 mW (○).

Results and Discussion

Since the original report of their development in 1993,[29] research of holographic polymer dispersed liquid crystal (HPDLC) has taken numerous approaches to enhancing electrooptic performance. Predominately, researchers have focused on adjusting the prepolymer formulation by varying monomer functionality[14,15] or adding components such as monofunctional reactive diluent,[16,17,20,29] surfactant,[18,19] and fluorinated monomer[30−32] and characterized the corresponding impact of these changes on electrooptic performance and polymer/LC morphology. In acrylate-based HPDLCs, fast polymerization kinetics and high monomer functionality are known to be critical for the development of HPDLCs with polymer/LC morphology that yields high diffraction efficiency (DE) and sufficient baseline transmission.[10−12] This work examines the influence of these two critical factors, polymerization kinetics and monomer functionality, on the formation and performance of thiol−ene-based HPDLCs.

1. Kinetics. The optical performance of acrylate-based HPDLCs improves with increasing polymerization rate. For example, the increased DE associated with the acrylate-based HPDLC samples containing *N*-vinylpyrrolidone (NVP) and octanoic acid have been recently correlated to the influence of these components on the polymerization rate in HPDLCs.[20,21] The most direct means to examine the influence of polymerization kinetics in photoreactive systems such as HPDLCs is by varying laser intensity, as the rate of photopolymerization is proportional to the square root of light intensity (with bimolecular termination).[33] Figure 2 plots selected transmission spectra of HPDLC reflection gratings formed from a trithiol/tetraene formulation polymerized over a wide range of laser power. In Figure 2, the peaks centered near 545 nm are associated with the selective reflection of white light from the fabricated HPDLC reflection gratings. Despite the increase in laser power, the reflection notch for the fabricated HPDLCs remains centered at 545 nm. Two phenomena critical to the overall DE of the grating are baseline transmission and the depth of the reflection notch. In Figure 2, the baseline transmission associated with each of the gratings is almost linear in the region shown and increases significantly with laser power. Increasing laser power also increases the depth of the reflection notch by reducing the transmission of light at 545 nm. By increasing baseline transmission and reflection notch depth, increasing laser power increases overall DE.

Table 1. Optical Performance of HPDLC Reflection Gratings Based on a Trithiol/tetraene Formulation Polymerized over a Range of Laser Power

laser power (mW)	transmission at 450 nm (%)	transmission at 545 nm (%)	overall DE (%)
51	21	23	28
95	58	30	49
193	71	32	54
287	70	20	65
388	69	15	71

Table 1 shows the influence of laser power on transmission at 450 nm (baseline transmission), transmission at 545 nm (notch transmission), and overall DE. Baseline transmission can be used as a measure of light scatter associated with droplet size, droplet density, and interfacial roughness.[9] As laser power is increased, the baseline transmission at 450 nm increases from 21% at 51 mW to 58% by simply increasing laser power to 95 mW. Further increasing laser power to 388 mW increases baseline transmission in this HPDLC formulation to almost 70%. Interestingly, the baseline transmission of HPDLC gratings written with laser powers of 193 mW or greater is nearly identical, indicating that light scattering in gratings written above this critical laser power is essentially equivalent. Most often, the source of reduced baseline transmission in HPDLCs is scattering losses associated with transmission of light through LC droplets. The depth of the reflection notch can be quantified by examining the percent transmission at 545 nm and can serve as a measure of the refractive index mismatch between the polymer and LC lamellae. In general, increasing laser intensity reduces transmission at 545 nm from approximately 30% (95 mW) to 15% (388 mW). Interestingly, the reflection grating written at 51 mW has lower transmission at 545 nm than gratings written at 95 and 193 mW. However, the reduced notch transmission of the grating written at 51 mW is likely related to increased scattering from larger LC droplets, rather than improved grating structure.

The influence of laser power on the optical behavior of HPDLC reflection gratings indicates that fast polymerization kinetics are also critical in the formation of thiol−ene-based HPDLCs. The impact of polymerization kinetics on the performance of fabricated HPDLC gratings is evident in the influence of laser power on DE. Increasing laser power increases DE from 28% to 71%. The significant increase in DE as a function of laser power is mostly due to the impact of polymerization kinetics on baseline transmission. Increased polymerization rate likely results in reduced LC droplet size, which corresponds to reduced scattering and increased baseline transmission.

