

Comparative Study on the Electrooptical Properties of Polymer-Dispersed Liquid Crystal Films with Different Mixtures of Monomers and Liquid Crystals

Farzana Ahmad,¹ Muhammad Jamil,^{1,2} Young Jae Jeon,¹ Lee Jin Woo,¹ Jae Eun Jung,³ Jae Eun Jang,³ Gae Hwang Lee,³ Jinsang Park⁴

¹Liquid Crystals Display Research Center, Department of Chemistry, Konkuk University, Seoul 143-701, Korea

²Division of International Studies, University College, Konkuk University, Seoul 143-701, Korea

³Samsung Advanced Institute of Technology, San 14, Nongseo-dong, Giheung-gu, Youngin-Si, Gyeonggi-do-446-712, Korea

⁴Westtown School, 975 Westtown Road, West Chester, Pennsylvania 19382-5700

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ABSTRACT: This article deals with the study of polymer-dispersed liquid crystal (PDLC) films that consisted of microdroplets of liquid crystals (LCs) dispersed in a polymer matrix. The PDLC films were fabricated by the photoinduced phase separation method under room-temperature conditions. To determine the extent of the effects of the molecular structures and their physical properties of different mixtures of mono-

mers and LCs on the morphology and electrooptical properties of the PDLC films, various mixtures were used. A detailed discussion of the obtained results is given. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1424–1430, 2011

Key words: dielectric properties; irradiation; liquid crystalline polymers (LCP); phase separation; photopolymerization

INTRODUCTION

Polymer-dispersed liquid crystal (PDLC) films are getting more attention, both industrially and institutionally, as electrooptic display materials because they do not require the polarizer and alignment layer to be switched to an electrically transparent state¹ and they show a quick electrooptical response, no leakage of materials, simple fabrication, low cost production, and ease of processing, which make them more focused over other technologies, such as liquid crystal (LC) displays.^{2,3} Therefore, PDLC films have promising applications for the fabrication of reflective and projection displays, windows shutters, and holographic recording media.^{4–7}

Several studies on the morphology and electrooptical properties of PDLC films have been done.^{7,8} It is recognized that the electrooptical properties and morphology of PDLCs depend on various factors, including the chemical structure, physical properties of the crosslinked monomers and LCs, and their preparation conditions (e.g., UV curing intensity, curing temperature) and on the PDLC preparation method [e.g., photoin-

duced phase separation, Solvent Induced Phase Separation (SIPS), Temperature induced Phase Separation (TIPS)].^{8–10} Earlier, different groups reported that PDLC films fabricated with rigid chains, having high molecular weights, and containing more than three functional groups of crosslinked monomers showed highly transmitted states at zero applied voltages.^{11–13}

Although many efforts have been made to find appropriate mixtures for high contrast ratios, fast response times, and low driving voltages for PDLCs, much research is still needed to explore the quality of suitable PDLC mixtures to attain high-quality electrooptical properties for displays.

Therefore, in this study, we appraised such issues of PDLCs. In this article, we deal with the comparative study of different monomers mixtures with different types of commercial LCs to investigate appropriate mixture properties. Furthermore, here, we discuss the extent of the effect of the monomer and LC properties on the electrooptical and morphological properties of PDLC displays. For this purpose, we used various monomers comprised of a bifunctional acrylate monomer biphenyl A-ethoxylate diacrylate (BPEDA) and monofunctional monomers [2-ethylhexyl acrylate (EHA), isobornyl acrylate (IBA), and methyl methacrylate (MMA)]. To compare the monomer properties, four different commercial LCs were used. Among the four types of LCs, two were cyanosubstituted LCs (BL001 AND BL002), and the other two were fluorsubstituted LCs (TL203 and TL205).

Correspondence to: Y. J. Jeon (yjjeon@konkuk.ac.kr) or J. E. Jung (jaeeun.jung@samsung.com).

