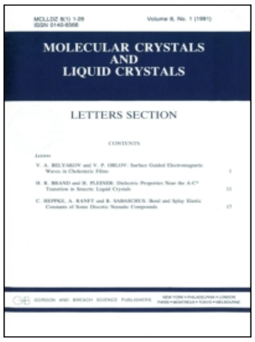


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Electro-optical properties of PDLC films using diethylenetriamine (DETA) hardener

M. Ellahi & M. Y. Rafique

To cite this article: M. Ellahi & M. Y. Rafique (2016) Electro-optical properties of PDLC films using diethylenetriamine (DETA) hardener, Molecular Crystals and Liquid Crystals, 638:1, 103-110, DOI: 10.1080/15421406.2016.1222037

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1222037

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2016, VOL. 638, 103–110
http://dx.doi.org/10.1080/15421406.2016.1222037

Electro-optical properties of PDLC films using diethylenetriamine (deta) hardener

M. Ellahi[a] and M. Y. Rafique[b]

[a]International Centre for Chemical and Biological Sciences (ICCBS), H.E.J. Research Institute of Chemistry, University of Karachi, Karachi, Pakistan; [b]Department of Physics, Comsats Institute of Information Technology, Lahore, Pakistan

ABSTRACT

The author's results obtained today and in previous works are summarized. The present work has been performed to investigate the effects of the structure and electro-optical (E-O) properties of epoxy resin based polymer dispersed liquid crystal (PDLC) films smart glass using Diethylenetriamine (DETA) as hardener with 4-cyano-4′-penthylbiphenyl (5CB) liquid crystal. In this study we have been prepared PDLC films by the thermal polymerization-induced phase separation (PIPS) method, with a thickness of 10.0 ± 1.0 μm controlled by a polyethylene terephathalate (PET) spacer and optimal preparation condition were 25% and 30% 5CB LC, respectively, with a curing time 7 hours at 70°c temperature. In addition, PDLC films were prepared with different amounts of DETA to investigate the best ratio of the hardener. Results showed that when the weight ratio of LC 5CB was 30% in PDLC and mol 3% of DETA hardener, then dispersed state of LC were well proportioned, and the variation of transmittance reached the highest value. The optical characterization of the PDLC film indicates an improvement of the angular transmission of visible light. Meanwhile, it is examined that by adjusting the mol% of hardener and LC 5CB content possesses good E-O properties with a low energy efficient method for preparing PDLC smart glass display technology.

KEYWORDS

Diethylenetriamine; electro-optical properties (E-O); epoxy resins; polymer dispersed liquid crystal; smart glass

1. Introduction

Recently, it is well known that the polymer liquid crystals (PDLC) films smart glass have been regularly investigated and successfully considered by the different scientific and technical methods as the suitable model system. A PDLC system consists of micron-sized birefriengent liquid crystalline domains, dispersed uniformly in an optically active and transparent polymer matrix, having spatially varying refractive index and efficient light scattering properties. In this context, the saving energy is one of the most significant issues related with global warming, and glass is often regarded as a less energy efficient constituent. A new class of glass, the so-called smart glass, is expected to be a solution for buildings and transport at ion vehicles to reduce heating and cooling energy. PDLC films (smart glasses) are a technologically important class of materials that find many applications as electrically switchable optical devices

---

CONTACT M. Ellahi, Ph.D. mujtaba.ellahi@gmail.com International Centre for Chemical and Biological Sciences (ICCBS), H. E. J. Research Institute of Chemistry, University of Karachi, 75270 Karachi, Pakistan.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

