The Electro-Optical Properties and Adhesion Strength of Epoxy-Polymercaptan-Based Polymer Dispersed Liquid Crystal Films

Gang Chen 1,†, Wei Hu 2,†, Le Zhou 2, Huimin Zhang 3, Ling Wang 4, Cuihong Zhang 3, Jian Sun 2, Lanying Zhang 2,*, Xiaotao Yuan 5,* and Siquan Zhu 1,6,*

1 School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, China; chengang6833@163.com
2 Department of Materials Science and Engineering, College of Engineering, Peking University, Beijing 100871, China; work.huwei@pku.edu.cn (W.H.); zhoul@pku.edu.cn (L.Z.); sunjian10@pku.edu.cn (J.S.)
3 Key Laboratory of Organic Polymer Photoelectric Materials, School of Science, Xijing University, Xi’an 710123, China; zhanghuimin850214@126.com (H.Z.); cuicui1008@126.com (C.Z.)
4 School of Materials Science and Engineering, Tianjin University, Tianjin 300072, China; iwang17@tju.edu.cn
5 Department of Chemistry and Chemical Engineering, School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China
6 Department of Ophthalmology, Beijing Anzhen Hospital of Capital Medical University, Beijing 100020, China
* Correspondence: zhanglanying@pku.edu.cn (L.Z.); yuanxt@ustb.edu.cn (X.Y.); siquanzhu@sina.com (S.Z.)
† These authors contributed equally to this work.

Abstract: Polymer dispersed liquid crystal (PDLC) films were prepared by thermal polymerization-induced phase separation in epoxy/polymercaptan/liquid crystal (LC)/accelerator mixtures. The effects of the concentration of LC and accelerator, the curing temperature, and the structure of epoxy monomer on the electro-optical (E–O) properties and adhesion strength of the PDLC films were studied systematically via E–O, peel strength, DSC, IR, and gel measurements. It showed that different polymer structures and the properties of the polymer can be obtained by changing the compositions and the curing temperature, which had significant impacts on the E–O properties of the PDLC films. Meanwhile, the polymer matrix with high glass-transition temperature (T_g) and small pore size will improve the adhesion strength of the PDLC film, and these kinds of epoxy-polymercaptan-based PDLC films have better performance than traditional acrylate-based PDLC in the aspect of the adhesion strength. This work may provide some inspiration in preparing epoxy-polymercaptan-based PDLC films, which both have excellent E–O performance and good adhesion strength, towards roll-to-roll processes and large-scale flexible applications.

Keywords: polymer dispersed liquid crystal; polymer network morphologies; electro-optical properties; adhesion strength

1. Introduction

Polymer dispersed liquid crystal (PDLC) film is a kind of composite material consisting of submicron-sized droplets of liquid crystal (LC) embedded within a polymer matrix [1–9] and has a unique electric-switchable property between transparent-state and opaque-state. In general, the ordinary refractive index (n_o) of LC is adjusted to match the refractive index (n_p) of the polymer matrix. Under the application of the electric field, the PDLC film will become transparent, for the LC molecules are induced to align along the same direction as the electric field. Once the electric field has been removed, the PDLC film becomes opaque, because of the random alignment of the LC molecules induced by the polymer matrix [2,10]. The PDLC films with this electro-optical property pave the way for multifarious applications of PDLC films such as smart windows, flexible displays,
and other various optical devices [11–13] and provide a rich platform for making new liquid-crystal-based devices [14–17].

The flexibility and large area are an obvious trend of the development of smart windows. PDLC can be made into the large-scale flexible film due to its combined unique E-O properties of LC [18–21] and some excellent properties of the polymer, such as excellent flexibility, outstanding adhesion strength [22], and the availability of large-scale flexible manufacturing. In the large-scale flexible PDLC films, two pieces of conductive polymer films are used as the substrates of the PDLC film. To guarantee the quality and the stability of the flexible PDLC films in the productive process and usage, the polymer matrix must have enough adhesive property to ensure that the PDLC film has enough adhesion strength between the substrates of the PDLC film.

Yang’s group has done many works to improve the adhesion strength of the PDLC films [14,17,23,24], however, the adhesion strength of the PDLC film based on the poly-acrylate still cannot completely satisfy the application requirements. The epoxy-based polymer has been widely used as the binder for encapsulation materials for semiconductor devices [25,26], intumescent fire-resistive coatings [27], etc. due to their remarkable adhesion and mechanical property.

Herein, to further research the effect of the compositions and technological conditions on the polymer structures, E-O properties, and adhesion strength of PDLC films, the epoxy-polymercaptan-based polymer was selected as the polymer matrix to improve the adhesion strength and several series of PDLC films were fabricated. The effects of the concentration of LC, the curing temperature, the concentration of accelerator and the structure of epoxy monomer on, the E-O properties and adhesion strength of these PDLC films have been systematically researched. Particularly, by roll-to-roll processes [14,17], which are the most widely-used processing method of flexible large-scale PDLC film, these PDLC films were fabricated with the flexible conductive PET films as the substrates, and the adhesion strength of the PDLC film was measured and compared with acrylate-based PDLC films.