2. Ene Monomer Functionality. Increasing monomer functionality typically results in increased cross-link density while shifting the polymer gel point to lower double bond conversion.[34,35] In polymerizations with trithiol, increasing ene monomer functionality from two to four shifts the gel point conversion from 71% to 41%. Complementary examination of LC phase separation in thiol−ene PDLCs has shown that phase separation occurs both through liquid−liquid and liquid−gel demixing.[23] In thiol−ene polymer/LC systems, delaying the transition of liquid−liquid to liquid−gel demixing by delaying the polymer gel point allows up to 25% more LC phase separation. In addition to the general influence of monomer functionality on LC phase separation, ene monomer functionality is influential on polymerization rate in thiol−ene PDLCs. Increasing allyl ether monomer functionality in polymerization with trithiol serves to increase the polymerization rate by as much as 90%.

The influence of ene monomer functionality on the performance of HPDLC reflection gratings is examined in Figure 3. Figure 3 shows transmission spectra of fabricated HPDLCs from stoichiometric mixtures of trithiol with diene, triene, or tetraene. As with increased laser intensity, increasing the functionality of the ene monomer increases baseline transmission (at 450 nm)

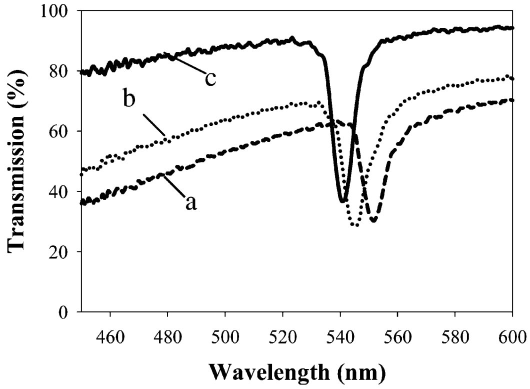

Figure 3. Transmission spectra of HPDLC reflection gratings containing trithiol polymerized with (a) diene, (b) triene, and (c) tetraene.

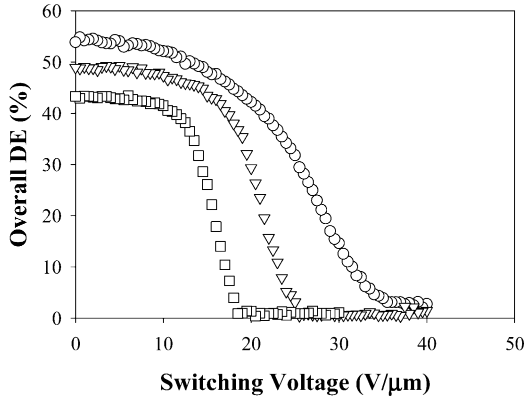

Figure 4. Overall diffraction efficiency (%) vs switching voltage (V/μm) of HPDLC reflection gratings containing trithiol polymerized with diene (□), triene (▽), and tetraene (○).

from 36% (diene) to 79% (tetraene). Increasing ene monomer functionality shifts the reflection notch toward lower wavelengths (blue shift) due to the increased shrinkage in more cross-linked thiol−ene polymers. The overall DE of HPDLC gratings significantly increases from 36% (diene) to 55% (tetraene) with increased ene monomer functionality.

Increasing ene monomer functionality is also influential on the switching performance of HPDLCs. Figure 4 is a plot of overall DE vs switching voltage (SV) for HPDLC formulations with increasing ene monomer functionality in polymerization with trithiol. As ene monomer functionality is increased, the voltage to attain 0% DE increases from 19 V/μm (diene) to 36 V/μm (tetraene). While ene monomer functionality is beneficial by increasing the overall DE and baseline transmission of HPDLC gratings, it also raises the voltage necessary to switch the diffraction grating.