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EXPERIMENTAL

Materials

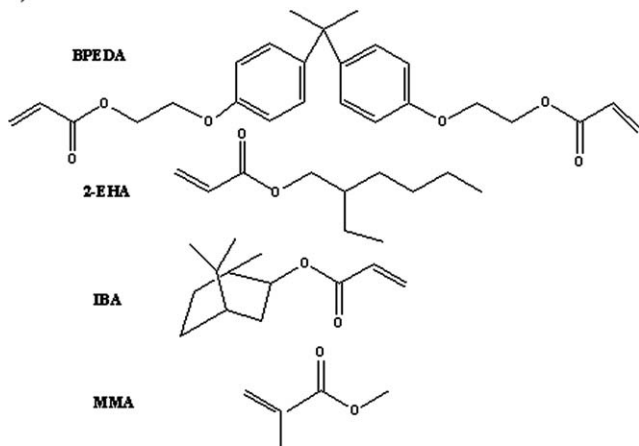
The investigated PDLC composite films were cured by three photocurable monomers mixtures: BPEDA (Sigma-Aldrich Chemical, USA), EHA (Sigma-Aldrich Chemical, USA), IBA (Sigma-Aldrich Chemical, USA), and MMA (Acros Organics, USA). The 2-hydroxy-2-methyl propiophenone (Darocure 1173, E-Merck Co., Licrilite, Germany) was used as the photoinitiator. Among the four nematic LCs that we used, two were cyanosubstituted [BL001 (E. Merck), a eutectic mixture of three cyanobiphenyls and a cyanoterphenyl,^{13,14} and BL002 (E. Merck), a eutectic mixture of 4-*n*-pentyl-4-cyanobiphenyl, alkyl, and oxyalkyl substituents],^{13,14} and two were fluorosubstituted [TL203 (E. Merck), a mixture of pentyl cyano-

TABLE I
Compositions of Various Mixtures of Monomers and LCs Used in the Formation of the PDLC Films

BPEDA or monomer	Monomers and LCs (wt %)			
	BL001	BL002	TL203	TL205
EHA	17 : 3 : 80	17 : 3 : 80	17 : 3 : 80	17 : 3 : 80
IBA	17 : 3 : 80	17 : 3 : 80	17 : 3 : 80	17 : 3 : 80
MMA	17 : 3 : 80	17 : 3 : 80	17 : 3 : 80	17 : 3 : 80

biphenyl blend with fluorosubstituted and chloro-substituted mesogens,¹⁵ and TL205 (E. Merck), a mixture of mesogens containing cyclohexane-fluorinated biphenyls and fluorinated terphenyls with aliphatic chains containing 2–5 carbon atoms].¹⁵ The chemical structures and the physical properties of the composites are shown in Figure 1.

1) Chemical structures of monomers



2) Physical properties of monomers and LCs

BPEDA: $n_p = 1.545$

EHA: $n_p = 1.436$; $\gamma = 1.7$ mPa

IBA: $n_p = 1.476$; $\gamma = 1.447$ mPa

MMA: $n_p = 1.414$; $\gamma = 0.6$ mPa

BL001 : $\Delta n = 0.2255$; $n_o = 1.5217$; $\Delta \varepsilon = +13.8$; $C_p = 58^\circ\text{C}$

BL002 : $\Delta n = 0.2460$; $n_o = 1.5250$; $\Delta \varepsilon = +17.2$; $C_p = 71^\circ\text{C}$

TL203 : $\Delta n = 0.2013$; $n_o = 1.5286$; $\Delta \varepsilon = +11.0$; $C_p = 74.6^\circ\text{C}$

TL205 : $\Delta n = 0.2175$; $n_o = 1.5270$; $\Delta \varepsilon = +5.0$; $C_p = 87.4^\circ\text{C}$

3) Photo-initiator

Darocure 1173:

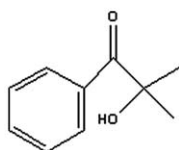


Figure 1 Chemical structures and some of physical characteristics of the monomers and LCs used in the formation of the PDLC films.