2. Materials and Methods

2.1. Materials

Nematic LC E8 ($T_{N-I} = 72.9 \, ^{\circ}C$, $n_o = 1.525$, $n_e = 1.773$) was obtained by mixing five mesogens according to literature [28]. Epoxide monomers, 2,2-Bis(4-glycidyloxy-phenyl)propane (DGEBA, >85.0%) and trimethylolpropane triglycidyl ether (TMPTGE) were purchased from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan and Beijing Hanlun Science and Technology Development Co., Ltd., Beijing, China, respectively. A mercaptan (SH) terminated liquid curing agent, CAPCURE® 3-800 (3-800) was purchased from Gabriel Performance Products, Ashtabula, OH, USA. Catalyst, 2,4,6-tris(dimethylaminomethyl)phenol (DMP-30, 95%) was purchased from Aladdin Industrial Corporation, Shanghai, China. The chemical structures of the compounds used here were shown in Figure 1. All of these materials were used as received without further purification.

![Figure 1. The chemical structures of the compounds used in this paper.](image)
2.2. Sample Preparation

As shown in Table 1, four groups of samples were prepared according to the feeding ratios. They were prepared in the same composition and procedure except the concentration of LC in Group A, the curing temperature in Group B, the concentration of DMP-30 in Group C, and the ratio of DGEBA/TMPTGE in Group D.

Table 1. The compositions and curing temperature of the samples used in this paper.

| Sample | Composition (DGEBA/TMPTGE/E8/DMP-30, wt.%) | Curing Temperature (°C) |
|--------|---------------------------------------------|-------------------------|
| Group A |                                             |                         |
| A1     | 8.12/24.38/32.50/35.00/0.20                 | 60                      |
| A2     | 7.50/22.50/30.00/40.00/0.20                 | 60                      |
| A3     | 6.87/20.63/27.50/45.00/0.20                 | 60                      |
| A4     | 6.25/18.75/25.00/50.00/0.20                 | 60                      |
| Group B |                                             |                         |
| B1     | 7.50/22.50/30.00/40.00/0.20                 | 45                      |
| B2     | 7.50/22.50/30.00/40.00/0.20                 | 60                      |
| B3     | 7.50/22.50/30.00/40.00/0.20                 | 75                      |
| B4     | 7.50/22.50/30.00/40.00/0.20                 | 90                      |
| Group C |                                             |                         |
| C1     | 7.50/22.50/30.00/40.00/0.05                 | 60                      |
| C2     | 7.50/22.50/30.00/40.00/0.10                 | 60                      |
| C3     | 7.50/22.50/30.00/40.00/0.20                 | 60                      |
| C4     | 7.50/22.50/30.00/40.00/0.40                 | 60                      |
| Group D |                                             |                         |
| D1     | 30.00/-/30.00/40.00/0.20                    | 60                      |
| D2     | 22.50/7.50/30.00/40.00/0.20                 | 60                      |
| D3     | 15.00/15.00/30.00/40.00/0.20                | 60                      |
| D4     | 7.50/22.50/30.00/40.00/0.20                 | 60                      |
| D5     | -/30.00/30.00/40.00/0.20                    | 60                      |

All of the samples listed in Table 1 were prepared by the following procedure. Firstly, each component in the sample was vigorously stirred together to obtain a homogenous syrup. Then, to measure the E-O properties of the PDLC films, the syrup was sandwiched between two substrates of transparent ITO-coated glasses by capillary action. And to measure the adhesion strength of the PDLC films, the syrup was sandwiched between two transparent and conductive PET films via a roll-to-roll process. The thickness of the PDLC film was adjusted to 20 ± 1 µm by polyethylene terephthalate (PET) spacers between two substrates of transparent ITO-coated glasses, or by glass spacers between two conductive PET films substrates. And to measure the DSC, IR spectra, and gel fraction of the polymer network, the syrup was poured into the centrifuge tube. After that, the sample was cured at a designed temperature in an oven for 24 h, so that the sample was completed.

2.3. Measurements

The E-O properties of the samples were measured by a liquid crystal parameter tester (LCT-5066C, The North LCD Engineering R&D Center, Changchun, China) at room temperature. A halogen laser beam (560 nm) was used as the incident light source, and an electric field (square wave, 100 Hz) was applied during the measurement. The voltage increases linearly with the time and 142 s is needed for increasing the voltage from 0 to 100 V.

To measure the morphologies, glass-transition temperature ($T_g$), IR spectrometry, and gel fraction of polymer structures, all of the samples were dipped in hexane (AR) (Beijing Tong Guang Fine Chemicals Company, Beijing, China) for twenty days at room temperature to fully extract the liquid crystalline molecules and then dried at 60 °C for one day. The morphologies of polymer structures of the PDLC films were observed by scanning electron microscopy (SEM, Hitachi S-4800, Hitachi, Tokyo, Japan). Thin layers of gold were coated onto the films to eliminate any electric charge problem. The $T_g$ was measured by
differential scanning calorimeter (PerkinElmer DSC 8000, Waltham, MA, USA). The heating rate is 40 °C/min. The IR spectra were measured by FT-IR Spectrometer (PerkinElmer Spectrum Two, Waltham, MA, USA).

As shown in Figure S1 in Supporting Information, the adhesion strength of the PDLC films with the flexible conductive PET film substrates was tested using a universal tensile testing machine (CMT6103, MTS Systems (China) Co., Ltd., Shenzhen, China) at the rate of 10 mm/min, and the tested PDLC film was in the size of 1.4 cm × 2.0 cm.

3. Results and Discussion

3.1. The Effect of the Concentration of LC on the E-O Properties and Adhesion Strength of the PDLC Films

The effect of the concentration of LC on the E-O properties and adhesion strength of the PDLC films has been researched in Group A. The weight ratio of DGEBA and TMPTGE was fixed at 1:3 and the curing temperature was 60 °C.

