Effects of Prepolymer Structure in Holographic Polymer Dispersed Liquid Crystal

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ABSTRACT: Three different types of polyols—poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), and poly(tetramethylene glycol)—with different molecular weights (\(M_n\)) were incorporated into the prepolymer structure, and the effects were examined with regard to the morphology and performance of holographic polymer dispersed liquid crystal. Among them, PEG showing the lowest glass transition temperature (\(T_g\)) exhibited the lowest threshold voltage (\(V_{th}\)), lowest operating voltage (\(V_{op}\)), and lowest diffraction efficiency with slow grating formation owing to its high viscosity of prepolymer mixture. The \(T_g\) decreased with increasing \(M_n\) because of the decreased crosslink density and hydrogen bonding, which reduced the anchoring strength, \(V_{th}\), and \(V_{op}\). PPG400 gave \(V_{th}\) and \(V_{op}\) of approximately 7 and 24 V, respectively, with a contrast ratio of approximately 12.

INTRODUCTION

Holographic polymer dispersed liquid crystals (HPDLCs) have many potential applications, such as displays and smart windows. However, these applications require a high diffraction efficiency (DE) and low driving voltage.1–3 The DE generally increases, when there is high mismatch of the refractive indices between the polymer and LC,4 which is due to the good phase separation of LC from a polymer. The driving voltage of HPDLC is generally high due primarily to the large anchoring energy and elastic deformation energy, which are caused by its smaller droplet size and strong interfacial interaction. The high driving voltage limits the applications of HPDLC devices with a suitable power supply.5.6 The LC regions are composed of randomly oriented nanosize droplets whose size depends on a number of factors, such as the monomer functionality, film composition, intensity and duration of irradiation, and curing temperature.7–13

The morphology and electro-optic properties of HPDLCs have attracted considerable interest.14–18 Recently, the effects of the prepolymer structure have received a great deal of attention. Pogue et al.19 reported the effects of varying the monomer functionality on the HPDLC gratings. Schulte et al.20 examined fluoro-substituted acrylate monomers and found that the presence of fluorine atoms at the LC/polymer interface of the HPDLC gratings can lower the anchoring strength and switching voltage. Kashima et al.21 reported the effects of the chain length of crosslinking agents of PDLC.

This study examined the effects of the viscosity and glass transition temperature (\(T_g\)) of the prepolymer on the grating formation kinetics, thermal, mechanical, morphological, and electro-optical performance of HPDLC. For this, prepolymer structures were varied systematically using three chemically different types of polyols—poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), and poly(tetramethylene glycol) (PTMG)—with molecular weights (\(M_n\)) of 300, 400, and 600, respectively. The molecular weights between the crosslinks (\(M_c\)) of the polymer network were also varied.

EXPERIMENTAL

Materials and Oligomer Synthesis

The films were prepared by polymerization-induced phase separation from a homogeneous mixture of polyurethane acrylate (PUA) oligomers, reactive diluents, additives, and LC in the presence of a photoinitiator and coinitiator.

To synthesize the PUA oligomers, a molar excess of hexane di-isocyanate (HDI) was reacted with the aforementioned types of polyol to form a HDI-terminated polyurethane prepolymer. The prepolymer was then capped with 2-hydroxyethyl acrylate (HEA), which is photosensitive, and was subjected to laser irradiation. The mixture composition of PUA was set to polyol/HDI/HEA = 1/2/2 (in moles). In this way, an increase in \(M_n\) causes an increase in the prepolymer molecular weight and molecular weight between the crosslinks (\(M_c\)), because the molar composition is fixed, regardless of

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the $M_n$. $N$-Vinyl pyrrolidone (NVP) was used as a reactive diluent. NVP reduces the viscosity, whereas PUA provides the mixture with high reactivity and a polymer with a highly networked structure. The composition of the PUA oligomer/diluent was fixed to 3/2 by weight.

A surfactant (octanoic acid) was used to reduce the switching field by lowering the interfacial tension between the LC and polymer. E7 (BL001, Merck), a eutectic mixture of three cyanobiphenyl and one cyanoterphenyl mixtures with positive dielectric anisotropy ($\Delta\varepsilon = 13.8$), was used as the LC at 40 wt %. Rose Bengal (RB) was used as the photoinitiator for holographic recording with an argon ion laser, because it displays broad absorption in the 450–560 nm region and a high-triplet quantum yield.22 A millimolar amount of $N$-phenylglycine (NPG) was added to the resulting mixture as a coinitiator.23,24 Table 1 lists the formulations to prepare the transmission mode of HPDLC.