Methods

Sample preparation

In the beginning, various homogeneous mixtures of LCs, bifunctional monomer, and monofunctional monomers were prepared by vigorous stirring for 1 day. The compositions of the mixtures are shown in Table I. A total of 0.3 wt % photoinitiator was added in the polymers and LC mixture. Furthermore, this mixture was introduced in between two pieces of indium tin oxide coated conductive glass by the capillary action. The microbead spacer, with a 5- μm (Sekisui Chemicals, Japan) diameter, was used to control the cell thickness. Finally, these cells were cured by UV light with a wavelength (λ) of 365 nm at room temperature for 5–10 min. After curing, the PDLC films were produced because of the phase separation between the photopolymerizable monomers and LC molecules. The fabricated PDLC films were investigated further for their morphology and electrooptical properties.

Measurements

Electrooptical properties and morphology. An LC droplet morphology in the polymer matrix was observed through a polarizing microscope (Olympus, Japan, model BX-60) at a magnification of 50 \times fitted with charge coupling device digital camera interfaced to a computer. The electrooptical responses were studied by the application of an electric field to the sample with a function generator [Ellisotech real time generating system (RTGS)].

RESULTS AND DISCUSSION

Microstructure of the PDLCs

Figure 2 shows the microstructure of the PDLCs containing mixtures of EHA, IBA, and MMA

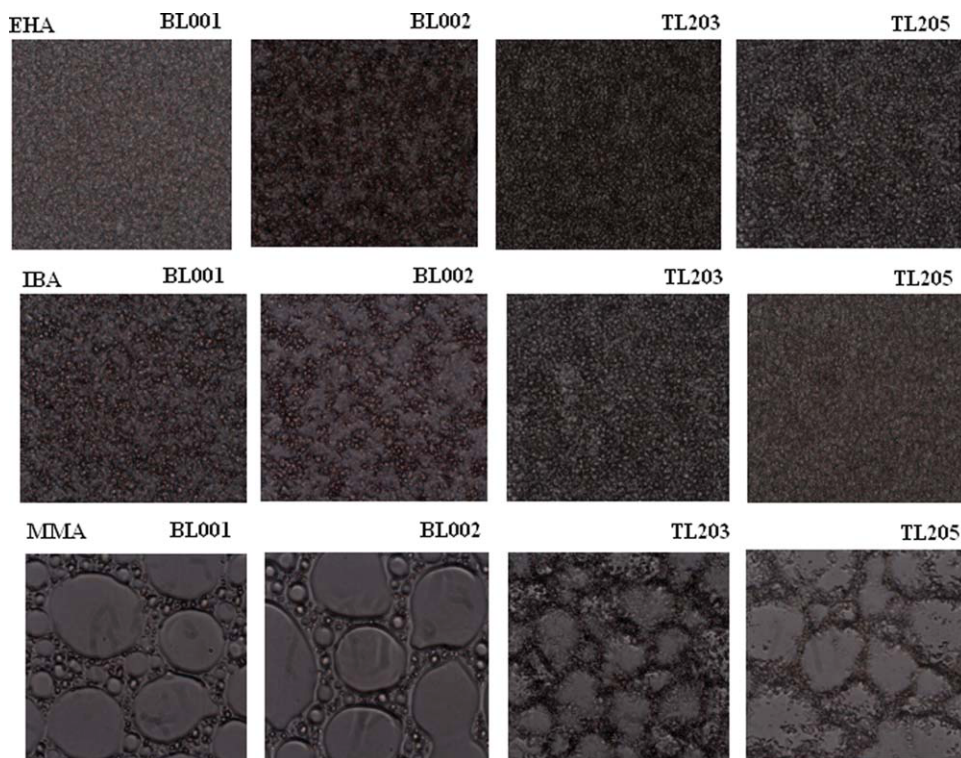


Figure 2 Microstructure of various PDLCs as observed through the microscope. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crosslinking monomers and the four LCs. It shows the uniform small domain sizes for the mixtures containing EHA and IBA and the nonuniform bigger domain size for the mixture containing MMA. The different droplet size found under the same conditions pointed out the dependence of the PDLC morphology on the monomer's physical and chemical properties. Earlier studies showed that the LC domain size depends on the composition of the photopolymerizable monomers, their structures, the rate of polymerization, and also some physical parameters, such as the viscosity, rate of diffusion, and solubility of LC in the polymer solution.^{11,12,16–19} In this case, the small domain size was possible because of the high viscosities of the composites (BPEDA, EHA, and IBA) and the high chain rigidity of the crosslinking monomer (BPEDA). Also, the branched and cyclic chain structures of the monomers (EHA and IBA, as shown in Fig. 1) may have been responsible for the complex diffusion of free radicals of the polymerizable monomers during polymerization, and this, in turn, made it difficult to coalesce the LC domain. Therefore, small LC droplets were formed.