As shown in Figure 2a–c, the transmittance of all samples in Group A increases as the applied voltage increases. Specifically, when the concentration of LC increases from 35 to 50 wt.%, the threshold voltage (V_th) and saturation voltage (V_sat) of samples A1–A4 decrease gradually. And the decay time (t_off) increases sharply as the concentration of LC increases from 35 to 50 wt.%, yet the rise time (t_on) does not change obviously. However, with the concentration of LC increasing from 35 to 50 wt.%, the contrast ratio (CR) of samples A1–A4 does not change linearly. When the concentration of LC is not more than 40 wt.%, sample A1 and A2 have a high contrast ratio that is beyond 100. However, further increase in the concentration of LC to 45 and 50 wt.% results in a remarkable decrease of CR due to the high vertical off-state transmittance (T_0). Here, the V_th and V_sat are defined as the voltages required for the transmittance to reach 10% or 90% of the maximum transmittance, respectively [4,5,10]. The t_on and t_off are defined as the time required for transmittance changing from 0% to 90.0% upon turn on, and from 100.0% to 10.0% upon turn off, respectively [6]. And the CR is defined as the value of T_sat/T_0, where the vertical saturation transmittance (T_sat) and T_0 are transmittances of the on- and off-states of PDLC films [5]. The adhesion strength of the PDLC films in Group A decreases gradually when the concentration of LC increases from 35 to 50 wt.%, as shown in Figure 2d.

Figure 2. (a) The voltage dependence of the transmittance, (b) the response time, (c) the saturation transmittance, off-state transmittance, contrast ratios, and (d) adhesion strength of samples A1–A4; (e) FTIR spectra and gel fractions and (f) DSC thermographs of the polymer matrix of samples A1–A4.
To explain the above results, the FTIR spectra, gel fractions, $T_g$ and morphologies of the polymer matrix of samples A1–A4 were measured, as shown in Figures 2e,f and 3. All of the gel fractions of samples A1–A4 are above 90 wt.% as shown in Figure 2e, which indicate the polymeric monomer has been reacted sufficiently. As shown in Figure 3, a significant contrast of the polymer structures between A1, A2 and A3, A4 can be found. To be specific, a typical porous polymer structure of PDLC films was observed when the concentration of LC is not more than 40 wt.%, which results in good E-O properties of sample A1 and A2. And the change in concentration of LC from 35% to 40% leads to the increase of pore size from sample A1 to A2, which is the main reason for the lower $V_{th}$ and $V_{sat}$, the slower $t_{off}$, and the higher CR of Sample A2 than Sample A1. This is because the LC molecules in a larger pore would decrease the specific surface area of the LC domain, and so the LC molecules in sample A2 are much more easily driven by an external electric field to orient along the direction of the electric field due to the weaker anchoring effect of polymer matrix on the LC molecules [7]. And the anchoring effect of polymer matrix on the LC molecules is the main driving force for reorienting the LC molecules to random alignment [2], so Sample A2 with larger pore size has a slower $t_{off}$ than Sample A1. However, when the concentration of LC increases to 45 and 50 wt.%, the polymer structures are composed of beads, and the liquid crystal phases are the continuous phases after phase separation. The continuous phase of LC molecules weakens the anchoring effect of polymer matrix on the LC molecules, so the LC molecules are easier to be driven by the electric field, which gives rise to lower $V_{th}$ and $V_{sat}$. And the sharp decrease of CR when the concentration of LC increases to 45 and 50 wt.% can also be attributed to this drastic change of polymer structures. In general, a higher CR can be obtained when the pore sizes can be comparable to the visible light [29]. However, the effective porous structure does not exist in samples A3 and A4, and the continuous phase of liquid crystal cannot scatter the incident light effectively, which results in a high $T_0$. Furthermore, as the concentration of LC increases, the size of the epoxy beads decreases and the molecular interactions between LC molecules and polymer matrix become much weaker, which results in the slower $t_{off}$ of sample A4 compared to sample A3.

![Figure 3. The polymer morphologies of samples A1–A4: (a) Sample A1; (b) Sample A2; (c) Sample A3; (d) Sample A4.](image)

The decrease of adhesion strength from sample A1 to sample A4 can be attributed to the change of the concentration of polymer matrix. For the adhesion strength is supported by the polymer matrix, the less concentration of the polymer matrix could not sustain
high adhesion strength. Meanwhile, the $T_g$ of the polymer matrix also has a significant influence on the adhesion strength of the PDLC films. As shown in Figure 2f, the $T_g$ of the polymer matrix of PDLC films increases gradually as the concentration of LC increases, which leads to that the polymer matrix has a smaller displacement when sustains the same tension. Despite the $T_g$ of the polymer matrix of sample A1 is lower than that of sample A2, the higher adhesion strength of sample A1 than that of sample A2 indicates that the concentration of polymer is a more fundamental factor to decides the adhesion strength. Although the $T_g$ of samples A1, A2 are lower than samples A3, A4, the lower adhesion strength of samples A3, A4 indicates that the continuous phase of the polymer matrix is crucial to the excellent adhesion strength and that the polymer density increases as the concentration of polymeric monomer decreases.

