



The regulation of polymer structures and electro-optical properties of epoxy-mercaptan-based phase separated liquid crystals / polymer composites



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ABSTRACT

Morphologies of polymer networks are playing a key role in affecting the electro-optical (E-O) properties of a polymer dispersed liquid crystals (PDLCs) material. In this paper, the relationships between the polymer morphologies and the E-O properties of PDLCs are investigated in an unexplored thermally curing system based on epoxy/low-molar-mass-mercaptan. The polymer morphologies in this curing system can be regulated from polymer beads to porous polymer matrix by varying the liquid crystals (LCs) contents, chemical structures of epoxy monomers, and functionality of thiol hardeners. Interestingly, great improvements of E-O properties occur as the polymer structures change from polymer beads to porous frameworks, even though with an abnormal low LCs contents. Eventually, the mechanism for the formation of different polymer structures are illustrated and the relationships between the E-O properties and polymer structures are established. This work provides new insights in morphology control and optimizing the E-O properties in thermally cured PDLCs films.

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1. Introduction

Polymer-dispersed liquid crystals (PDLC) films represent an important class of electrically switchable composites materials and have attracted intensive scientific studies due to their combination of electrically responsive/birefringent characteristic of liquid crystals (LCs) and many excellent properties of polymer such as good mechanical strength, well flexibility and easy processability [1–3]. In their most common form, PDLC films have a phase-separated polymer framework where liquid-crystalline droplets are

uniformly dispersed [4]. This phase-separated composite has a spatially varying refractive index (RI) and efficiently scatters light, making it opaque. Additionally, the light scattering state can be switched off by applying an electric field to realign the orientations of LCs due to a good match of the ordinary RI of LCs and that of polymer. This electro-optical (E-O) properties of PDLC films make them attractive in applications such as flexible displays, smart windows and other optical devices [5–10].

Typically, a PDLC film can be obtained by polymerization induced phase separation via UV or thermal curing [11–15]. The UV curing method is fast and solvent-free. However, a yellow stain may occur after polymerization and the bonding power is relatively weak. Moreover, the volatile polymeric monomers are detrimental to health [16,17]. Compared with UV initiated polymerization, thermally induced phase separation presents the following advantages such as well processability, less contamination, lower cost, strong bonding energy, and no yellow stain, therefore arises much more attention [14,18,19]. The first instance of thermally cured PDLC films were reported by Doane et al. using the epoxy/polyamine curing system [1]. The E-O properties of the as-made films

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could be optimized by controlling the size, spacing and distribution of liquid-crystalline microdroplets within the solid polymer. Then, they also carried out the preparation of the films from the epoxy/poly-thiol system, and revealed that the driving voltages of the films were strongly correlated with the resistivity of the materials [20–22]. Previous works in our group reported the preparation of PDLC films from epoxy/low-molar-mass-amine system, and investigations of the impacts of chemical structures of epoxy monomers and amine, contents of LCs and catalysts on the E-O properties of the films were systematically carried out [17,23–26].

All these above works on PDLC films suggests that the comprehensive performances of the films, especially E-O properties, are closely related with the structures and the compositions of the film. Generally, decreasing the LCs content will worsen the E-O properties of PDLC films, accompanied with increasing of the threshold (V_{th})/saturation (V_{sat}) voltages and decreasing of contrast ratios (CRs) because the sizes of LCs droplets within the porous polymer structures are smaller as LCs content decreases. Here, V_{th} and V_{sat} are defined as the voltages required for the transmittance to reach 10% or 90% of the maximum transmittance, respectively [27–30]. CR is defined as the value of T_{on}/T_{off} , where T_{on} and T_{off} are transmittances of the on- and off-states of PDLC films [25]. However, although increasing the LCs content can greatly improve the E-O properties, it will not only increase the cost of the film, but also deteriorate the mechanical strength, especially the peeling strength of the film due to the low polymer content, which is not beneficial for the film to be used in practical applications. Even though great efforts have been carried out to optimize the polymer structures within the film, up till now, it is still a great challenge to achieve a PDLC film with both excellent E-O properties and high mechanical strength (high polymer content) at the same time.

To allow further understanding the impacts of polymer structures on the E-O properties of PDLC films, the presented work prepared a series of PDLC films in epoxy/low-molar-mass-mercaptan system. We systematically examined the impacts of LC content, curing temperature, epoxy monomers and thiol functionality on the phase-separated structures of polymer, and found that the polymer morphologies have great impacts on the E-O properties of the as-made PDLC films in this curing system, especially a great improvement of E-O properties was observed by turning the polymer structures from epoxy beads to porous frameworks, even though involving a decrease of LCs content. This work is meaningful not only for optimizing PDLC films performances but also offering new insights into regulating morphologies of epoxy-mercaptan-based PDLC films.