Moreover, the monomer containing rigid chain segments showed a greater chemical affinity with the LC molecules because of its similar rigid molecular structure; it was also supposed to give smaller phase separations and a smaller domain size.^{12,20,21}

Figure 2 shows a nonuniform larger droplet size for the MMA monomer. This morphology was possibly caused by the slow polymerization rate²² and low viscosity of MMA. Collectively, these may have provided enough time for large droplets to diffuse into the polymer matrix during slow polymerization, and accordingly, larger LC droplets may have formed.

Electrooptical studies of the PDLCs

Transmittance

Figure 3 shows the transmittance properties of PDLCs plotted against the voltage for the various mixtures of PDLC with EHA, IBA, and MMA monomers and four LCs. In accordance, when the type of monomer and LC properties were changed, changes in the off-state transmittance (T_{off}), threshold voltage (V_{th}), and the driving voltage for all of the mixtures were observed.

In the PDLCs, T_{off} depended on the polymer refractive index (n_p) mismatch with the ordinary refractive index (n_o) of the LCs. As this mismatch increased between the refractive indices of the two, the transmittance of light increased, and a more opaque state appeared at zero voltage.^{23,24}

We evaluated T_{off} for different monomer mixtures, and it is plotted in Figure 4 against the variation in the refractive indices of the LCs with the monomers

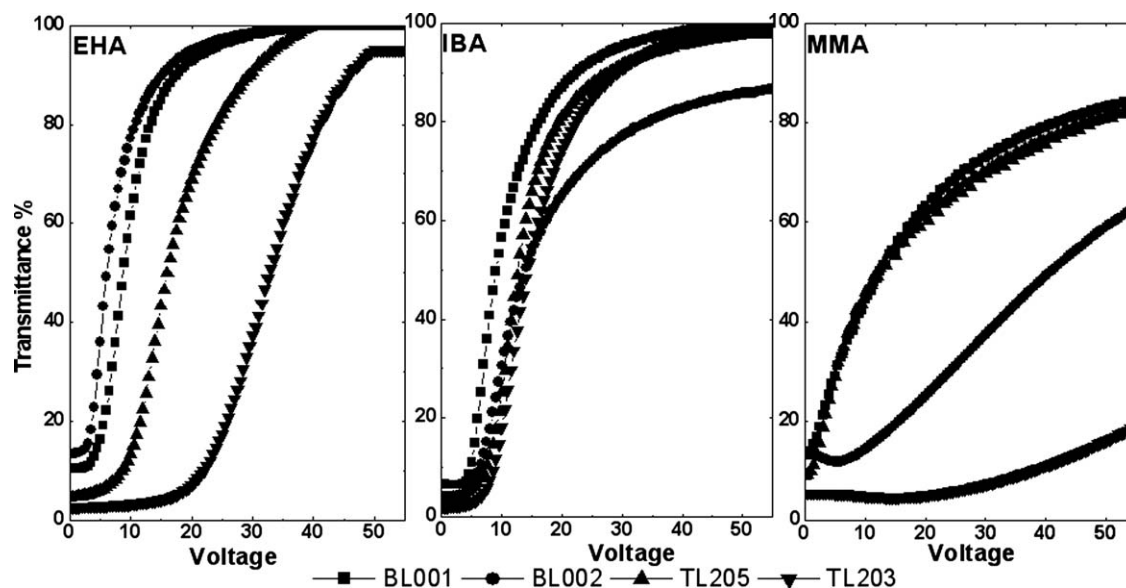


Figure 3 Percentage transmittances of various PDLCs with different LCs and monomer mixtures plotted against the applied voltage.