This change of the polymer structures from porous structure to epoxy beads can be ascribed to the inhomogeneous gelation process for the chain ring-opening polymerization of epoxy monomers and polymercaptan [30]. To be specific, the curing process starts with the formation of microgel particles resulting from the curing of polymeric monomers. As the curing reaction progresses, the size of these microgel particles increases continually for the microgel particles to react with the uncured monomers or other microgel particles. The polymerization rate depends on the concentration of monomers [31]. When the concentration of LC is low enough, such as 35 wt.%, the microgel particles have more possibilities to react with the uncured monomers and other microgel particles, so the microgel particles become large and coalesce gradually at the same time, which leads to the formation of a continuous polymer phase. Meanwhile, the fast polymerization rate leads to the insufficient phase separation of polymer and LC. The continuous polymer phase and the insufficient phase separation result in the polymer porous structure with a smaller pore size (Figure 3a). As the concentration of the LC increases to 40 wt.%, the polymerization rate becomes slower and a better phase separation occurs, leading to a continuous polymer phase with a larger pore size (Figure 3b). However, accompanied with the further increase of the concentration of LC, there are not enough microgel particles and uncured monomers to polymerize and coalesce into a continuous polymer phase, so the further polymerization of the microgel particles leads to the formation of interconnected microspheres until the curing reaction terminates (Figure 3c,d). Meanwhile, the liquid crystal phase is changed into a continuous phase. The higher the concentration of LC is, the less the concentration of the polymeric monomer is, so the size of the interconnected microspheres becomes smaller as the concentration of LC increases from 45 wt.% (Figure 3c) to 50 wt.% (Figure 3d).

3.2. The Effect of the Curing Temperature on the E-O Properties and Adhesion Strength of the PDLC Films

The effect of the curing temperature on the E-O properties and adhesion strength of the PDLC films has been researched in Group B. Here, the weight ratio of DGEBA and TMPTGE was fixed at 1:3 and the curing temperature was 60 °C. As shown in Figure 4a–c, when the curing temperature is 45 °C, the PDLC film has very low driven voltages, but the CR is too low for the high $T_0$. With the gradual increase of the curing temperature from 45 to 75 °C, the $V_{th}$, $V_{sat}$, and CR increase gradually and the $t_{off}$ decreases. When the curing temperature is 90 °C, the E-O properties of sample B4 are too bad because of the high $T_0$ and the low $T_s$. And every sample in Group B has a very fast $t_{on}$. The adhesion strength increases gradually when the curing temperature increases from 60 to 90 °C, but the adhesion strength of sample B1 is a little higher than that of sample B2, as shown in Figure 4d.

The low CR of samples B1 and B4 can be explained by their microstructure. The FTIR spectra, gel fractions, $T_g$ and morphologies of the polymer matrix of samples B1–B4 were measured, as shown in Figures 4e,f and 5. All of the gel fractions of samples B1–B4 are above 94 wt.% as shown in Figure 4e, which indicates the polymeric monomer has been reacted sufficiently. As shown in Figure 5a, a nonhomogeneous porous structure can be found in sample B1. Diameters of some larger pores are more than 10 μm and others are less than 1 μm, which could not scatter the visible light effectively. The formation of
the nonhomogeneous porous structure can be ascribed to the bad intersolubility of the polymeric monomer and the LC molecules at 45 °C, which leads to that the pores with smaller size were formed in the monomer-rich regions and the pores with larger size were formed in the LC-rich regions [31]. As the curing temperature rises to 60 °C, a typical polymer porous structure has been formed and sample B2 renders excellent E-O properties. However, the further increase of curing temperature to 75 °C gives rise to smaller pore size, which results in a higher $V_{th}$ and $V_{sat}$ of sample B3. The smaller pore size is formed due to the faster curing rate and the good intersolubility of LC molecules and polymer [29] in the higher curing temperature. The better intersolubility of LC molecular and polymer decelerates the phase separation of the LC molecular and polymer, and the faster curing rate leads to the fast formation of the polymer matrix. So, there is not enough time for sufficient phase separation, which induces the formation of the porous polymer with a smaller pore size. For the same reason, when the curing temperature increases to 90 °C, a polymer structure of infinitesimal aspheric pore has been formed in sample B4, as shown in Figure 5d.

Although the $T_g$ of sample B3 is lower than that of B2 (Figure 4f), the adhesion strength of sample B3 is higher than that of sample B2, which indicates that the pore size of the polymer matrix could markedly influence the adhesion strength of PDLC film, and the polymer matrix with small pore size has large adhesion strength. The highest $T_g$ and smallest pore size of sample B4 leads to the highest adhesion strength in Group B. However, the adhesion strength of sample B1 has a little higher than that of sample B2, which can be ascribed to the higher $T_g$ and nonhomogeneous porous polymer structure of the sample B1, yet this nonhomogeneous porous polymer structure is not beneficial to the E-O properties of the PDLC film.

![Figure 4](image_url) **Figure 4.** (a) The voltage dependence of the transmittance, (b) the response time, (c) the saturation transmittance, off-state transmittance, contrast ratios, and (d) adhesion strength of samples B1–B4; (e) FTIR spectra and gel fractions and (f) DSC thermographs of the polymer matrix of samples B1–B4.
Figure 5. The polymer morphologies of samples B1–B4: (a) Sample B1; (b) Sample B2; (c) Sample B3; (d) Sample B4.

3.3. The Effect of the Concentration of DMP-30 on the E-O Properties and Adhesion Strength of the PDLC Films

The accelerator plays a very important role in the polymerization rate of the epoxy resin. Here, DMP-30 was chosen as the accelerator in our curing system and the effect of different concentrations of DMP-30 on the E-O properties and adhesion strength of the PDLC films has been researched in Group C.