The subsequent increase of overall DE and SV with ene monomer functionality may be a direct result of polymer/LC morphology. Figure 5 compares the morphology of HPDLCs made from the formulations examined in Figures 3 and 4. Similar to previous examination of the morphology of NOA65-based HPDLCs,[9] these thiol−ene-based HPDLCs exhibit droplet morphology in the LC lamellae. Comparing parts a−c of Figure 5, LC droplet size decreases as ene monomer functionality increases. As shown in Table 2, average LC droplet size for HPDLCs decrease from 160 nm (diene, Figure 5a) to 50 nm (tetraene, Figure 5c). In influencing LC droplet size, ene monomer functionality also dictates the grating structure of the HPDLCs. As ene monomer functionality is decreased, the width of the polymer lamellae decreases from approximately 100 nm (tetraene) to 40 nm (triene). In examining Figure 5a, it is difficult to see any grating structure for the diene as the LC droplets are so large that polymer lamellae are difficult to detect.[36] Interestingly, while LC droplets in HPDLCs made up of diene and triene exhibit spherical droplets, LC droplets in the tetraene are ellipsoidal. HPDLCs fabricated from NOA65 were classified to have spherical droplets of 80−100 nm.[9]

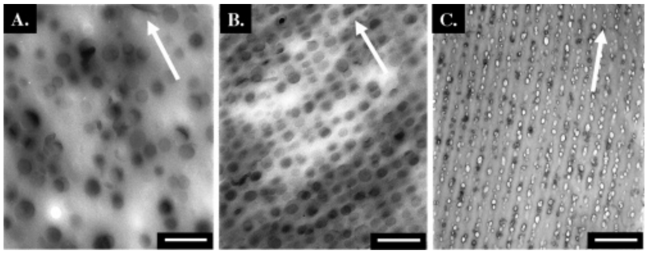

Figure 5. Transmission electron micrographs of HPDLC morphology for formulations containing trithiol polymerized with (a) diene, (b) triene, and (c) tetraene. The arrow is parallel to the direction of the polymer and LC lamellae for each micrograph. Scale bar is 500 nm.

From Figure 5, it can be concluded that the influence of ene monomer functionality on the optical performance of HPDLC reflection gratings is associated with a reduction in LC droplet size and improved grating structure. By increasing the polymerization rate, higher ene monomer functionality reduces the time for LC droplet growth and coalescence. At the same time, increasing ene monomer functionality shifts the transition from liquid−liquid to liquid−gel demixing to much earlier double bond conversion. Altering the evolution of LC demixing in the formation of HPDLCs serves to further reduce the time for LC droplet growth and coalescence in these systems, thus reducing LC droplet size. The decreased LC droplet size due to increasing ene monomer functionality decreases light scattering, resulting in increased baseline transmission and ultimately higher DE. While reduced LC droplet size inherently improves HPDLC optical performance, smaller LC droplets are known to need much larger voltages to switch.[10−12]

3. Thiol Monomer Functionality. The influence of thiol monomer on thiol−ene polymerization kinetics has been most often associated with chemical composition of the thiol monomer, with mercaptopropionate compounds polymerizing much faster than mercaptoacetate or aliphatic thiols.[24,25] Examination of the influence of thiol monomer functionality on the formation of PDLCs has shown that thiol monomer functionality has no effect on polymerization kinetics, unlike ene monomer functionality.[23] Despite not influencing polymerization kinetics in PDLCs, thiol monomer functionality is influential on the LC phase separation process and LC droplet size in thiol−ene PDLCs. Examining the performance of HPDLCs made with increasing thiol functionality is therefore a direct means to determine the influence of varying thiol−ene polymer gel point from 33% to 50% conversion in systems with equivalent polymerization kinetics.

To examine the influence of thiol functionality in HPDLC formulations, transmission spectra of HPDLC reflection gratings written in formulations with increasing thiol monomer functionality in polymerization with tetraene are shown in Figure 6. Interestingly, unlike ene monomer functionality, the optical performance of HPDLCs is not directly correlated to thiol monomer functionality. While increasing thiol monomer functionality from two to three increases baseline transmission and overall DE, increasing thiol monomer functionality from three to four serves to reduce HPDLC performance in these areas. HPDLC gratings containing trithiol monomer have a DE of 57% in comparison to the 43% DE of the dithiol and tetrathiol

Table 2. Comparison of the Polymer/LC Morphology for HPDLC Reflection Gratings Fabricated from Formulations of Various Thiol and Ene Monomer Functionality

formulation	droplet size (nm)	droplet shape	polymer lamellae width (nm)	transmission at 450 nm (%)	overall DE (%)
trithiol/diene (Figure 5a)	160	spherical		36	36
trithiol/triene (Figure 5b)	120	spherical	40	46	45
trithiol/tetraene (Figure 5c)	50 (width), 70 (length)	ellipsoidal	100	79	55
dithiol/tetraene (Figure 8a)	100	spherical	60	40	43
tetrathiol/tetraene (Figure 8b)	35	spherical		61	44

