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Influence of non-reactive solvent on optical performance, photopolymerization kinetics and morphology of nanoporous polymer gratings

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Abstract

A study of nanoporous polymer gratings, with controllable nanostructured porosity, as a function of grating performance, photopolymerization kinetics and morphology is presented. Modifying the standard holographic polymer dispersed liquid crystal (H-PDLC) system, by including a non-reactive solvent, results in a layered, nanoporous morphology and produces reflective optical elements with excellent optical performance of broadband reflection. The addition of the non-reactive solvent in the pre-polymer mixture results in a morphology typified by void/polymer layer-by-layer structures if sufficient optical energy is used during the holographic writing process. The duration and intensity of optical exposure necessary to form well-aligned nanoporous structures can only be obtained in the modified system by (a) illumination under longer time of holographic interference patterning (30 min) or (b) illumination under very short time of holographic interference patterning (30 s) and followed by post-curing using homogeneous optical exposure for 60 min. Comparatively, a typical H-PDLC is formed in less than 1 min. To further understand the differences in the formation of these two analogous materials, the temporal dynamics of the photoinitiation and polymerization (propagation) kinetics were examined. It is shown herein that the writing exposure gives a cross-linked polymer network that is denser in the bright regions. With 60% (or even 45%) acrylate conversion, almost no free monomer would be left after the writing. Continued exposure serves primarily to add cross-links. This has the

tendency to collapse the network, especially the less dense portions, which in effect get glued down to the more dense parts. To the extent that the solvent increases the mobility of the polymer network, this process will be aided. Equally important, the size of the periodic nanopores can be varied from 10 to 50 nm by controlling either the LC concentration in the pre-polymer mixture or by controlling the time of the homogeneous post-cure.

Keywords

Nanoporous polymer; Holographic polymer dispersed liquid crystal; Photopolymerization kinetics; Phase separation

1. Introduction

Polymer Dispersed Liquid Crystals (PDLCs) were first demonstrated in 1986, when Doane and coworkers developed a phase separation system where the nematic liquid crystal (LC) droplets were spontaneously phase separated within the solid polymers during the photopolymerization process [1]. In addition, they showed that the LC droplet size, and the electro-optical switching ability, of the polymer/LC composite can be modified by varying the LC concentration [1,2]. Because of the large dielectric anisotropy and optical birefringence of the incorporated nematic LC in the composite, the optical state of the PDLC film could be switched “on” and “off” by applying an electric field [3]. Subsequently, Bunning and coworkers combined the optical holographic technique and PDLC materials to produce holographic polymer dispersed liquid crystals (H-PDLCs) materials to fabricate transmission or reflection gratings in a single step process [4–6]. H-PDLCs have potential application in display systems, electro-optical filters, free space optical switches, and photonic crystal switchable lasers [7–14]. In the standard H-PDLC system used for electrically switchable gratings, the pre-polymer mixture contains a photoinitiator/coinitiator, monomer, and LC. The mixture is dispensed in between two conductive glass slides and exposed to holographic interference patterning. The interference pattern created by two or more coincidently coherent laser beams creates bright and dark fringes. As previously documented, the monomer is polymerized to the greatest extent in the bright regions. The spatially varying polymerization kinetics results in chemical potential gradients for both reactive and non-reactive species that cause monomer to diffuse from the dark regions to the light regions and non-reactive components, such as the LC, to diffuse from the light regions to the dark regions. Similar to PDLCs, H-PDLCs exhibit polymerization-induced phase separation typified in a morphology consisting of alternating periods of polymer and LC, with the LC embedded as small droplets in the dark regions. At a controlled thickness for the grating film, the efficiency of these holographically written polymeric gratings is determined by the refractive index mismatch between the polymer-rich and the LC-rich regions. The shape and the amount of phase-separated LC droplets determine the electro-optic performance of gratings [15–18].