[1–3]. PDLC films are formed by LC micro domain sizeembedded in a polymer matrix. PDLC can be used not only for smart windows, but also for displays and tunable optical modulators [4]. In turn off state, no electric filed is applied between ITO electrodes, the orientation (i.e. director) of liquid crystal molecules inside each droplet are different in different domain size. When the incident light of electromagnetic wave having a specific polarization [5] perpendicularly enters into PDLC, the refractive index [6] inside each droplet (with respect to the incident light) is determined by the director. For this reason, the directors in the droplets are arbitrarily distributed, so most of the refractive index inside the droplets is different from the refractive index of polymer surrounding the droplets. According to the Snell Law, the incident light will be refracted at the interface between liquid crystal and polymer. There are thousands of micron domain size distributed in 10 μm volume of PDLC, so thousands time of refraction occur when the Incident light passing through PDLC, the light is sprinkled, and an opaque milky whitest ate observed in other side. PDLC films can be prepared by five different techniques: Thermally Induced Phase Separation (TIPS), Polymerization Induced Phase Separation (PIPS), Solvent-Induced Phase Separation (SIPS), and microencapsulation process (MP). Each technique produces PDLCs with different properties and characteristics. Generally, the most suitable method to prepare PDLC devices is PIPS method via heat curing technique is more consistent to provide homogeneity, simple processing, less pollution, cheaper, strong bonding power, and forms a homogeneous morphology of polymer networks [7–10]. The main advantages of PIPS method of heat curing process are, it requires no evaporation, the fabrication process is relatively simple, clean, and solvent free. It also has advantage over Ultra-Violet (U.V.) curing PIPS methods because it avoids both the changes in LC properties produced by U.V. irradiation and the resulting contamination of radical initiator reagents [11]. Among the different families of cross-linking resins, epoxies are extensively used due to their excellent performance, coupled with very easy convention methods and limited cost. Previously, we have studied two groups with influence of the multi-functional epoxy monomers structure and characterization on the electro-optical properties and morphology of PDLC films [12,13]. Having all these in view, the present work concern with research of epoxy resins system with Diethylenetriamine (DETA) as hardener to investigate briefly study the electro-optical properties on polymer network of PDLC films. In this paper, we have been studied the optical properties of PDLC films with4-cyano-4′-penthylbiphenyl (5CB) LC with same LC concentrations, thicknesses, and curing times; comprehensively.

The present study devoted to investigate an example of fabrication method by using 4-cyano-4′-penthylbiphenyl (5CB) LC with epoxy resins structure. Furthermore, in this paper in both systems, we have tried to show the Diethylenetriamine (DETA) as hardener with variable mol% and different composition feed ratio.

2. Experimental setup

2.1. Materials

In this research, the PDLC films have fabricated by PIPS heat curing process. The 4-cyano-4′-penthylbiphenyl (5CB) LC used in this study was (Shijiazhuang Yongsheng Huatsing Liquid Crystal Co., Ltd). The curable epoxy resins used were Poly propylene glycol diglycidyl ether (PPGDE, Sigma-Aldrich Company) containing alkyl group (-*R*) having crosslinked network. Its refractive index is 1.464. Ethylene glycol diglycidyl ether (EGDE) resin (XY 669, Anhui Hengyuan Chemical Co., Ltd.) It is a di-fucntional viscous fluid liquid having yellowish color epoxy monomer containing short flexible chain length. Its refractive index is 1.463,

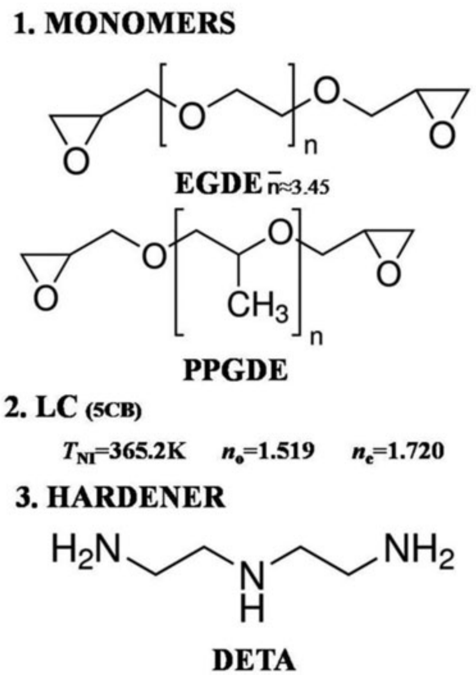


Figure 1. Chemical structures, names and abbreviations of the materials used.

