# Influence of thiol monomers on optical and switching properties of polymer-dispersed liquid crystals

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## Abstract

Polymer-dispersed liquid crystals (PDLCs) were synthesized via the radical photopolymerization of isotropic mixtures comprising a cyanobiphenyl nematic liquid-crystalline mixture and monomers. The optical and switching properties of the PDLCs depended on the polymerization initiators and thiol monomers used. The polymerization initiators used were 1-hydroxycyclohexyl phenyl ketone (CPK) and 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (PPO), while the thiol monomers used were 1,4 bis(3 mercaptobutyroyloxy)butane (B2), trimethylolpropane tris(3-mercaptobutylate) (T3), and pentaerythritol tetrakis(3 mercaptobutylate) (T4). The PDLCs prepared using PPO exhibited superior optical switching performance compared with those prepared using CPK. Particularly, the PDLCs fabricated with PPO and B2 exhibited a high initial haze value of 94.2 % at 0 V, which decreased to 11.0 % upon the application of an electric field of 100 V. The initial haze values of the PDLCs containing B2, T3, and T4 followed the order B2 > T3 > T4. At 100 V, the haze values of the PDLCs containing B2, T3, and T4 were nearly identical and in the range from 11.0 % to 12.6 %. These results indicate that the optical and switching properties of PDLCs are strongly influenced by small amounts of thiol monomers and the type of polymerization initiator used.

## Key words

polymer-dispersed liquid crystal, photopolymerization, polymerization initiator, thiol monomer, optical properties

## 1. Introduction

Polymer-dispersed liquid crystals (PDLCs) come under a highly versatile class of materials that have recently gained significant attention (Agarwal et al., 2025). One primary development target of PDLCs is switchable devices, such as dimmable windows (He et al., 2022). In PDLCs, micron-sized droplets of low-molecular-weight nematic liquid crystals (NLCs) are dispersed within a polymer network. These droplets exhibit light-scattering behavior and appear white and opaque; their opacity changes to transparency upon the application of an electric field. PDLCs are typically formed by inducing phase separation between a polymer and an NLC via solvent induced phase separation, thermally induced phase separation, and polymerization-induced phase separation (PIPS) (Sutherland et al., 1993; Doane et al., 1986; Ujiie et al., 2021). PDLC films are fabricated by sandwiching a polymerizable composite between two substrates coated with transparent conductive electrodes. Glass and plastic plates are the commonly used substrates. For plastic substrates, PIPS is preferred over other phase separation methods to avoid the degradation caused by the solvents or heat. PIPS enables the precise structural control of PDLC films. In PIPS, PDLC films are produced by ultraviolet (UV) curing mixtures comprising vinyl monomers and NLCs. The transmitted light intensity of PDLC films can be controlled by varying the applied voltage (Agarwal et al., 2025; Nata et al., 2024). Controlling the electric-field responsiveness and optical properties of PDLCs is essential not only for their application in dimming devices but also for advancing fundamental research on liquid crystalline materials (Agarwal et al., 2025). In this study, we investigated the effect of multifunctional secondary thiols on PDLC properties, and the findings indicated that the optical properties and electric-field responsiveness of the PDLCs significantly varied because they depended on the type of multifunctional secondary thiols used.

## 2. Experimentals

The composition of the cyanobiphenyl nematic liquid crystalline mixture (LCM) used in the experiments is shown in Figure 1. The LCM was mixed with vinyl monomers. A po-

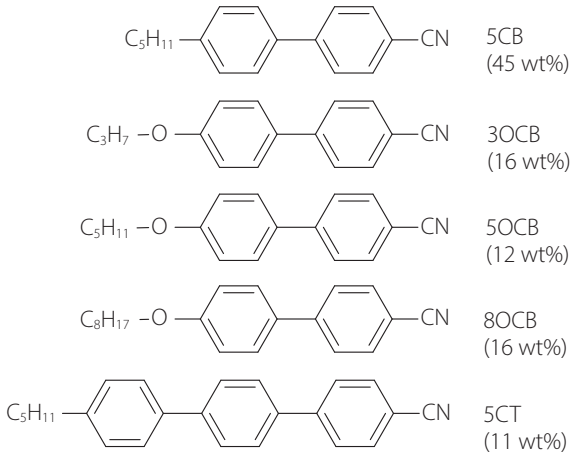


Figure 1: Composition of the nematic liquid-crystalline mixture (Nematic range: –54 to 71 °C)