As shown in Figure 6a–c, the $V_{th}$ and $V_{sat}$ are almost stable when the concentration of DMP-30 is not more than 0.2 wt.%, and the further increase of the concentration of DMP-30 results in the increase of the $V_{th}$ and $V_{sat}$. From 0.05 to 0.4 wt.% of the concentration of DMP-30, $t_{off}$ decreases dramatically, the $CR$ increases notably and $t_{on}$ is almost unchanged. The $T_{g}$ of these samples have a little decline with the increase of the concentration of DMP-30. The adhesion strength increases as the concentration of DMP-30 increases from 0.05 to 0.4 wt.%, as shown in Figure 6d.

The FTIR spectra, gel fractions, $T_g$, and morphologies of the polymer matrix of samples C1–C4 were measured, as shown in Figures 6e,f and 7. All of the gel fractions of samples C1–C4 are above 93 wt.% as shown in Figure 6e, which indicate the polymeric monomer has been reacted sufficiently. It can be found that a porous polymer structure has been formed in all of the samples. The porous polymer structure with nearly equal pore size has been formed when the concentration of DMP-30 is not more than 0.2 wt.%, which leads to similar $V_{th}$, $V_{sat}$, and $CR$ of the samples C1–C3. The further increase of the concentration of DMP-30 induces the obvious decrease of the pore size of polymer structure, which leads to the obvious increase of $V_{th}$ and $V_{sat}$. All of the samples have a very fast $t_{on}$, and the $t_{off}$ decreases gradually when the concentration of DMP-30 increases from 0.05 to 0.4 wt.%, for the decrease of the pore size. The biggest $CR$ is obtained when the concentration of DMP-30 is 0.4 wt.%, for the comparable size of the pore size and the wavelength of visible light. This is because the $CR$ is defined as the value of $T_s/T_0$, and in general, the more light was scattered by the PDLC films, the lower the $T_0$ is. When the pore size is comparable to the wavelength of the visible light, the degree of scattering is the biggest, which results to the lowest $T_0$. Thus, the biggest $CR$ can be obtained. The decrease of the pore size with the increase of the concentration of DMP-30 can be ascribed to the change of curing rate. The DMP-30 can effectively accelerate the curing rate, which results in the fast formation of the polymer network before the sufficient phase separation. The more the concentration of
DMP-30 is, the faster the curing rate is, so the pore size decreases with the increase of the concentration of DMP-30.

![Figure 6](image)

**Figure 6.** (a) The voltage dependence of the transmittance, (b) the response time, (c) the saturation transmittance, off-state transmittance, contrast ratios, and (d) adhesion strength of samples C1–C4; (e) FTIR spectra and gel fractions and (f) DSC thermographs of the polymer matrix of samples C1–C4.

![Figure 7](image)

**Figure 7.** The polymer morphologies of samples C1–C4: (a) Sample C1; (b) Sample C2; (c) Sample C3; (d) Sample C4.

The increase of adhesion strength with the increase of the concentration of DMP-30 is because of the decrease in the pore size of the polymer matrix (Figure 7), which is a similar change rule to the one mentioned above. And the upward tendency of $T_g$ of the polymer
matrix (Figure 6f) is another important factor that leads to the increase of adhesion strength. The highest \( T_g \) and smallest pore size of sample C4 leads to the highest adhesion strength in Group C.

3.4. The Effect of the Structure of Epoxy Monomer on the E-O Properties and Adhesion Strength of the PDLC Films

The effect of the structure of epoxy monomer on the E-O properties and adhesion strength of the PDLC films has been researched in Group D. Here, two kinds of epoxy monomer, DGEBA and TMPTGE have been used, with the former having a rigid core in the molecular structure and the latter having a flexible molecular structure.

As shown in Figure 8a–c, with the increase of the concentration of TMPTGE, the \( V_{th} \) and \( V_{sat} \) of the sample in Group D decrease gradually, and \( t_{off} \) becomes faster gradually except for sample D5. All of the samples in Group D have a very fast \( t_{on} \) that is less than 4 ms. The samples containing DGEBA have higher CR, and the CR becomes higher with the increase of the concentration of TMPTGE. The very low CR of sample D5 is due to the high \( T_0 \), as shown in Figure 8a,c. As shown in Figure 8d, the adhesion strength of the PDLC film decreases gradually when the weight ratio of DGEBA/TMPTGE changed from 4:0 to 0:4.

![Figure 8](image-url)

**Figure 8.** (a) The voltage dependence of the transmittance, (b) the response time, (c) the saturation transmittance, off-state transmittance, contrast ratios, and (d) adhesion strength of samples D1–D5; (e) FTIR spectra and gel fractions and (f) DSC thermographs of the polymer matrix of samples D1–D5.

The FTIR spectra, gel fractions, \( T_g \), and morphologies of the polymer matrix of samples D1–D5 were measured, as shown in Figures 8e,f and 9. All of the gel fraction of samples D1–D5 are above 92 wt.%, which indicate the polymeric monomer has been reacted sufficiently. It can be found that typical porous polymer structures of PDLC were observed in samples D1–D4. And with the increase of the concentration of TMPTGE, the pore size increases gradually, which gives rise to the gradual decrease of \( V_{th} \) and \( V_{sat} \), the gradual rise of CR from sample D1 to sample D4. However, sample D5, which does not contain DGEBA, has a disparate polymer structure that is a co-existent framework of polymer porous structure with large size and interconnected microspheres, and the interconnected microspheres balls are distributed within the porous structure. This co-existent framework results in a
high $T_0$ and low CR. The increase of the pore size from sample D1 to sample D5 can be ascribed to the dilution effect of TMPTGE. The viscosity of DGEBA is much higher than that of TMPTGE. When the ratio of DGEBA/TMPTGE changes from 4:0 to 0:4, the viscosity of syrup decreases gradually, so a more sufficient phase separation occurs in the process of polymerization, which leads to the large pore size.