$[n_{o(LC)} - n_p]$. To better understand, we put a linear trend line over the data; this showed that T_{off} decreased with increasing difference $[n_{o(LC)} - n_p]$. This figure also indicates a more opaque state for IBA for TL203 LC, whereas the light transmittance property increased from EHA to the monomer types. This behavior revealed that the opaque state decreased with decreasing n_p values. This can also be stated as the dependence of off state transmittance (T_{off}) on the molecular structure of the monomers. Figure 4 reveals that the opaque state of the PDLCs decreased with decreasing structural complexity of the crosslinking monomers.

V_{th}

The applied voltage, at which the transmission approached 10% of the maximum, was V_{th} . Once the applied voltage was lower than the threshold value, there was no induced arrangement in the LC droplets, and the sample was in its off state.²⁵ Earlier many studies have reported the dependence of V_{th} on many factors, for example, the PDLC cell thickness, and process of fabrication and LC types.²⁶

According to theory^{2,26} [eq. (1)], V_{th} depends on the reciprocal size of the LC droplets (R):

$$V_{th} \cong \frac{d}{R} \left[\frac{K(\omega^2 - 1)}{\epsilon_0 \Delta \epsilon} \right]^{1/2} \quad (1)$$

where d is the film thickness, K is the effective elastic constant, $\Delta \epsilon$ is the dielectric anisotropy of the LCs, ω is the aspect ratio of elongated droplet, and ϵ_0 is the vacuum dielectric constant. Dielectric stu-

dies of various PDLC composite materials have clearly indicated that the dielectric anisotropy plays a major role in obtaining a low operating V_{th} .²⁷⁻³² From mean field theory, the dielectric anisotropy of an LC compound is governed by the dipole moment and its angle of inclination with respect to the principle molecular axis.^{33,34} We evaluated the V_{th} values, and they are plotted in Figure 5 against the dielectric anisotropic values of the LCs. We found a decrease in V_{th} with increasing dielectric anisotropy values in accordance with the theory.^{2,26}

Moreover, V_{th} plotted against the monomer types in Figure 6 showed an increase in V_{th} from MMA to IBA monomer type for the cyanosubstituted LCs,

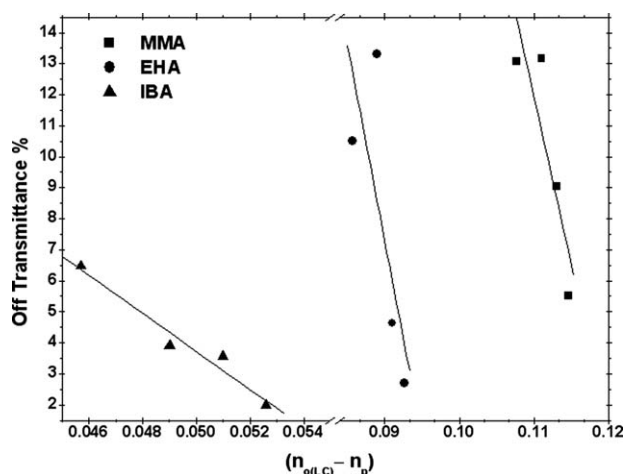


Figure 4 Percentage transmittances of various PDLCs at zero applied voltage plotted as a function of the difference in the LC refractive index from the monomer refractive index.

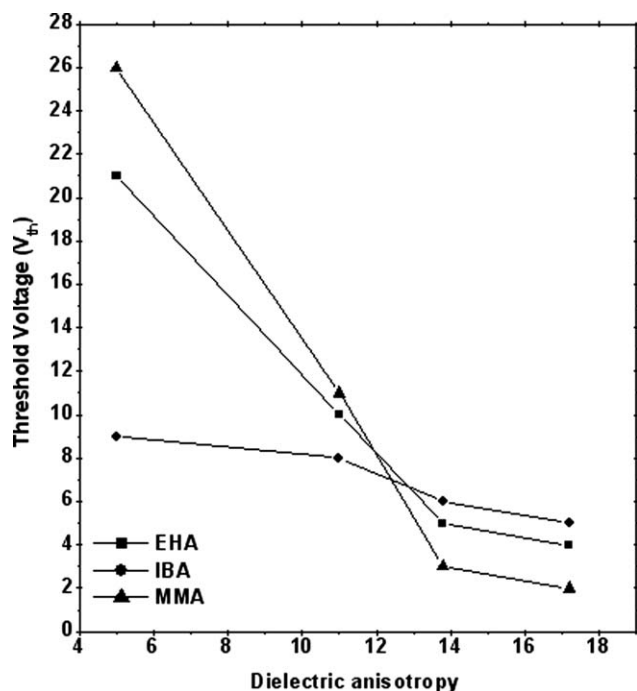


Figure 5 Change in V_{th} as a function of the dielectric anisotropy values of various LCs.