Table 1: Composition of polymerization initiators and thiol monomers

| PDLC | Initiator | Thiol monomer (wt%) | | |
|---|---|---|---|---|
| | | B2 | T3 | T4 |
| CB2 | CPK 2 wt% | 2 | – | – |
| CT3 | | – | 2 | – |
| CT4 | | – | – | 2 |
| TB2 | PPO 2 wt% | 2 | – | – |
| TT3 | | – | 2 | – |
| TT4 | | – | – | 2 |

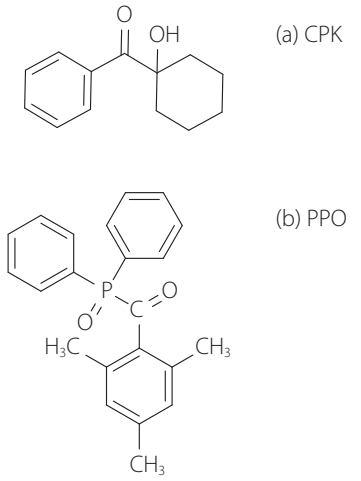


Figure 2: Polymerization initiator structures

Note: CPK = 1-hydroxycyclohexyl-phenyl ketone, PPO = 2,4,6-trimethylbenzoyl-diphenylphosphine oxide.

lymerization initiator and a thiol monomer were thereafter dissolved in the mixture to obtain a polymerizable composite to which spherical spacers were added subsequently (Table 1). The weight ratios of the LCM, vinyl monomers, polymerization initiator, and thiol monomer were maintained at 60:36:2:2 wt%, respectively. The polymerization initiators used were 1 hydroxycyclohexyl-phenyl ketone (CPK) and 2,4,6 trimethylbenzoyl-diphenylphosphine oxide (PPO; Figure 2). Three multifunctional secondary thiols (Figure 3) were used as the monomers: 1,4-bis(3-mercaptobutyryloxy)butane (B2), trimethylolpropane tris(3-mercaptobutylate) (T3), and pentaerythritol tetrakis(3-mercaptobutylate) (T4).

The polymerizable composite was sandwiched between two indium-tin-oxide–coated glass substrates with an 8-µm cell gap maintained using spherical spacers. Photopolymerization was performed under UV irradiation (wavelength = 365 nm, intensity = 34 mWcm$^{-2}$, distance = 150 mm, and temperature = 24 °C). After 90 s of irradiation, the polymer and LCM were phase separated fully. The infrared (IR) spectra of the composite were observed using a Fourier transform IR spectrometer (Shimadzu IRAffinity-1). The thermal properties

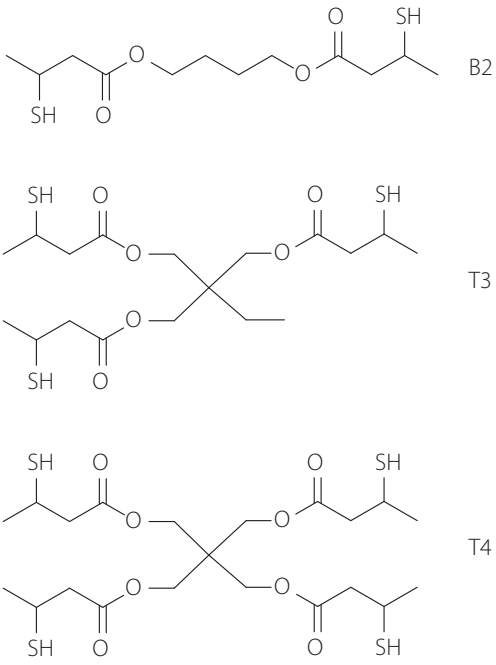


Figure 3: Multifunctional thiol monomer structures

Note: B2 = 1,4-bis(3-mercaptobutyroyloxy)butane, T3 = trimethylolpropane tris(3-mercaptobutylate), T4 = pentaerythritol tetrakis(3-mercaptobutylate).

of the composite were examined using differential scanning calorimetry (Mettler Toledo DSC1). The haze values were measured using a haze meter (Nippon Denshoku Industries, NDH 8000).