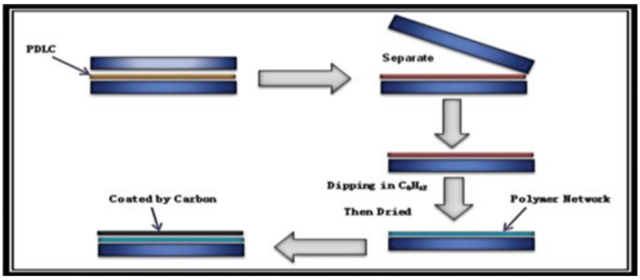
Table 1. The compositions of the samples A1–A3 studied.

	Epoxy Resins (75 wt%) (7 hours at 70°C)	
Sample	PPGDE/EGDE/DETA/mol%	5CB-LC/wt%
A1	1.0/3.0/1.0	25
A2	2.0/2.0/2.0	25
A3	3.0/1.0/3.0	25

and Diethylenetriamine (DETA) (Sigma-Aldrich Company) used as hardener having 1.484 refractive index. DETA is a polyamine hardener for epoxy resins. The chemical structures of these materials are shown in Fig. 1. All of the above materials were used as received without additional purification. The compositions of curable epoxy monomers/hardener/LC mixtures are listed in Table 1 and Table 2 for 7.0 hours at 70°C same time and temperature, respectively. Functionality is referred to standard functional of numerous curable epoxy monomers. It is calculated by $Fav = \Sigma\Phi i\ fi$, where Fav is the average functionality of composite resin, Φi and fi stand for the relative proportion and functionality, respectively [14]. In both systems, the PDLC films were obtained by the PIPS via heat curing procedure.

Table 2. The compositions of the samples B1–B3 studied.

	Epoxy Resins (70 wt%) (7 hours at 70°C)	
Sample	PPGDE/EGDE/DETA/mol%	5CB-LC/wt%
B1	1.0/6.0/1.0	30
B2	1.0/4.0/2.0	30
B3	1.0/2.0/3.0	30



Scheme 1. A schematic diagram of the processing of PDLC films.

2.2. Sample preparation

The samples were prepared consisting of heat curable epoxy monomers, hardener and the different amount of 25% and 30% of 4-cyano-4′-penthylbiphenyl (5CB) LC. Initially, the compounds were mixed in various percentages and stirred for 3 hours until they had been homogenized. After that, based on capillary action, the mixtures were sandwiched between two pieces of indium tin oxide (ITO) coated glass substrates, with a thickness of $10.0 \pm 1.0\ \mu$m controlled by a polyethylene terephathalate (PET) spacer and optimal preparation condition were 25% and 30% 4-cyano-4′-penthylbiphenyl (5CB) LC with a curing time 7.0 hours at 70°C temperature.

In scheme 1, a schematic diagram of the processing of PDLC films. As shown in scheme 1, the samples were first separated and dipped in cyclo hexane (C_6H_{12}) at room temperature to extract the LC molecules for about 72 h. Then the films with polymer networks were dried for 12 h under vacuum. After the samples were sputtered with carbon, the microstructures of the networks were observed by the SEM. The SEM images were then treated statistically using a method suggested for estimation of both LC domain size distribution and average droplet size.

2.3. Analysis and measurement

The morphology of PDLC samples was observed by scanning electron microscopy (SEM) (ZEISS, EVO18, Germany). The electro-optical (E-O) properties of PDLC films were studied using a liquid crystal device (LCD) parameters tester (LCT-5016C, Changchun Liancheng Instrument Co., Ltd.). A halogen tungsten lamp was used as an incident light source and the incident wavelength (λ) through the samples was fixed with the wavelength (λ) filter (632.8nm).

3. Experimental results and discussion

3.1a. Morphology of polymer network at 7.0 hours at 70°C with 25% (5CB) LC

In order to measure the domain size, Fig. 2a shows the morphology of SEM micrographs of the polymer network of the samples A1–A3. The morphology of PDLC systems is dependent on the mol% ratio, curing conditions, time, temperature, chemical structures materials, and details of the film formation technique [15].