![Figure 9. The polymer morphologies of samples D1–D5: (a) Sample D1; (b) Sample D2; (c) Sample D3; (d) Sample D4; (e) Sample D5.](image)

The decrease of the adhesion strength from sample D1 to sample D5 is the combined effect of the $T_g$ and pore size of the polymer matrix. As shown in Figure 8f, the $T_g$ of the polymer matrix decreases when the weight ratio of DGEBA/TMPTGE changed from 4:0 to 1:3. This decrease of the $T_g$ and the increase of the pore size lead to the decline of the adhesion strength with the increase of concentration of TMPTGE. Although sample D5 has higher $T_g$ than sample D4, the adhesion strength of sample D5 decreases further for the large pore size.

It is worth noting that the $t_{off}$ becomes slower with the decrease in the pore size in Group D, which is opposite to the general study result that the porous structure with a small pore size leads to a faster $t_{off}$. This unusual phenomenon may be ascribed to the different epoxy monomers. The response times ($t_{on}$ and $t_{off}$) of PDLC films are governed by many factors: the size, shape, and director configuration of the LC droplet; the value of the deformation constants and rotational viscosity coefficient; the anchoring effect of polymer matrix on the LC molecules [2]. That general study result is obtained only in the case that the same polymeric monomers have been used, for the anchoring effect of polymer matrix on the LC molecules cannot be a constant if the polymeric monomer has been changed. In samples D1–D5, two kinds of epoxy monomers, DGEBA and TMPTGE, have been used, and the change of the ratio of DGEBA and TMPTGE leads to a dramatic change of the property of the polymer matrix, especially anchoring effect of polymer matrix on the LC molecules. For example, the $T_g$ of the polymer matrix in Group D decreases sharply when the weight ratio of DGEBA/TMPTGE changed from 4:0 to 0:4. And as described below, the refractive index of the polymer matrix changes when a different ratio of DGEBA and TMPTGE has been used. Thus, general study results could not be suitable for the interpretation of the change of the $t_{off}$ in Group D. And the result of Group D indicates the regulation of the polymeric monomer structure is an effective way to adjust the anchoring effect of polymer matrix on the LC molecules, and optimize the driven voltage and decay time simultaneously.
As shown in Figure 8a,c, it can be found that accompanied by the change of the ratio of DGEBA/TMPTGE, the $T_s$ of the PDLC films in Group D changes gradually, and the $T_s$ reaches a maximum when the ratio of DGEBA/TMPTGE equals 1:3. In general, the $T_s$ is decided by the matching degree of the $n_o$ of LC and $n_p$ of polymer matrix. The higher the matching degree of the $n_o$ of LC and $n_p$ of polymer matrix, the higher the $T_s$ will be [2]. Here, the $n_o$ of LC is almost unchanged, so it can be deduced that the $n_p$ of polymer matrix changes sharply with the change of the ratio of DGEBA/TMPTGE. When the ratio of DGEBA/TMPTGE is 1:3, the matching degree is the highest, so the highest $T_s$ has been achieved.

### 3.5. The Advantage of Adhesion Strength of the Epoxy-Polymercaptan-Based PDLC Films

As mentioned in the introduction, the epoxy-based polymer has been widely used as the binder due to its remarkable adhesion and adhesion property. Thus, we tried to compare adhesion strength of our epoxy-polymercaptan-based polymer dispersed liquid crystal films with other different LC-polymer composites. Here the optimized sample A2 was selected to measure the adhesion strength for the excellent comprehensive E-O properties. As shown in Figure 10, this adhesion strength has giant advantages over traditional acrylate-based PDLC and acrylate-based polymer-dispersed and stabilized liquid crystals [14,17,23].

![Figure 10.](image)

**Figure 10.** The adhesion strength of different LC-polymer composites: (A) The optimized sample in this work; (B) acrylate-based polymer-dispersed and stabilized liquid crystals (PD&SLC) doped with 5.0 wt.% ITO/SiO$_2$ nanocrystals reported by Xiao Liang et al. [14]; (C) acrylate-based PD&SLC doped with 5.0 wt.% Cs$_x$WO$_3$/PVP nanorods [17]; (D) acrylate-based polymer dispersed liquid crystals reported by Haonan Lin et al. [23]; (E) acrylate-based polymer dispersed liquid crystals of which the adhesion strength has been improved by doping with 3-(trimethoxysilyl)propyl methacrylate reported by Haonan Lin et al. [23].