Recently we have demonstrated a nanoporous polymer reflection grating with high efficiency and broad reflection bandwidth that is produced when a non-reactive solvent is mixed into the standard H-PDLC system [19]. In contrast to the standard H-PDLC system, where the index contrast comes from the difference between polymer ($n_{\text{polymer}} \sim 1.5$) and

LC ($n_{LC} \sim 1.63$), this passive grating (modified H-PDLC) with high optical performance is based on the high index contrast between the polymer ($n_{\text{polymer}} \sim 1.5$) and air voids ($n_{\text{void}} = 1$). The non-reactive solvent mixed in the pre-polymer mixtures is phase-separated from the polymer during the holographic writing. Subsequent evaporation of the patterned non-reactive solvent from the film, after holographic fabrication, leads to the development of highly reflective gratings. The resulting periodic nanoporous polymer structure has been demonstrated to be useful in sensing applications where they provide distinct advantages due to the large surface-to-volume ratio and high optical performance [20–23].

While the techniques used to form the standard H-PDLC and the modified H-PDLC are the same, the time scales for formation of highly reflective gratings are dramatically different. In the modified H-PDLC containing non-reactive solvents, high diffraction efficiency gratings are observed only if either the pre-polymer mixture is exposed to (1) holographic exposure exceeding 10 min or (2) short holographic exposure (~ 30 s) followed by post-cure under homogeneous light for >30 min. This is in direct contrast to the standard H-PDLC system where the grating efficiency reaches a maximum within a minute [24,25]. Extra writing or post-curing time in the traditional H-PDLC system typically decreases the efficiency [24–28].

We present herein an examination of the grating formation both temporally and as a function of LC concentration for the modified H-PDLC which incorporates a non-reactive solvent. This information is supplemented with corresponding analysis of the polymerization kinetics and morphology. The kinetics of the polymerization process were examined by monitoring the polymerization rate and double bond conversion with real-time infrared spectroscopy (RTIR) [29,30] during holographic exposure. RTIR spectroscopy has previously proved a useful tool to study photopolymerization kinetics and the contribution of each component in the H-PDLC system. Together, the analysis is used to propose a model to describe the formation of the periodically arranged nanopores between the layered polymeric planes generated from the modified H-PDLC system.

2. Experimental

The pre-polymer mixture used here consisted of fixed 1 weight percentage (wt.%) photoinitiator (Rose Bengal, Spectra Group Limited), 3 wt.% coinitiator (N-phenylglycine, Aldrich), and 10 wt.% solubilizing monomer (NVP, Aldrich) [19]. The concentration of acrylate monomer (dipentaerythritol hydroxypentaacrylate, Aldrich), liquid crystal (TL213, $n_0 = 1.527$, $n_e = 1.766$, EM Industries, Merck), and non-reactive solvent (acetone, Aldrich) are varied as specified in the remainder of this article and the figures. All chemical materials were used as received without further purification and the mixtures were homogenized to solutions by using a mixer and sonicator before sample preparation. Samples were prepared by sandwiching 15 μL of the pre-polymer mixture (containing a small amount of 5 μm glass rods as spacers) between two glass slides. The enclosed sample was subsequently exposed to the holographic interference patterning using a single laser beam and a prism [31]. The Ar^+ laser, operating at 514 nm with 100 mW exposure power, had a fixed exposure time of 30 s for the first holographic writing process. Then the sandwiched sample was either kept under the holographic writing for an additional length of time or post-cured with a 75 W white

light source with a tungsten lamp for different lengths of times. After full exposure and/or curing the sandwiched sample was opened using a blade. To maintain the whole piece of polymer film the gold-coated glass slide was used as the top plate and the film was situated at the bottom plate. The acetone was completely evaporated after 5 min.

A Shimadzu UV-3101PC spectrophotometer working in transmission mode was used to characterize the optical transmission of the resulting grating samples. The morphology of the samples was observed by bright-field transmission electron microscopy (BFTEM) [6]. For the BFTEM measurements, the sample preparation was as follows: the cross-sections of the films were prepared by fracturing the sample in liquid N₂ and mounting them on their edges in conductive silver paint. The TEM samples were prepared by ultramicrotomy at room temperature from epoxy blocks. As a result, the bright regions of the image show air voids filled by the epoxy while the dark regions show the polymer. BFTEM was conducted on a Jeol 100CX TEM operating at 100 keV.