The composition feed ratio of samples A1–A3 with 25% (5CB) LC content and similar heating temperatures is listed in Table 1. Figure 2a shows the domain size morphology of the polymer network of PDLC system for samples A1–A3. Diethylenetriamine (DETA) reacts

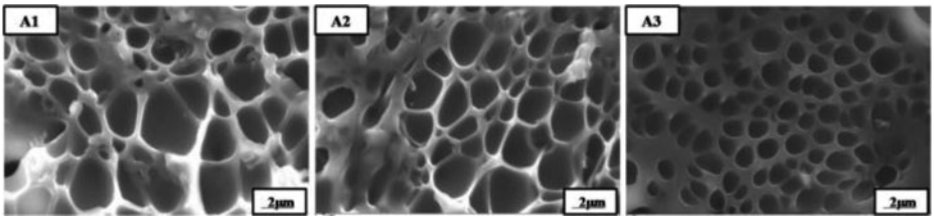


Figure 2.a. SEM micrographs of the polymer networks of the samples A1–A3.

with the epoxy monomers to form polymeric network with the ring opening addition polymerization reaction process. To begin with the hydroxyl group (-OH) opened and adds a new epoxy ring to form polymer network chain of the PDLC systems. In addition, the DETA hydroxyl group (-OH) then capable to form a link with one more epoxy group to form continue polymer network chain. It can be seen that the LC domain size of the polymer network decreasing with constant mol% of hardener DETA. The effects of the structure of alkoxy chain length and flexible di-functional curable epoxy monomer EGDE on PDLC films were showed the microstructures of the PDLC films as shown in Fig. 2a. When polymerization was initiated, the molecular weight and cross-linking density of the polymer network increase and hence the solubility of the LC decreases leading to the formation of domain size. This was related to the relative content of the curable epoxy monomers composition and the 25% of (5CB) LC content. The average LC domains sizes have been observed of all samples approximately 2.5 μm, 2.1 μm, and 1.9 μm for samples A1–A3, respectively. It can be clearly seen that the LC domain size have different variations with increasing the mol% of PPGDE shown in Fig. 2a.

The solubility of the LC decreases stiffening polymers until the LC phase separates and form domain size during the heat curing method. Domain size controlled by the relative amounts of the epoxy resins, the rate of polymerization, and some physical parameters such as the viscosity, diffusion rate, and solubility of the LC in the polymer [16]. In this paper, the LC domain size and cross-linking density were mainly influenced by the relative ratio of the EGDE and PPGDE. Epoxy monomers mostly influences to form cross-linking density with alkoxy group chain length with increasing PPGDE which increases the cross-linking density of PDLC films. For a perfect system, the relative content of the heat curable monomers and LC have a great effect on the microstructure of the polymer matrix. Consequently, the size of the LC domains mol 2% DETA hardener is ideal and smooth with a curing time 7.0 hours at 70°C temperature.

3.1b. Morphology of polymer network at 7.0 hours at 70°C with 30% (5CB) LC

It is evident from Fig. 2b that morphology is appreciably influence by adding the Diethylenetriamine (DETA) hydroxyl group (-OH) as a hardener in samples B1–B3. Previously, we have been prepared the epoxy monomers based PDLC films with 2, 2′-(ethylene di oxy)bis (ethylamine) EDBEA is a polyamine hardener [12,13]. The DETA accelerates the rate of polymer network reaction speedily and prepare the PDLC films with reducing the domain size of PDLC system at same time and temperature as shown in Fig. 2b. We have prepared samples B1–B3 with mol 2% hardener at same temperature and time but different composition feed ratio of PPGDE and EGDE. The average LC domains sizes have been observed of all samples approximately 3.7 μm, 2.8 μm, and 2.0 μm for samples B1–B3, respectively.

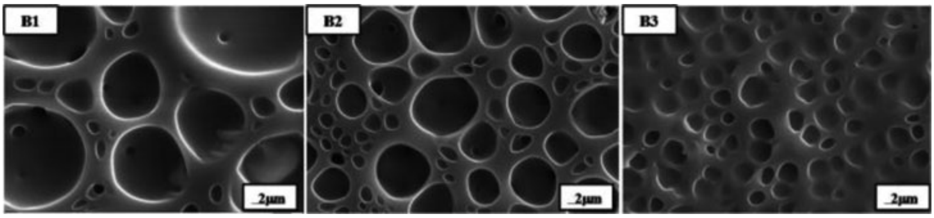


Figure 2.b. SEM micrographs of the polymer networks of the samples B1–B3.