whereas the opposite effect appeared for the fluoro-substituted LCs. This behavior may have been due to some physical phenomenon and the properties involved in the monomer and LCs, such as the viscosity of the monomers, the polarities of the LC molecules, and the droplet size.^{11,35}

Electrooptic response time

The dependence of the response time of the PDLCs with dielectric anisotropy and applied volt-

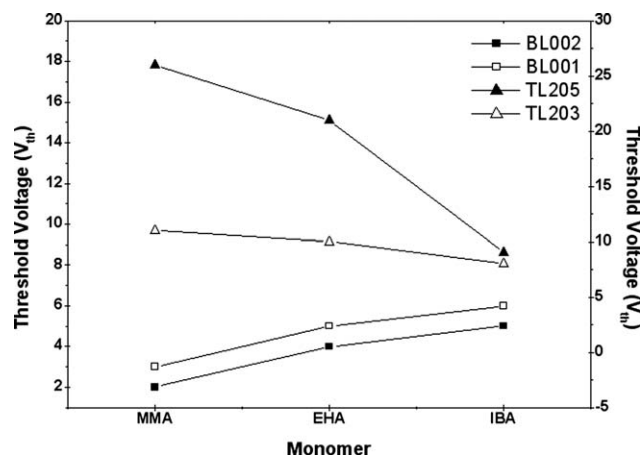


Figure 6 Change in V_{th} of the various PDLC films as a function of the different monomer types used.

age is shown in Figures 7 and 8, respectively. The optical response, or response time, is the sum of the total time ($t_{on} + t_{off}$, where t_{on} is the rise time and t_{off} is the delay time); t_{on} is the time required for the film to reach 90% response from 10% of T_{off} . t_{off} is the time needed for film to reach 10% response from 90% of the on-state level. The smaller the sums of these two indices are, the quicker the response time of the film will be. t_{on} is mainly a function of the electric field, thickness of the film, viscosity, resistivity, and dielectric anisotropy. The decay time depends on the viscosity and elasticity of the LCs and on the shape and size of the droplets formed.³⁶ According to theory,^{26,37} the response times are principally governed by the droplet size and shape, viscosity, elastic constants, anchoring forces, and drive