### 4. Conclusions

In conclusion, we prepared several series of PDLC films by thermal polymerization-induced phase separation in epoxy/polymercaptan/liquid crystal (LC)/accelerator mixtures and found that the E-O properties and adhesion strength of these PDLC films can be adjusted flexibly by changing the compositions and the curing temperature. IR and gel measurements showed that the polymeric monomer has been reacted sufficiently after thermal-curing. The optimal E-O property of the PDLC film can be obtained in a homogeneous porous polymer structure with proper pore size and match of the refractive index. The polymer structure, the refractive index and the anchoring effect of the polymer matrix...
on the LC molecules can be adjusted by changing the structure of the epoxy monomer at the same time, providing an effective way to optimize the driven voltage and decay time simultaneously. And the alteration of the concentration of LC, the concentration of accelerator and the curing temperature can only influence the polymer structure. Meanwhile, the DSC measurements showed the $T_g$ of the polymer matrix can be adjusted by changing the compositions and the curing temperature. And the polymer matrix with high $T_g$ and small pore size will improve the adhesion strength of the PDLC film, and these kinds of epoxy-polymercaptan-based PDLC films have better performance than traditional acrylate-based PDLC in the aspect of the adhesion strength. This work may provide some inspiration in preparing epoxy-polymercaptan-based PDLC films, which both have excellent E-O performance and good adhesion strength, towards roll-to-roll processes and large-scale flexible applications.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/cryst11060576/s1, Figure S1: The measurement of the adhesion strength of the PDLC films: (a) The principle illustrator of the measurement of the adhesion strength and (b) the digital photograph of the adhesion strength testing process.

Author Contributions: Conceptualization, G.C., W.H., and S.Z.; Data curation, C.Z. and J.S.; Funding acquisition, J.S. and L.Z. (Lanying Zhang); Investigation, G.C., W.H., L.Z. (Le Zhou), and L.W.; Methodology, G.C., W.H., and L.Z. (Le Zhou); Project administration, X.Y. and S.Z.; Resources, G.C., H.Z., and L.Z. (Lanying Zhang); Supervision, X.Y. and S.Z.; Validation, X.Y. and S.Z.; Visualization, G.C. and C.Z.; Writing—original draft, G.C.; Writing—review & editing, G.C., W.H., and L.Z. (Lanying Zhang), L.W., L.Z. (Le Zhou), and S.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the National Key R&D Program of China (2019YFC1904702), the National Natural Science Foundation of China (NSFC) (Grant no. 51903004).

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Higgins, D.A. Probing the mesoscopic chemical and physical properties of polymer-dispersed liquid crystals. *Adv. Mater.* 2000, 12, 251–264. [CrossRef]
2. Doane, J.W.; Golemme, A.; West, J.L.; Whitehead, J.B.; Wu, B.-G. Polymer Dispersed Liquid Crystals for Display Application. *Mol. Cryst. Liq. Cryst.* 1988, 165, 511–532. [CrossRef]
3. Sun, Y.; Zhang, C.; Zhou, L.; Fang, H.; Huang, J.; Ma, H.; Zhang, Y.; Yang, J.; Zhang, L.-Y.; Song, P.; et al. Effect of a Polymercaptan Material on the Electro-Optical Properties of Polymer-Dispersed Liquid Crystal Films. *Molecules* 2017, 22, 43. [CrossRef] [PubMed]
4. Amundson, K.; van Blaaderen, A.; Wiltzius, P. Morphology and electro-optic properties of polymer-dispersed liquid-crystal films. *Phys. Rev. E* 1997, 55, 1646–1654. [CrossRef]
5. Maschke, U.; Coqueret, X.; Benmouna, M. Electro-Optical Properties of Polymer-Dispersed Liquid Crystals. *Macromol. Rapid Commun.* 2002, 23, 159–170. [CrossRef]
6. Murai, H.; Gotoh, T. Stabilization of Epoxy-Based Polymer-Dispersed Liquid Crystal Films by Addition of Excess Hardener. *Mol. Cryst. Liq. Cryst.* 1993, 226, 13–23. [CrossRef]
7. Li, W.; Cheng, Z.; Pan, G.; Liu, H.; Cao, H.; Yang, Z.; Yang, H. Effects of the mixture composition on the microstructure of polymer matrix and light scattering properties of liquid crystal/photo-polymerizable monomers composites. *Opt. Mater.* 2008, 31, 434–439. [CrossRef]
8. Chen, M.; Hu, W.; Liang, X.; Zhang, H.; Zhang, C.; Song, P.; Zhang, L.; Li, F.; Chen, F.; Yang, H. The regulation of polymer structures and electro-optical properties of epoxy-mercaptan-based phase separated liquid crystals/polymer composites. *Polymer* 2017, 127, 1–7. [CrossRef]
9. Montgomery, G.P.; Vaz, N.A. Contrast ratios of polymer-dispersed liquid crystal films. *Appl. Opt.* 1987, 26, 738–743. [CrossRef]
10. Mucha, M. Polymer as an important component of blends and composites with liquid crystals. *Prog. Polym. Sci.* 2003, 28, 837–873. [CrossRef]
11. Baetens, R.; Jelle, B.P.; Gustavsen, A. Properties, requirements and possibilities of smart windows for dynamic daylight and solar energy control in buildings: A state-of-the-art review. *Sol. Energy Mater. Sol. Cells* 2010, 94, 87–105. [CrossRef]
12. Sheraw, C.D.; Zhou, L.; Huang, J.R.; Gundlach, D.J.; Jackson, T.N.; Kane, M.G.; Hill, I.G.; Hammond, M.S.; Campi, J.; Greening, B.K.; et al. Organic thin-film transistor-driven polymer-dispersed liquid crystal displays on flexible polymeric substrates. *Appl. Phys. Lett.* 2002, 80, 1088–1090. [CrossRef]

13. Mach, P.; Rodriguez, S.J.; Nortrup, R.; Wiltzius, P.; Rogers, J.A. Monolithically integrated, flexible display of polymer-dispersed liquid crystal driven by rubber-stamped organic thin-film transistors. *Appl. Phys. Lett.* 2001, 78, 3592–3594. [CrossRef]