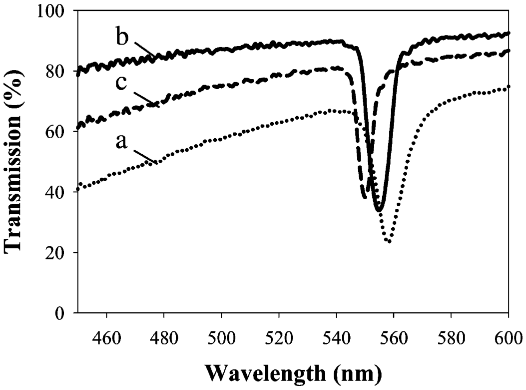

Figure 6. Transmission spectra of HPDLC reflection gratings based containing tetraene polymerized with (a) dithiol, (b) trithiol, and (c) tetrathiol.

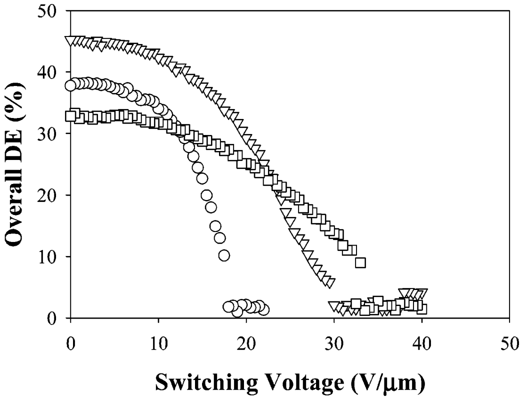

Figure 7. Overall diffraction efficiency (%) vs switching voltage (V/μm) of HPDLC reflection gratings containing tetraene polymerized with dithiol (○), trithiol (▽), and tetrathiol (□).

systems. Much of the improvement in DE with the inclusion of trithiol is due to improved baseline transmission.

In contrast to the DE results, the influence on SV is directly correlated to thiol monomer functionality. Shown in Figure 7 is the evolution of overall DE vs SV for HPDLC formulations containing increasing thiol functionality increases SV from 18 V/μm (dithiol), to 30 V/μm (trithiol), to 33 V/ μm (tetrathiol). Similar to ene monomer functionality, the direct correlation between increasing thiol monomer functionality and SV may be associated with a reduction in LC droplet size.

Examination of the morphology of HPDLCs made with increasing thiol monomer functionality can help understand the means by which thiol monomer functionality influences DE and SV. Figure 8 shows micrographs of HPDLC reflection gratings made from dithiol/tetraene (a) and tetrathiol/tetraene (b). The morphology of these gratings can be compared to the trithiol/tetraene HPDLC shown in Figure 5c. These micrographs show that LC droplet size decreases with increasing thiol monomer functionality, as seen with ene monomer functionality as well. This dependence is further illustrated in Table 2. Samples made from dithiol/tetraene and tetrathiol/tetraene have average LC droplet sizes of 100 and 35 nm, respectively.

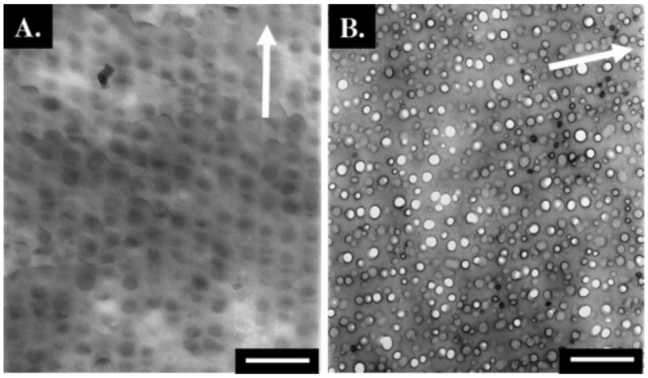

Figure 8. Transmission electron micrographs of HPDLC morphology for formulations containing tetraene polymerized with (a) dithiol and (b) tetrathiol. The arrow is parallel to the direction of the polymer and LC lamellae for each micrograph. Scale bar is 500 nm.