**Grating Formation**

To fabricate holographic grating, the mixture was sandwiched between two indium-tin-oxide (ITO)-coated glass plates with a gap of 20 $\mu$m, which was adjusted using a bead spacer. The sample was irradiated with an Ar-ion laser (514 nm) at intensity of 120 mW cm$^{-2}$ for a period of 180 s. The incident beam angle between the two lasers outside the cell was set to 13°. The interference pattern was determined using Bragg’s law ($\Lambda = \lambda/2\sin(\theta/2)$, where $\Lambda$ = grating spacing, $\lambda$ = wavelength of the writing beam). The grating morphology was visualized by scanning electron microscopy (SEM). For this, one side of the ITO glass was removed, and the sample was soaked in methanol for 24 h before removing the LC. Grating formation was not possible with 3000$M_n$ due to the high viscosity.

**Measurements**

The dynamic DE was probed using a photodiode during the holographic polymerization using an Ar-ion laser. The DE was defined as the diffracted intensity divided by the sum of the diffracted and transmitted intensity.25 The electro-optical properties of the film were determined by probing with a He–Ne laser (633 nm), because the material is not sensitive to red light. A square wave voltage operating from 0 to 80 V was applied across the film to drive the shutter. The tensile properties of the LC-free films were measured at room temperature using a Universal Testing Machine (Lloyd) at a crosshead speed of 200 mm min$^{-1}$. The specimens were prepared according to ASTM D-1822. Thermal analyses were carried out by differential scanning calorimetry (DSC, Seiko DSC 220) from 70 to 100°C at a heating rate of 10°C min$^{-1}$. Viscosity of the compound was measured at room temperature using a vibration type viscometer (Vibro viscometer, SV-10, A&D, Japan). It was found that the viscosity of PEG prepolymer (1800 cP) was much greater than that of PPG (950 cP) and PTMG (1050 cP) at the same $M_n$ (400).

**RESULTS AND DISCUSSION**

**Thermal Properties**

Figure 1 shows the DSC thermograms of the cured films prepared from PEG, PPG, and PTMG. The glass transition temperature, that is, the temperature corresponding to the inflection point of the curve was clear with the PEG- and PPG-based films, where the transition temperature ($T_g$) decreased with increasing $M_n$ of polyol. This was attributed to the lower crosslinking density and number of urethane groups. $T_g$ is related to the crosslinking density of the polymer network according to the following equation:26

$$T_g = A + \frac{B}{M_n}$$  \hspace{1cm} (1)
where $A$ and $B$ are constants, and $M_c$ corresponds to the oligomer or prepolymer molecular weights. Table 1 shows the increases in $M_c$ with increasing $M_n$ of polyol.

On the other hand, the urethane group density decreased with increasing $M_n$ of polyol, because urethane groups are formed by chemical reactions between the terminal OH groups of the polyols and the isocyanate groups of HDI. These urethane groups impart rigidity and strong intermolecular interactions via hydrogen bonding to augment the $T_g$.

With regard to the PTMG-based polymer networks, the $T_g$ was observed only with 3000$M_c$ which is higher than the other two types of polyol, at the same $M_n$. The $T_g$s of the other $M_c$ values for PTMG were not observed by DSC up to 70 °C.

**Mechanical Properties**

The mechanical properties of the films are important with regard to the operating performance of HPDLC, because LC molecules anchored on the polymer surfaces are subject to repeated deflection after applying the voltage. Figure 2 shows the stress–strain behavior of the LC-free films. Regardless of the type of polyol, the initial modulus and break strength increase with decreasing $M_n$ of polyol, whereas the elongation at break decreases. This is mainly due to the effects of the $M_n$ of the polyol on the $T_g$, as well as the crosslinking density of the polymer network in accordance with the ideal rubber theory as follows:

$$G_0 = \frac{\rho RT}{M_c}$$

where $\rho$, $R$, and $T$ are the density, gas constant, and absolute temperature, respectively. The increase in $M_c$ is accompanied by an increase in $M_n$, as aforementioned. With regard to the effect of the polyol type, PTMG exhibited the highest modulus and strength, whereas PEG had the lowest values in accordance with the $T_g$. Films with a small elastic modulus are

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**FIGURE 1** DSC curves of the LC-free films of various molecular weights of (a) PPG, (b) PEG, and (c) PTMG.

**FIGURE 2** Stress–strain behavior of the LC-free films containing various types and molecular weights of polyol.
expected to have a low threshold and operating voltage due to the low anchoring strength at the polymer–LC interface.28

DE

Figure 3 shows the real time DE of the film during photopolymerization. The DE overshoot was the most pronounced with PPG showing a maximum at 10–20 s, followed by an asymptotic decrease to a steady value, which was the highest with PPG 400. A tiny overshoot was also observed with the other two types of polyol depending on the $M_n$. The overshoot at the initial stage of grating formation was attributed to the low compound viscosity, which causes rapid diffusion, followed by fast curing, grating formation, and phase separation. Rapid curing would induce an increase viscosity leading to a slow diffusion and steady state.