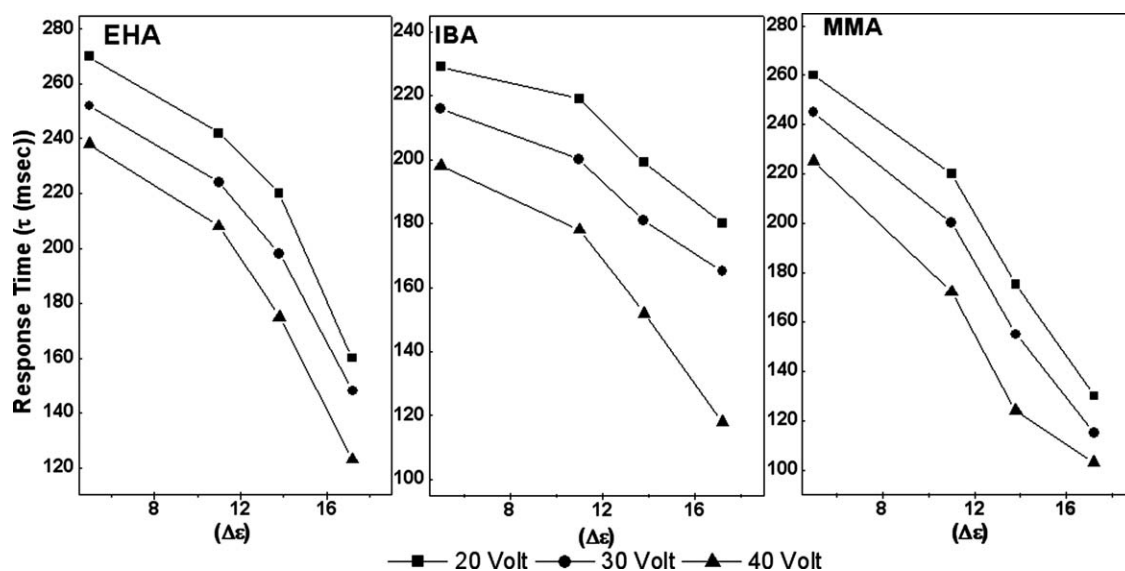


Figure 7 Response time of the various PDLC films at different applied voltages versus the dielectric anisotropy values of the LCs used.

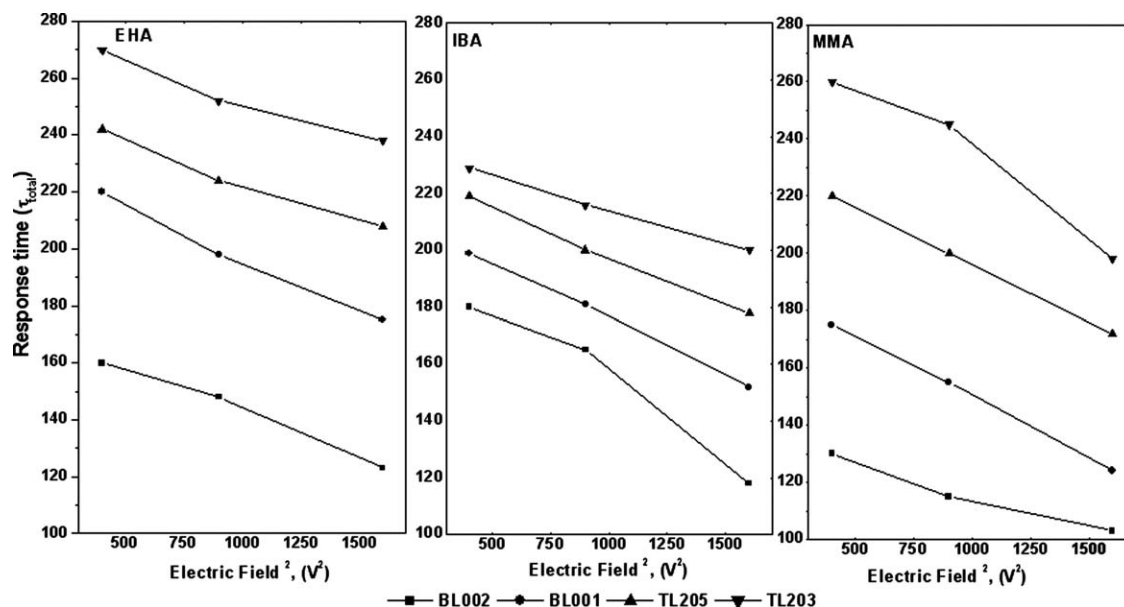


Figure 8 Response time versus the square applied electric field of the PDLCs for various monomers.

voltage, and the total response time (τ_{total}) can be computed as follows:

$$\tau_{\text{total}} \cong \frac{\gamma}{\Delta\epsilon V^2} \quad (2)$$

where γ is the rotational viscosity coefficient and V is the applied electric field. As shown in Figure 7, τ_{total} decreased with increasing dielectric constant values of the LCs. It is according to theory²⁶ that the response times were inversely related to the dielectric anisotropy values. The cyanosubstituted LCs showed the fastest response time, whereas the fluorosubstituted LCs showed slower response time because of their high and low dielectric anisotropy values, respectively.