The photopolymerization kinetics were examined with RTIR spectroscopy. This system adapted a standard Thermo Electron Nexus 670 FTIR by adding a horizontal transmission accessory with photopolymerization capability, described in detail previously [29]. Samples were polymerized between NaCl slides. Examination of the polymerization (both real-time and post-cure) of formulations with and without non-reactive solvent was performed by flood-lit curing with an EFOS Acticure 4000 high pressure mercury lamp, using a 250–500 nm filter. The influence of post-cure time on double bond conversion was examined in reflection gratings inscribed on NaCl slides.

3. Results and discussion

Holographic exposure of the standard H-PDLC system yields a spatially varying interference pattern of bright and dark fringes controlled by the laser wavelength and interference angle of the beams. When used to initiate polymerization of the standard H-PDLC, the spatially varying interference pattern causes monomer to polymerize in the bright fringes (polymer-rich) and the LC to phase separate in the dark fringes (LC-rich). Here the term “rich” is used to indicate that each region does not consist solely of these materials, as residual LC is trapped in the polymer-rich region and polymer network is prevalent within the LC-rich region. The extent of the phase separation determines the index contrast and further determines the optical performance of the reflection gratings. Normally initial loadings of more than 30 wt.% LC are necessary to yield sufficient phase separation of the LC in H-PDLC systems. Previous examination of grating efficiency as a function of holographic writing time indicates the grating is formed completely after 1 min of holographic exposure [6]. The photopolymerization stops within one minute and the diffusion of the monomer and the LCs also stops within a very short time. However, the presence of a non-reactive solvent in the standard H-PDLC system changed this behavior drastically. Specifically, we found that the time for generating a grating with high efficiency is much greater than 1 min. Fig. 1 plots transmission spectra for samples with different holographic writing times (5, 10, 30, 60 min). The transmission spectra were taken from the films after the sandwiched cell was opened and the volatile organic solvent evaporated off. After 5 min of holographic exposure, the notch is barely observable. As holographic

exposure time is increased, both an increase in diffraction efficiency and a red shift are evident. Only after 60 min holographic exposure is the grating completely formed with a diffraction efficiency of approximately 55%. The results are completely different from the samples fabricated using the standard H-PDLC system, which yields grating samples of 60% reflectivity under one min of holographic writing [6].

To further understand the formation of these systems, the modified H-PDLC formulation was exposed to 30 s of holographic exposure, followed by flood-lit post-exposure ranging from 10 min to 24 h. Fig. 2 plots the corresponding transmission spectra, taken again from nanoporous gratings that have been opened allowing the solvent to evaporate. As in Fig. 1, the diffraction efficiency of the reflection notch increases with exposure time while the notch position red shifts. As evident from Fig. 2, 60 min of post-cure with homogenous light creates a reflection grating with higher efficiency (70%) and increased bandwidth (50 nm). It is evident in both Figs. 1 and 2 that incorporating the non-reactive solvent into the standard H-PDLC system increases the time needed for obtaining a reflection grating with high efficiency. The efficiency of grating samples fabricated by the standard H-PDLC system reaches a maximum in one minute [26], and further holographic writing or post-curing does not enhance the grating efficiency. However, the efficiency of the grating samples fabricated by the modified H-PDLC system containing additional non-reactive solvents continues to increase with longer holographic writing or post-curing time. In the case of post-curing, the reflection efficiency reaches a steady maximum value (~80%) after 24 h post-curing time.

Comparing Figs. 1 and 2, the initial stage of phase separation in the holographic writing or homogeneous post-cure is fundamentally the same in these two cases. The red shift of the Bragg wavelength ($\lambda_{\text{Bragg}} = 2n_{\text{ave}}\Lambda$) indicates that the effective grating spacing (Λ) continues to increase with longer holographic writing or homogeneous post-curing in samples with the same composition (fixed average refractive index, n_{ave}). This red shift of the Bragg wave-length shows that the phase-separation induced growth of the polymer remains active during subsequent holographic writing and homogeneous post-curing. In addition, there is an intermediate state between a slight phase separation and a better separation. The samples in Fig. 1 (curve of 10 min) and Fig. 2 (curve of 30 min) all indicate such a state since low transmittance of the polymer film is observed in those two samples. We speculate that the scattering in those samples is due to incomplete phase separation of the LC/non-reactive solvent during the short holographic writing time and homogeneous post-curing time.