14. Liang, X.; Guo, S.; Chen, M.; Li, C.; Wang, Q.; Zou, C.; Zhang, C.; Zhang, L.; Guo, S.; Yang, H. A temperature and electric field-responsive flexible smart film with full broadband optical modulation. *Mater. Horiz.* 2017, 4, 878–884. [CrossRef]

15. Guo, S.-M.; Liang, X.; Zhang, C.-H.; Chen, M.; Shen, C.; Zhang, L.-Y.; Yuan, X.; He, B.-F.; Yang, H. Preparation of a Thermally Light-Transmittance-Controllable Film from a Coexistent System of Polymer-Dispersed Liquid and Polymer-Stabilized Liquid Crystals. *ACS Appl. Mater. Interfaces* 2017, 9, 2942–2947. [CrossRef] [PubMed]

16. Wang, L.; Urban, A.M.; Li, Q. Nature-Inspired Emerging Chiral Liquid Crystal Nanostructures: From Molecular Self-Assembly to DNA Mesophase and Nanocolloids. *Adv. Mater.* 2018, 1801335. [CrossRef]

17. Liang, X.; Guo, C.; Chen, M.; Guo, S.; Zhang, L.; Li, F.; Guo, S.; Yang, H. A roll-to-roll process for multi-responsive soft-matter composite films containing Cs3WO7 nanorods for energy-efficient smart window applications. *Nanoscale Horiz.* 2017, 2, 319–325. [CrossRef] [PubMed]

18. Wang, L.; Li, Q. Photochromism into nanosystems: Towards lighting up the future nanoworld. *Chem. Soc. Rev.* 2018, 47, 1044–1097. [CrossRef]

19. Gutiérrez-Cuevas, K.G.; Wang, L.; Zheng, Z.-G.; Bisoyi, H.K.; Li, G.; Tan, L.-S.; Vaia, R.A.; Li, Q. Frequency-Driven Self-Organized Helical Superstructures Loaded with Mesogen-Grafted Silica Nanoparticles. *Angew. Chem. Int. Ed.* 2016, 55, 13090–13094. [CrossRef]

20. Wang, L. Self-activating liquid crystal devices for smart laser protection. *Liq. Cryst.* 2016, 43, 2062–2078. [CrossRef]

21. Wang, L.; Li, Q. Stimuli-Directing Self-Organized 3D Liquid-Crystalline Nanostructures: From Materials Design to Photonic Applications. *Adv. Funct. Mater.* 2016, 26, 10–28. [CrossRef]

22. Belmonte, A.; Fernández-Francos, X.; Serra, À.; De la Flor, S. Phenomenological characterization of sequential dual-curing of off-stoichiometric “thiol-epoxy” systems: Towards applicability. *Mater. Des.* 2017, 113, 116–127. [CrossRef]

23. Lin, H.; Zhang, S.; Saeed, M.H.; Zhou, L.; Gao, H.; Huang, J.; Zhang, L.; Yang, H.; Xiao, J.; Gao, Y. Effects of the methacrylate monomers with different end groups on the morphologies, electro-optical and mechanical properties of polymer dispersed liquid crystals composite films. *Liq. Cryst.* 2020. [CrossRef]

24. Zhang, T.; Kashima, M.; Zhang, M.; Liu, F.; Song, P.; Zhao, X.; Zhang, C.; Cao, H.; Yang, H. Effects of the functionality of epoxy monomer on the electro-optical properties of thermally-cured polymer dispersed liquid crystal films. *RSC Adv.* 2012, 2, 2144–2148. [CrossRef]

25. Ho, T.-H.; Wang, C.-S. Modification of epoxy resin with siloxane containing phenol aralkyl epoxy resin for electronic encapsulation application. *Eur. Polym. J.* 2001, 37, 267–274. [CrossRef]

26. Ho, T.-H.; Wang, C.-S. Modification of epoxy resins with polysiloxane thermoplastic polyurethane for electronic encapsulation: 1. *Polymer* 1996, 37, 2733–2747. [CrossRef]

27. Wang, G.; Yang, J. Influences of molecular weight of epoxy binder on fire protection of waterborne intumescent fire resistive coating. *Surf. Coat. Technol.* 2012, 206, 2146–2151. [CrossRef]

28. Bronnikov, S.; Kostromin, S.; Zuev, V. Polymer-Dispersed Liquid Crystals: Progress in Preparation, Investigation, and Application. *J. Macromol. Sci. Part B* 2013, 52, 1718–1735. [CrossRef]

29. Smith, G.W.; Vaz, N.A. The relationship between formation kinetics and microdroplet size of epoxy-based polymer-dispersed liquid crystals. *Liq. Cryst.* 1998, 3, 543–571. [CrossRef]

30. Vidil, T.; Tournilhac, F.; Musso, S.; Robisson, A.; Leibler, L. Control of reactions and network structures of epoxy thermosets. *Prog. Polym. Sci.* 2016, 62, 126–179. [CrossRef]

31. Shen, W.; Wang, L.; Zhang, T.; Chen, G.; Li, C.; Chen, M.; Zhang, C.; Zhang, L.; Li, K.; Yang, Z.; et al. Electrically switchable light transmittance of epoxy-mercaptan polymer/nematic liquid crystal composites with controllable microstructures. *Polymers* 2019, 160, 53–64. [CrossRef]