### 3. Preparation of the PDLC films

The composite prepared using the LCM, monomers, and initiator was an isotropic transparent liquid. The PDLC film obtained via UV irradiation (365 nm) was white and opaque (Figure 4 (a)). The film became transparent upon the application of an electric field of 100 V (Figure 4 (b)). Figure 5 shows the IR spectra of the PDLC film and the polymerizable composite comprising the LCM and monomers. The stretching vibration of the vinyl groups at 1637 cm$^{-1}$ observed in the composite was absent in the PDLC film. This IR results indicated that the polymerization of the vinyl monomers was complete.

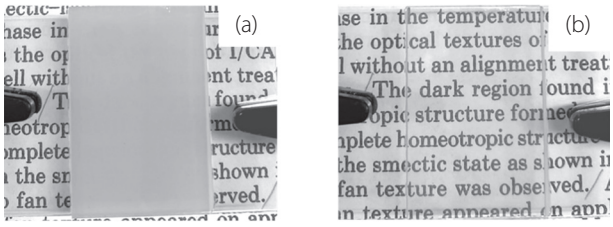


Figure 4: Polymerizable composite at (a) 0 V and (b) 100 V

### 4. Influence of the thiol monomers

Figures 6 and 7 show the electro-optical characteristics of

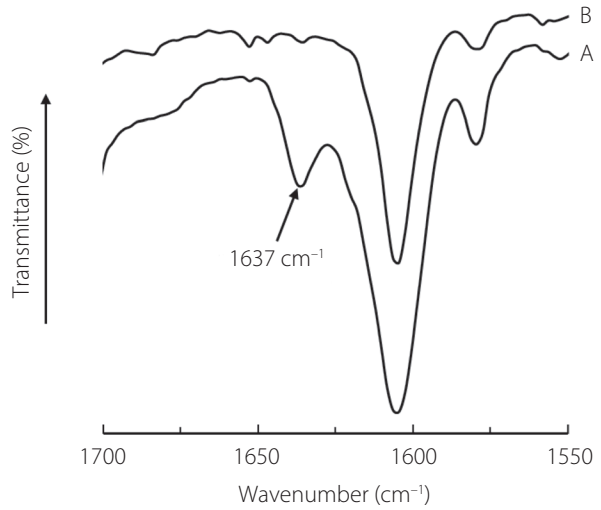


Figure 5: Infrared spectra of the (A) polymerizable composite and (B) polymer-dispersed liquid crystal (PDLC) film obtained using 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (PPO) and 1,4 bis(3-mercaptobutyroyloxy)butane (B2)

Note: The polymerizable composite exhibited a stretching vibration of the vinyl groups at 1637 $cm^{-1}$; however, this vibration was absent in the PDLC film.

the PDLCs. Table 2 summarizes the combinations of polymerization initiators and thiol monomers used in the PDLCs. In all of the PDLC films, the initial state was opaque and the haze value decreased as the applied voltage increased. As shown in Figure 6, CB2 exhibited the highest initial haze value (90.2 % at a driving voltage of 0 V). Its haze value decreased by 18.5 % when the driving voltage was increased to 100 V. Figures 6 and 7 show that the haze values strongly depend on the