From Fig. 2b it can be seen that at the constant mol% ratio of DETA hardener decreased the number of LC domains and the LC domain size distribution was narrow, which would make the PDLC films easier to drive in practical devices. Furthermore, to illustrate the effect of DETA, the electro-optical (E-O) properties of the PDLC system needed to be studied.

3.2a. Electro-optical (E-O) properties of PDLC films at 7.0 hours at 70°C

The electro-optical (E-O) properties are very important to assess LC system. The E-O properties of PDLC systems mainly depend on the chemical nature of the epoxy monomers, hardener, and LC content. As well as, the effect of epoxy monomers structures on PDLC systems can be obtained by the E-O properties of samples A1–A3. The transmittance applied voltage curves of samples A1–A3 are shown in Fig. 3a. It can be seen from Fig. 3a, that transmittance of the samples reached the saturation level, when the applied voltage increased. Comparatively, studies showed that the Fig. 3a with Fig. 2a, the morphology of the polymer network in the PDLC systems had a vital effect on the E-O properties of the PDLC films. Good E-O properties of the PDLC systems can be obtained when the microstructure of the PDLC film is appropriate. It is well examined that when the DETA hardener reached in sample A3 mol 3%, PPGDE mol 3%, and EGDE mol 1% then transmittance of the PDLC films were very best and good.

3.2b. Electro-optical (E-O) properties of PDLC films at 7.0 hours at 70°C

The applied voltage transmittance curves of samples B1–B3 are shown in Fig. 3b. In heating process, the epoxy monomers and hardener (EDBEA) reacted to form a polymer matrix and the LC coalesced; resulting the phase separation process occurred. When the heating time was insufficient, the LC domain sizes were formed relatively big. When this occurred the films were

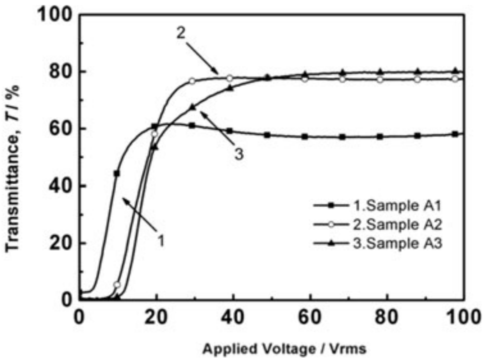


Figure 3.a. Applied voltage dependence of transmittance for samples A1–A3.

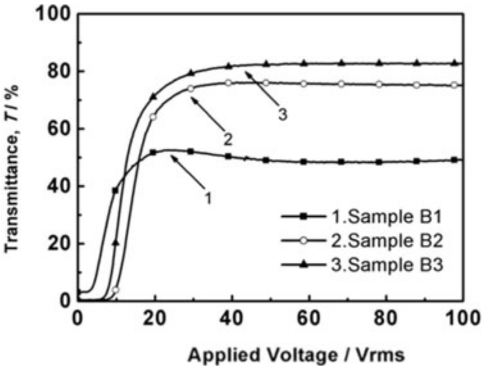


Figure 3.b. Applied voltage dependence of transmittance for samples B1–B3.

hard to drive since the anchoring energy at the boundary between the polymer matrix and LC droplets was large when the LC domain size were small, and small LC domains suppress light scattering in the visible region [17].

Progressively, with the passage of time more epoxy monomers and DETA hardener reacted to form the polymer matrix and the LC separated from the polymer matrix, forming more and larger domain size; then the film became easier to drive [18]. For the sample B3 prepared with EGDE mol 2%, DETA hardener mol 3%, and 5CB (LC) 30% then dispersed state of LC were well proportioned, and the variation of transmittance reached the highest value to get a good response to the electric field. In the meantime, the optical characterization of the PDLC film indicates an improvement of the angular transmission of visible light.