In comparing the performance of HPDLCs with increasing thiol monomer functionality, the best optical performance in the HPDLCs examined here is in the formulation containing trithiol/tetraene. Similar to thiol–ene-based PDLCs, LC droplet size decreases with increasing thiol monomer functionality due to the influence of thiol monomer functionality on gel point. As shown in Figure 8a, samples based on dithiol/tetraene have large LC droplets, 100 nm in size. Increasing thiol monomer functionality to three in the polymerization of trithiol/tetraene results in reduction of LC droplet size to 50 nm, correspondingly reducing scatter and increasing baseline transmission and overall DE. Further increasing thiol functionality to four, in the polymerization of tetrathiol/tetraene, reduces LC droplet size to 35 nm. Interestingly, such droplet size reduction actually increases baseline transmission in comparison to HPDLCs based on trithiol. Such behavior illustrates the importance of grating structure as a whole to the optical performance of HPDLCs. In comparing Figure 8b to Figure 5c, it is evident that the grating structure in the sample containing trithiol/tetraene (Figure 5c) is much more defined than tetrathiol/tetraene (Figure 8b), as the tetrathiol/tetraene morphology shows numerous LC droplets sporadically placed in the polymer lamellae. Despite the smaller LC droplet size, the lack of well-defined grating structure in the tetrathiol/tetraene HPDLC morphology reduces baseline transmission as the LC droplets present in the polymer-rich regions increase scatter as the refractive index mismatch of the polymer and LC regions decreases. It is possible that shifting the polymer gel point from 41% to 33% by increasing thiol functionality from three to four limits the amount of time for LC to diffuse completely into the LC regions, resulting in phase-separated LC droplets in the polymer regions.

4. Stoichiometry. Previous examination of thiol–ene-based HPDLCs has compared the performance of a NOA65-based grating to an HPDLC formulation containing a 1:1 molar ratio of tetrathiol and diene (ene deficient).[9] Surprisingly, despite the nonstoichiometric ratio of thiol to ene, the ene deficient tetrathiol/diene formulation performed comparatively to NOA65. Thiol–ene reaction stoichiometry has been known to change the polymer gel point and polymerization kinetics.[24,25,37] Like

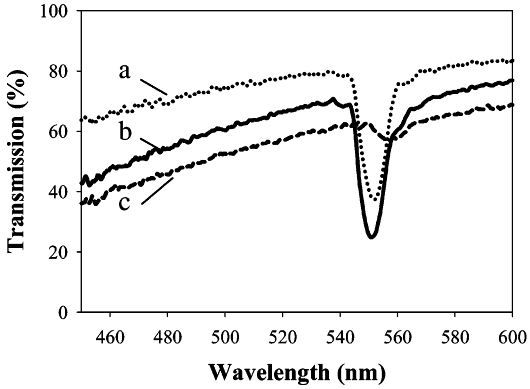

Figure 9. Transmission spectra of HPDLC reflection gratings based on the polymerization of mixtures of trithiol/diene with various stoichiometry: (a) 1:0.66 (excess thiol), (b) 1:1 (stoichiometric), and (c) 1:1.33 (excess ene).

ene and thiol monomer functionality, the influence of thiol−ene stoichiometry on polymerization kinetics and LC phase separation has been recently examined in the thiol−ene-based PDLC system.[23] Examination of the polymerization behavior of a trithiol/diene PDLC shows that reducing ene concentration (ene deficient) results in a marked increase in polymerization rate while simultaneously increasing LC phase separation.

The influence of thiol−ene stoichiometry was examined in an HPDLC formulation containing trithiol and diene. The stoichiometric (1:1 stoichiometric ratio) system was compared to HPDLC formulations containing 1:1.33 (excess ene) and 1:0.66 (excess thiol) stoichiometric ratios of trithiol to diene. The reactive portion of the 1:1.33 trithiol/diene formulation contains 10% more double bonds (ene) than thiol groups, while the 1:0.66 trithiol/diene formulation contains 10% more thiol groups than double bonds (ene). Examination of thiol and ene conversion of the polymerization of these mixtures by real-time infrared (RTIR) spectroscopy shows that, in the case of 1:0.66 trithiol to diene, diene conversion goes to 100% while trithiol conversion is limited to 66%.[23] In RTIR examination of the 1:1.33 trithiol to diene formulation, diene conversion is upward of 75% while thiol conversion is 100%.[23]

The influence of thiol−ene stoichiometry on the performance of HPDLC reflection gratings is examined in Figure 9. The transmission spectra of reflection gratings made from the trithiol/diene mixtures show that ene monomer concentration is influential on the formation of these materials. Samples containing excess ene (1:1.33) have DE $<$ 1%. On the other hand, samples containing excess thiol (1:0.66) have DE that is comparable to the stoichiometric (1:1) formulation. Interestingly, the 1:0.66 trithiol to diene formulation increases baseline transmission at 450 nm from 44% (1:1) to 63%.