It is noteworthy that the photopolymerization-induced phase separation still occurs even though the grating sample is exposed to homogeneous post-curing instead of continuous holographic writing. In the standard H-PDLC system, longer times for holographic writing or post-cure do not enhance the grating efficiency, and the photopolymerization stops almost immediately after the brief period of holographic writing [24,25]. To further understand the influence of the non-reactive solvent on photopolymerization kinetics during grating structure formation, acrylate conversion was examined in the samples fabricated by standard and by modified H-PDLC systems using RTIR spectroscopy. Fig. 3, a plot of the percent acrylate conversion versus time, shows that the H-PDLC formulations containing the non-

reactive solvent exhibited greater acrylate double bond conversion. Adding 20 wt.% non-reactive solvent increases the acrylate double bond conversion from around 45% in the standard H-PDLC formulation to upwards of 60% in the modified H-PDLC system. The addition of the non-reactive solvent in the pre-polymer mixture increases the rate of photopolymerization, evident by the initial slope of the conversion versus time plots (Fig. 3). The influence of the non-reactive solvent on the double bond conversion and polymerization rate is attributed to the plasticization of the densely cross-linked polymer network. Adding solvent increases the non-reactive free volume of the polymerizing system. Increasing the non-reactive free volume in such a diffusion-limited reaction environment is conducive to greater monomer mobility, thereby increasing double bond conversion and the polymerization rate in the formation of plastic materials.

The addition of the non-reactive solvent is also influential during the homogeneous post-curing process. The percentage of acrylate conversion is plotted against post-cure time in Fig. 4. In this comparison, the reflection gratings from the modified H-PDLC formulation and the standard H-PDLC formulation were written between NaCl slides. The homogeneous post-cure of these gratings was subsequently examined with RTIR. As expected, adding the non-reactive solvent in the modified H-PDLC system facilitates greater acrylate double bond conversion than the standard H-PDLC formulation. It should be noted that the percent conversion reported here is not based on the original number of double bonds in the formulations, but based on the number of double bonds remaining after holographic illumination. Because of the diffusional limitations in the standard H-PDLC formulation, post-curing the grating with UV/ Visible light leads to only 20% conversion of the remaining double bonds. From Fig. 4, it is expected that upwards of 55% of acrylate double bonds remain after the original polymerization in the grating sample fabricated by standard H-PDLC system. Therefore, approximately 10% additional conversion is achieved through post-curing. In contrast, the grating sample fabricated using the modified H-PDLC system containing a non-reactive solvent has greater than 40% conversion of the remaining acrylate double bonds. Similar to Fig. 3, adding the non-reactive solvent diminishes the diffusional constraints of the system, facilitating enhanced monomer mobility and thus leading to greater acrylate double bond conversion. From Fig. 3, approximately 40% of the acrylate double bonds may remain after the initial polymerization from brief holographic writing. Converting 40% of the remaining double bonds in the modified H-PDLC system increases overall conversion by more than 16%, moderately greater than the standard H-PDLC formulation.