2. Experimental

2.1. Materials

Fig. 1 shows the chemical structures of the materials used. Nematic LCs, SLC-1717, was purchased from Shijiazhuang Yongsheng Huatsing Liquid Crystal Co., Ltd. Three kinds of hardeners with different functionalities, Trimethylpropane tris(2-mercaptoacetate) (3S, 85%), Pentaerythritol tetrakis(2-mercaptoacetate) (4S, >85%) and Dipentaerythritol hexakis(3-mercaptoacetate) (6S, 90%), were purchased from J&K scientific Ltd., Tokyo Chemical Industry Co., Ltd. and Frontier Scientific, Inc., respectively. Epoxy monomers, 1,4-bis((2,3-epoxypropoxy)methyl)cyclohexane (BEC, 95%) and Diglycidyl 1,2-cyclohexanedicarboxylate (DCD, 95%), were obtained from Tianjin Heowns Biochem LLC. N-(4-Pyridyl)dimethylamine (DMAP, 99%) obtained from Aladdin is used as the accelerator. All these materials were used without further purification.

2.2. Sample preparation

Four groups of samples, Group A, Group B, Group C and Group D, were prepared according to the feeding ratios listed in Table 1. They were prepared in the same conditions except the curing temperatures applied in Group A, the LCs content in Group B, the composition of epoxy monomers in Group C and the functionalities of thiols used in Group D.

All the samples were prepared according to the following procedures (Scheme 1). Firstly, each component of the sample was mixed thoroughly according to the feeding ratio in Table 1 to obtain a homogeneously syrup (Scheme 1a). Then, the syrup was sandwiched between two substrates of transparent ITO-coated glasses by capillary action as shown in Scheme 1b. The thickness of the cell was adjusted to $30 \pm 1 \mu\text{m}$ by polyethylene terephthalate (PET) spacers. After that, the epoxy-thiol based PDLC film was made by curing the sample at a designed temperature in an oven (Scheme 1c).

2.3. Measurements

The morphologies of the PDLC films were observed by scanning electron microscopy (SEM, S-4800). All samples were dipped in hexane (AR) for about seven days at room temperature to fully extract the liquid crystalline molecules, and then dried in vacuum for 24 h; thin layers of gold were coated onto the films to eliminate any electric charge problem.

FT-IR spectra were obtained on a BrukerVector-22 FT-IR spectrophotometer using a KBr pellet over a range of $4000\text{--}600 \text{ cm}^{-1}$.

The E-O properties of all samples were measured by a liquid crystal device parameter tester (LCT-5016C, Changchun Liancheng Instrument Co. Ltd., China) at room temperature. A halogen laser beam (560 nm) was used as the incident light source. The transmittances of the PDLC films were recorded by a photodiode, which were further monitored by a digital storage oscilloscope. The distance between the detector and the samples was approximately 300 mm, and an electric field (square wave, 50 Hz) was applied during the measurement.

The UV–Vis spectra of the sample was obtained by a UV/vis/NIR spectrophotometer (Perkin Elmer, Lambda 950). The transmittance of a blank cell was normalized as 100%.

3. Results and discussion

It is well known that the curing temperature plays an imperative role in the curing process of a PDLC film, because it not only impacts the viscosity of the syrup and the compatibility between polymeric monomers and LCs, but also influence the curing rate of system [31]. Samples in Group A prepared in different curing temperatures were investigated to find the proper curing temperature. From SEM observations in Fig. 2, it can be seen that when the curing temperatures were below 313.15 K, the morphologies of polymer matrix in Sample A1 and A2 had heterogeneous porous structures (Fig. 2a and b). Actually, the two separated phases of LC domains and polymer in Sample A1 and A2 could be even distinguished from naked eyes. After increasing the curing temperature to 333.15 K, a homogenous porous polymer structure of Sample A3 can be observed in Fig. 2c. Further raising the temperature to 353.15 K can also obtained a homogenous porous polymer structure of Sample A4, but a drastic decrease of pore sizes can be observed in Fig. 2d. These impacts of various curing temperatures on the resulted polymer structures can be explained by the following explanation. When the temperature was below a critical solubility temperature, the two phases of LCs and polymeric monomers were immiscible. LCs were separated out of the syrup and coalesced into large

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