From Figure 9, it is clear that ene monomer concentration is very influential on the optical performance of HPDLCs. LC is known to be much more soluble in ene monomer than in thiol monomer. In formulations containing excess ene monomer, it is probable that the additional ene monomer reduces the thermodynamic driving force for LC phase separation during both the liquid−liquid and liquid−gel demixing process, resulting in limited LC phase separation and poor grating structure. Reducing ene monomer concentration in the thiol−ene mixture serves to increase LC phase separation while also increasing polymerization rate. The result of the influence of increased LC phase separation and polymerization kinetics in 1:0.66 trithiol to diene formulations is increased baseline transmission and overall DE.

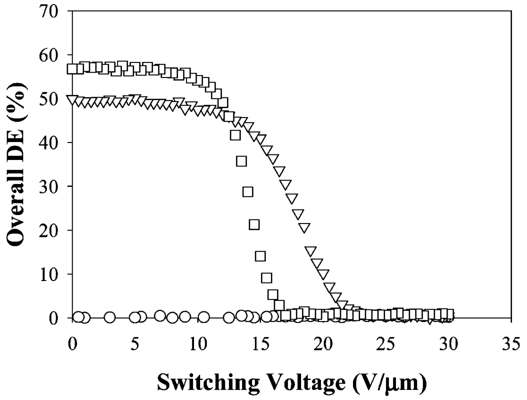

Figure 10. Overall diffraction efficiency (%) vs switching voltage (V/μm) of HPDLC reflection gratings based on the polymerization of mixtures of trithiol/diene with various stoichiometry: 1:0.66 (excess thiol) (□), 1:1 (stoichiometric) (▽), and 1:1.33 (excess ene) (○).

The influence of polymerization kinetics is once again evident in examining the influence of thiol−ene stoichiometry on the SV of HPDLC reflection gratings. Figure 10, a plot of overall DE vs SV for formulations containing various ratios of trithiol and diene, shows that samples containing excess thiol monomer (1:0.66) exhibit higher SV. In comparing the stoichiometric trithiol/diene mixture to the 1:0.66 trithiol/diene (excess thiol) mixture, the switching voltage increases from 16 to 22 V/um. This increase in SV is likely due to the influence of the increased polymerization rate in samples that contain excess thiol monomer.[23] Similar to ene monomer functionality, the increase in polymerization rate in these systems serves to reduce LC droplet size, thereby increasing the voltage necessary to effectively switch the reflection grating.

Conclusion

The electrooptical performance and morphology of HPDLC reflection gratings were characterized to further understand the impact of polymerization rate, gel point conversion, and excess monomer on the development of high-performance thiol−ene-based HPDLCs. To this end, HPDLC formulations containing increasing ene monomer functionality, increasing thiol monomer functionality, and nonstoichiometric mixture of thiol and ene monomer were examined. The optical performance of thiol−ene-based HPDLCs improves with increasing laser power, as the increased polymerization rate reduces LC droplet size, resulting in enhanced baseline transmission and overall diffraction efficiency (DE). Interestingly, the impact of monomer functionality in thiol−ene systems is dependent on the type of monomer. Increasing ene monomer functionality improves the optical performance of HPDLCs by reducing LC droplet size from 160 nm (trithiol/diene) to 50 nm (trithiol/tetraene). While increasing thiol monomer functionality also reduces LC droplet size to some degree, the electrooptic properties of HPDLC reflection gratings do not appear to be as dependent on thiol monomer functionality. HPDLCs made from trithiol/tetraene have more highly defined grating structure than tetrathiol/tetraene HPDLCs, subsequently increasing baseline transmission and overall DE. Surprisingly, systems with excess thiol monomer exhibit increased baseline transmission and overall DE in comparison to stoichiometric formulations. Optimal HPDLC performance is found in thiol−ene polymerizations with fast polymerization kinetics and moderate gel point conversion.

Acknowledgment. This work was completed at Wright-Patterson Air Force Base in Dayton, OH. Funding from the

AFOSR/NL and the ML Directorate of AFRL is also gratefully acknowledged.

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MA061829M