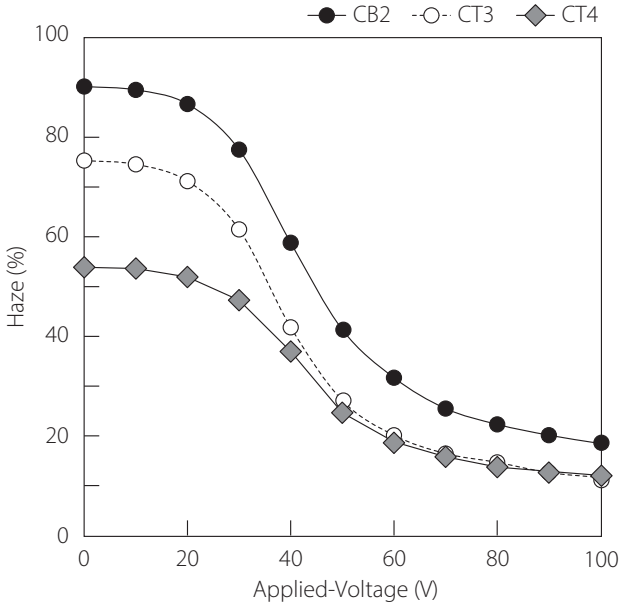


Figure 6: Applied-voltage dependence of the haze values of the polymer-dispersed liquid crystals (PDLCs) obtained using 1-hydroxycyclohexyl-phenyl ketone (CPK)

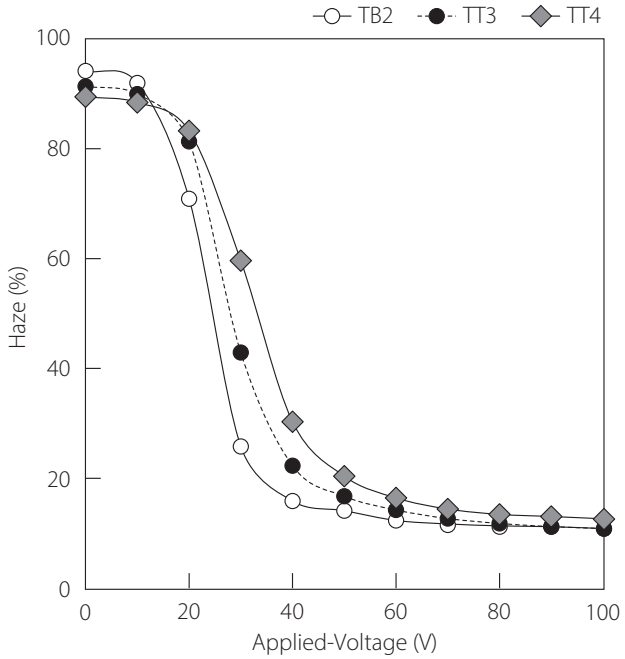


Figure 7: Applied-voltage dependence of the haze values of the polymer-dispersed liquid crystals (PDLCs) obtained using 2,4,6 trimethylbenzoyl-diphenylphosphine oxide (PPO)

Table 2: Haze values of the polymer-dispersed liquid crystals

| PDLC | Haze (%) | | |
|---|---|---|---|
| | 0 V | 30 V | 100 V |
| CB2 | 90.2 | 77.5 | 18.5 |
| CT3 | 75.3 | 61.5 | 12.1 |
| CT4 | 53.9 | 47.3 | 12.1 |
| TB2 | 94.2 | 25.8 | 11.0 |
| TT3 | 91.4 | 42.9 | 11.0 |
| TT4 | 89.5 | 59.6 | 12.6 |

type of initiator and thiol monomer used. The haze values of the PDLCs prepared using PPO and CPK also depended on the thiol monomers used. However, the PDLCs obtained using PPO exhibited higher initial haze values and lower haze values under an electric field than those obtained using CPK. This trend is consistent with the results reported for other PDLC films (Nata et al., 2024).

The multifunctional thiol monomers used in this study are crosslinking agents containing secondary thiol groups. Their local crosslinking densities show the following order: B2 < T3 < T4. While the bifunctional B2 is expected to distribute crosslinking points uniformly throughout the polymer, the tetrafunctional T4, with concentrated crosslinking points, is thought to form heterogeneous regions where areas of high crosslinking density coexist with areas of low density. This spatial heterogeneity in crosslinking density is the cause of the results shown in Figures 6 and 7.

## 5. Conclusions

This study investigated the optical and switching properties of PDLCs prepared using multifunctional secondary thiol monomers. The performance of the PDLCs was significantly influenced by even small amounts of the thiol monomers. The results also showed that even minor differences in the PDLC components could markedly affect the PDLC performance.

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