By analyzing the curves of samples A1–A3 and B1–B3, it can be observed that the E-O properties of samples B1–B3 were no worse than those of samples A1–A3.

4. Conclusions

The optimized condition for fabricating PDLC films containing 4-cyano-4′-penthylbiphenyl (5CB) wasfoundtobetheweight%ofLC25% and 30%, respectively. We have been investigated two PDLC film systems. The System1, at 7.0 hours at 70°C using curable epoxy monomers with heat curing processes mol%, composition ratio, various molecular structures and at different mol feed ratio hardener DETA, which effects the morphology of the PDLC systems. Additionally, the effect on microstructures of the PDLC systems was strongly influenced by the hydroxyl group (-OH), which in turn influenced the E-O properties of PDLC systems. The effect of the composition of the mixture and curing temperature on the microstructure of the polymer network were examined. Moreover, using different mol% DETA variable driving voltages were optimized.

In system 2, using the 3 mol% DETA hardener effects the immaculate morphology and E-O properties of PDLC systems of B2. In addition, with different amounts of hardener reduce the domain size of PDLC system which gradually decreases as mention Fig. 2b with good E-O properties. As a result, this study presents a low energy method for preparing PDLC films as well as our experimental findings will help more to understand the extent of epoxy monomers and LCs for further developments in the PDLC smart glass field.

In both systems, the sample A3 and B3 have the best result and show significant advantages for manufacturing PDLC films smart glass and developing the PDLC market.

Acknowledgments

This work was supported by the HEC fund for distinguished Young Scholars and the research fund of the State Key Laboratory for Advanced Metals and Materials. The authors wish to express appreciation to the QUA University and University of Karachi for laboratory experiment support and technical assistance.

References

[1] Doane, J. W., Vaz, N. A., Wu, B. G., & Zumer, S. (1986). *J. Appl. Phys. Lett.*, *48*, 269–271.
[2] Kitzerow, H. S. (1994). *J. Liq. Cryst.*, *16*(1), 1–31.
[3] Kim, Y. B., et al. (2009). *J. Thin Solid Films*, *517*(10), 3066–3069.
[4] Park, S., & Hong, J. W. (2009). *J. Thin Solid Films*, *517*(10), 3183–3186.
[5] Ellahi, M., Gao, Y., & Rafique, M. Y. (2013). *J. Am. J. Eng. Res.*, *2*(3), 01–06.
[6] Lee, S. H., Lee, S. L., & Kim, H. Y. (1998). *J. Appl. Phys. Lett.*, *73*, 2881–2883.
[7] Ellahi, M., et al. (2013). *J. Int. J. Sci. Technol. Res.*, *2*(3), 127–131.
[8] Yun, H. J., et al. (2012). *J. Liq. Cryst.*, *39*, 1141–1148.
[9] Farzana, A., Jamil, M., Lee, J. W., & Jeon, Y. J. (2012). *J. Colloid Polym. Sci.*, *290*(7), 599–606.
[10] Farzana, A., Jamil, M., Lee, J. W., Ri, Y. H., & Jeon, Y. J. (2014). *J. Mod. Opt.*, *61*(12), 1027–1032.
[11] Murai, H., & Gotoh, T. (1993). *J. Mol. Cryst. Liq. Cryst.*, *226*(1), 13–26.
[12] Ellahi, M., et al. (2013). *J. Polym. Bull.*, *70*(11), 2967–2980.
[13] Ellahi, M., et al. (2014). *J. Soft Mater.*, *12*(3), 339–345.
[14] De Sarkar, M., Gill, N. L., Whitehead, J. B., & Crawford, G. P. (2003). *J. Macromolecules*, *36*(3), 630–638.
[15] Song, P., et al. (2012). *J. Liq.Cryst.*, *39*(3), 313–321.
[16] Song, P., et al. (2012). *J. Liq. Cryst.*, *39*(9), 1131–1140.
[17] Ellahi, M., Rafique, M. Y., Ishtiaque, S., Ali, M. F., & Memon, J. (2015). *J. Mater. Focus*, *4*(03), 197–201.
[18] Ellahi, M., et al. (2015). *J. Polym. Bull. 72*(11), 2917–2930.