Among the three types of polyols, PEG gives the slowest and lowest grating formation because of the high compound viscosity, which was noted during the experiment. The high viscosity of PEG was attributed to its polar nature. The tiny DE overshoot noted only with 400 $M_n$ confirmed it to be due to the low viscosity of the prepolymer. When the compound viscosity was too high, the entire process is controlled by slow diffusion, giving rise to poor grating formation and DE. PTMG shows similar grating formation dynamics with PPG but at a slow rate.

Table 1 and Figure 4 present the steady-state DEs as functions of the type and $M_n$ of polyol. Regardless of the polyol type, 400$M_n$ imparts the greatest DE than the others, suggesting that $M_n$ is a parameter to control grating formation in terms of the compound viscosity and reactivity. The film was barely formed with 3000$M_n$ due to the high prepolymer viscosity and low HEA concentration to form networks.

Morphology

Morphology control is a key issue in optimizing the overall performance of HPDLC films in many contributions.29–31 Figure 5 shows SEM images of the transmission gratings. The dark layers with debris of holes at the interfaces are the original locations of the LC droplets that had been separated by dense polymer regions. Theoretically, the grating spacing should be 1267 nm according to Bragg’s law. Nevertheless, the fabricated grating spacing was actually 1086 nm due to shrinkage upon polymerization.32

Although well-defined grating structures are obtained, polymer–LC phase separation in terms of the LC layer width was greater with PPG and PTMG and with 400 $M_n$ prepolymer. In addition, debris of LC droplets at the surfaces is large and visible for PPG and PTMC, whereas it is hardly seen for PEG, implying the droplet size is smaller with PEG. The extent of phase separation observed by SEM agrees with the DE discussed earlier. This is related to the appropriate compound viscosity. The viscosities of the PPG and PTMG prepolymers were suitably low to allow adequate diffusion and phase separation, as noted from the real time data. In contrast, the PEG series showed a narrow LC region, which is indicative of limited phase separation due to the high prepolymer viscosity, which slows the entire process.

Electro-Optical Properties

Figure 6 shows the DE of the film as a function of the applied voltage. After applying the electric field, the DE decreased in an inverse sinusoidal manner to a constant value of approximately 3% in all films. A significant difference in $V_{th}$, $V_{op}$, and off-state DE was observed between the three groups. $V_{th}$ and $V_{op}$ were lowest with the PEG-based films and highest with the PTMG-based films in accordance with $T_g$. The same results were also reported by Du et al.8 and Senyurt et al.28 who used polyacrylate as prepolymer. According to Kashima et al.,21 low characteristic voltage with a low $T_g$ is due to the small anchoring energy of LC molecules on the film surface.

PPG generally shows the highest off-state DE and contrast ratio but $V_{th}$ similar to the PEG-based films. On the other hand, a high $M_n$ gives a low $V_{th}$ and $V_{op}$ in accordance with the low $T_g$. In particular, PPG400 exhibited a $V_{th}$ and $V_{op}$ of approximately 7 and 24 V, respectively, with a contrast ratio of approximately 12.
CONCLUSIONS

The effects of the molecular weight ($M_n$) and type of polyol (PPG, PEG, and PTMG) on the morphology, thermal, mechanical, and electro-optical properties of the HPDLC films were studied in the rubbery state of the polymer film. $T_g$, tensile modulus, and strength of the LC-free film decreased with increasing $M_n$ from 300 to 600 because of the increased $M_c$. The decreased $T_g$ subsequently reduced the anchoring energy, threshold, and driving voltage of the film.

FIGURE 5 SEM images of the gratings containing various molecular weights of (a) PPG (b) PEG, and (c) PTMG.
On the other hand, the viscosity increased with increasing $M_n$ and $M_c$, whereas the curing kinetics and polymer-LC phase separation decreased. At a low (300) and high (600) $M_n$, the low and high viscosity induced rapid and slow cure kinetics, respectively, giving rise to inappropriate phase separation and grating formation. Phase separation was the greatest only at an intermediate $M_n$ (400) to give the greatest DE.

Among the three types of polyols, PPG and PTMG imparted an appropriate viscosity to give sufficient diffusion and phase separation, as noted from the real time data. In contrast, PEG showed high viscosity, which slowed the entire phase separation, as noted from the real time data. In conclusion, the electro-optical performance of HPDLC can be optimized by the appropriate molecular architecture of the polyol. The results may provide important advantages for the manufacture of HPDLC films.

ACKNOWLEDGMENT

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