The applied electric field interacts with the LCs via the dielectric torque of the LCs to reorient the molecular configuration within each droplet. For a sufficiently strong field and high dielectric torque, the axes of nearly all of the molecules point speedily along the field direction, and each droplet predicts a refractive index close to n_o to the incoming light. As n_o approaches n_p , the light transmits without refraction, and a transparent state appears. Consequently, when LC has a high dielectric anisotropy, the PDLC films take less voltage and less time to produce a transparent state.²⁴

Figure 8 shows the response time as a function of the square applied electric field. It shows that τ_{total} decreased with increasing square applied voltage values for various LCs in diverse monomer mixtures, as according theory²⁶ and eq. (2).

Figure 8 shows that every LC, with respect to the response time as a function of the applied

electric field, showed interactions with different monomer mixtures, as found by different slope values at different applied voltages. Moreover, the LCs showed faster response times in the MMA monomer mixture at different applied voltages, compared with the other monomer mixtures. This was because, in the case of reorientation fields, the dynamic response of a nematic droplet depends on the relative strength of the electric field and elastic forces acting on the nematic LCs, which drive the droplet reorientation. In addition, these factors are affected by the dielectric, elastic, and viscosity properties of the nematic and on the morphology of the nematic droplets and the polymer network.³⁸

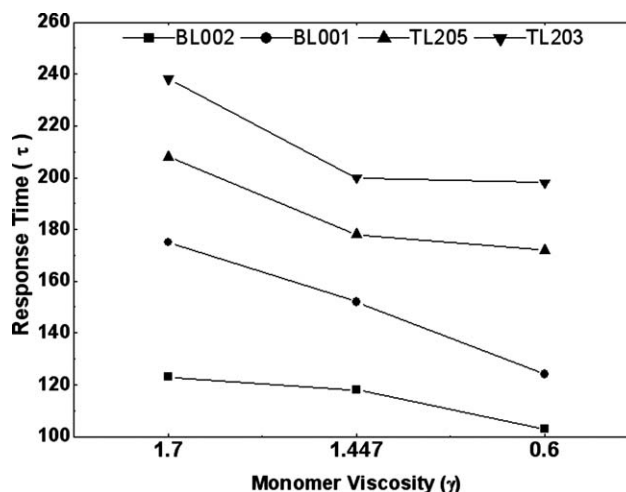


Figure 9 Response time of the PDLC films at an applied voltage of 40 plotted against the different monomer viscosities.

In accordance with this explanation, the data in Figures 7 and 8, as measured at an applied voltage of 40, were rearranged and replotted as the response time as a function of the monomer viscosities (Fig. 9). Figure 9 indicates that response time decreased with decreasing monomer viscosity from the EHA to MMA monomers types. According to this scenario, MMA showed a faster response time than the EHA-type monomer. This clearly revealed the dependence of the response time of the LCs with the monomers' physical properties, for example, the viscosity, because it is indicated in eq. (2) that the response time decreases with decreasing polymer viscosity.

CONCLUSIONS

In this comparative study, the PDLC films fabricated with the photoinduced phase separation method with one bifunctional monomer and three monofunctional crosslinking monomers with four LCs substituted with cyano and fluoro groups were investigated to study the effect of the monomers and LC structures and their physical properties on the morphology and electrooptical properties. The rigid, branched, and cyclic alkyl chain structure of the crosslinking monomers showed a small domain size, low T_{off} , and high V_{th} . Conversely, MMA, with a simple molecular structure, exhibited high T_{off} and low V_{th} values for the cyanosubstituted LCs. Moreover, T_{off} decreased with increasing refractive index difference of the LCs with the monomer refractive index. Also, the opaque state of the PDLCs decreased with decreasing structural complexity of the crosslinking monomers.

Our findings revealed that the response time depended also on the viscosity of the monomer; the methacrylate monomer with a low viscosity showed a faster response time than IBA, whereas the branched alkyl chain monomer (EHA) showed a slow response time. In addition, the cyanosubstituted LCs showed a low V_{th} and a faster response time than the fluorosubstituted LCs. Moreover, V_{th} and the response time decreased with increasing dielectric anisotropy and applied voltage.

Our results were correlated with the monomers viscosities, structural complexities, sizes of the LC droplets, and dielectric properties of the LCs and demonstrated the validity of the theoretical indications present in literature. From our analysis, we concluded that our experimental findings will help more to understand the extent of monomers and LCs for further developments in the PDLC field.

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