To further understand the influence of additional curing on the morphology of the nonporous gratings, the samples were examined with bright-field transmission electron microscopy (BFTEM). Shown in Fig. 5 are BFTEM micrographs of the grating samples from 30 s duration of holographic exposure followed by homogeneous post-cure times of 30 and 60 min. One can see that as the time of post-curing increases, the void (lighter coloration) size and density increases correspondingly. In the standard H-PDLC system of writing a grating for a given LC concentration, the resulting LC droplet size can be controlled by changing the rate of photopolymerization [6]. Once the LC droplets have phase separated, the droplet size corresponding to the growth speed of the pre-polymer mixture is governed by the diffusion of LC from bright to dark regions. The bright regions consist of primarily small-

diameter droplets due to the increased rate of photopolymerization (some small droplets do not have enough time to diffuse to lower intensity regions). In contrast, the dark regions have the largest diameter droplets. In the modified H-PDLC system, containing non-reactive solvent, the 60 min-sample clearly shows a grating consisting of phase-separated void lamellae. Small spherical domains (~50 nm) are present in that sample and are evidence of a nucleation and growth phenomenon. For the 60 min-sample, individual domains below 50 nm are evident with no indication of void coalescence. These small domain sizes of voids allow the film to be non-scattering, while at the same time producing the large index contrast to the polymer-rich region. Thus, by controlling the post-cure time, one can control the size of the nanopores and the corresponded optical performance of grating samples.

Examination of the temporal evolution of the nanoporous grating, the kinetics of the polymerization, and resulting morphology allows us to speculate as to the mechanism for the formation of the void lamella. Fig. 6 schematically represents the dynamics of grating formation. Initially the additional non-reactive solvent in pre-polymer mixture tends to increase the local polymerization rate in the bright region and gives a cross-linked polymer network that is denser in the bright regions compared to the dark region. The gelation happens rapidly in the bright region and a cross-linked structure is generated, but in the dark region the monomer is depleted due to the high concentration of LCs/non-reactive solvent that co-exists with monomer of low concentration. With 60% (or even 45%) acrylate conversion, almost no free monomer would be left after the holographic writing. At this point the grating sample is a gel-like thin film consisting of polymer, monomer, LCs, and non-reactive solvent. No phase-separated voids could be observed without further writing or post-curing, even after the sample was opened to allow the non-reactive solvent to evaporate. Continued exposure (holographic writing or homogeneous post-curing) serves primarily to add the cross-linking. This has the tendency to collapse the network, especially the less dense portions, which in effect get glued down to the more dense part. To the extent that the non-reactive solvent increases the mobility of the polymer network, this process will be aided. The process essentially stops after 60 min homogeneous post-cure and nicely phase-separated void lamella can be observed through evaporating the non-reactive solvent by opening the sandwiched sample.

In the standard H-PDLC grating no refractive index contrast could be observed for an LC concentration of 18 wt.% [6], but in the modified H-PDLC system a reflection grating of high optical performance with 70% reflectivity and 40 nm reflection bandwidth could be fabricated with a pre-polymer containing only 3 wt.% LC (Fig. 7 curve (b)). Upon increasing the concentration of the LC, the spectral response of the Bragg wavelength (λ_{Bragg}) shifts to a longer wavelength and the reflection bandwidth increases considerably. The baseline transmittance at wavelengths outside the notch is also considerably lower, which implies more scattering in the grating structure with higher LC concentration. To understand the red shift of λ_{Bragg} and increased reflective bandwidth with increasing LC concentration, we examined the cross-sectional morphology of grating samples using BFTEM, which is commonly used to observe the microstructure of reflection gratings fabricated by a standard H-PDLC system [6]. Fig. 8 is the cross-sectional BFTEM micrograph of grating samples, clearly showing that the size of voids (white regions)

increases with increasing LC concentration in the pre-polymer mixture. The morphology of a sample that contains 3 wt.% LC shows a slightly two-phase structure (Fig. 8a) and as the LC concentration increases, much larger voids and wider void-rich lamellae (50–60 nm) periodically separated by a polymer-rich region are observed (Fig. 8b). As the voids become larger, the cross-linked polymers in the void-rich region develop a bead-like structure. These void-rich regions are composed of discrete, spherical droplets with a small amount of polymer bridging the voids without the sample collapsing. The sample with a high concentration LC has a bicontinuous morphology in the void-rich regions and some phase-separated droplets in the polymer-rich regions. According to the Bragg condition, $\lambda_{\text{Bragg}} = 2n_{\text{ave}}\Lambda$, the λ_{Bragg} can be determined by grating spacing (Λ) and average refractive index (n_{ave}) of the sample [6]. From the observation of transmission spectra and morphology of grating samples we can conclude that the red shift of λ_{Bragg} is the result of (1) the increase of n_{ave} due to the higher LC concentration; and (2) the increase of Λ due to the larger size of voids in the sample generated by higher LC concentration.

We would like to give a brief discussion about the role of LC. We have observed that no reflection notch could be observed if no LC was added in the modified H-PDLC formulation (Fig. 7 curve (a)). From our recent publication we found out similar reflection could be fabricated by replacing LC/acetone with formamide which is a highly polar solvent [32]. That observation may offer an explanation of why the LC is necessary to fabricate ordered, nanoporous polymer film from the H-PDLC/non-reactive solvent system. The commercial nematic LC contains surfactant-like molecules, therefore, we speculate that during the holographic patterning in H-PDLC/non-reactive solvent system, the LC/acetone forms an emulsion in the photo-polymer fluid. The ordered, nanoporous structure appears when the phase-separated acetone evaporates upon exposing the polymerized film to air.

4. Conclusion

We have investigated the temporal evolution of the grating formation, photopolymerization kinetics, and morphology of gratings formed from a modified H-PDLC system containing a non-reactive solvent. During the initial short time of holographic writing, the non-reactive solvent increases the double bond conversion and the photopolymerization rate in the local bright region. The writing exposure gives a cross-linked polymer network that is denser in the bright regions. With 60% (or even 45%) acrylate conversion, almost no free monomer would be left after the writing. Continued exposure serves primarily to add cross-links. This has the tendency to collapse the network, especially the less dense portions, which in effect get glued down to the more dense parts. To the extent that the solvent increases the mobility of the polymer network, this process will be aided. The voids ranging from 10 to 50 nm separated by the layered polymer matrix could be controlled by either the homogeneous post-curing time or LC concentration in the pre-polymer mixture.

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Fig. 1.

The transmission spectra of grating samples fabricated using the modified H-PDLC system containing a non-reactive solvent as a function of holographic writing times.

(Acetone:LC:Monomer = 20 wt. %:20 wt. %: 46 wt. %.)

Fig. 2.

The transmission spectra of reflection grating samples as a function of different times of homogeneous post-curing generated by a 75 W white light source with a tungsten lamp. Samples were exposed to 30 s holographic exposure before the homogeneous post-curing. (Acetone:LC:Monomer = 20 wt. %:20 wt. %:46 wt. %.)

Fig. 3.

Dynamic observation of acrylate conversion during homogenous exposure of the H-PDLC formulations. The solid line is recorded from the standard H-PDLC mixture while the dash line is from the modified H-PDLC mixture containing non-reactive solvent. (Standard H-PDLC mixture LC:Monomer = 20 wt. %:66 wt. %; Modified H-PDLC mixture Acetone:LC:Monomer = 20 wt. %:20 wt. %:46 wt. %.)

Fig. 4.

Dynamic observation of acrylate conversion as a function of homogeneous post-cure time. (Standard H-PDLC mixture LC:Monomer = 20 wt. %:66 wt. %; Modified H-PDLC mixture Acetone:LC:Monomer = 20 wt. %:20 wt. %:46 wt. %).

Fig. 5. BFTEM morphology of cross-sectional fracture surface of reflection grating formed using different homogeneous post-curing times of (a) 30 min and (b) 60 min. (Acetone:LC:Monomer = 20 wt. %:20 wt. %:46 wt. %).

Fig. 6. The formation of wide-reflection bandgap holographic gratings fabricated using the modified H-PDLC system.

Fig. 7.

The transmission spectra of the reflection gratings of (a) 0 wt.%, (b) 3 wt.%, (c) 20 wt.% and (d) 30 wt.% LC concentration in the pre-polymer mixture of fixing 20 wt.% acetone concentration and varying monomer concentration.

Fig. 8. BFTEM micrographs of the cross-sectional fracture surface of the reflection gratings formed using (a) 3 wt.%, (b) 20 wt.% LC concentrations in the pre-polymer mixture.