

Investigations on the effect of polymer precursors chain lengths on the electro-optical properties of polymer dispersed liquid crystal (PDLC) films

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In this study, the effects of various chain lengths of polymer precursors on the electro-optical properties of polymer-dispersed liquid crystal (PDLC) films have been investigated. For this purpose, PDLC-films were prepared by inserting the three different precursor of different chain lengths into mixtures of liquid crystal (LC) and polymers. Such mixtures were dropped on ITO-glass and were cured under the UV irradiation to make PDLC films. The electro-optical (EO) properties of the PDLC films were characterized by measuring their haze, transmittance and contrast ratio (CR). Further, the relationship between the electro-optical properties according to the chain length of the precursor liquid crystal (LC) droplet size was measured. The obtained results revealed that the longer the chain length of the monomer, the larger the size of the liquid crystal droplet. Also, for the viscous the polymer matrix, the lower the threshold voltage and the higher the ON transmittance was observed.

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1. Introduction

Polymer-dispersed liquid crystals (PDLCs) are an important class of electrically switchable materials, wherein the micrometer-sized liquid crystal droplets are embedded in a polymer matrix [1–5]. Without the applied electric field, PDLC films exhibit a milky white scattering state due to the random orientation of liquid crystal (LC) droplets in the polymer matrix [5–7].

Once the electric field of sufficient strength is applied, these films become transparent and this phenomenon is attributed to the alignment of LC droplets along the direction of the electric field, provided that the ordinary refractive index n_o of LC precisely matches with the refractive index n_p of polymer matrix [8–10]. Recently, PDLC films have gained much attention owing to various useful features. PDLC films contain electrically switchable features from a light scattering state to a transparent state without using the polarizers and alignment layers [11–12].

Upon competing with major characteristics of PDLC films are their rapid reaction time, low fabrication cost, no material leakage, and few steps straightforward production methods, which provide them an advantage over other display technologies [13–14]. In their most common configuration, PDLCs are made using the phase separation process, which produces micron-sized domains of LCs that are randomly scattered in a polymer matrix [13–14, 24–30].

Previous research studies [15–19, 24–30] have shown that PDLC films have only low transmittance and high haze, at the stage when no voltage is applied, making them

very opaque. On the other hand, when voltage is applied, these films exhibit high transmittance and low haze. As a result, such films are required to be transparent like a general glass medium. However, with the passage of time as the display market expands and technology develops due to the practical use of PDLC in recent years, consumer interest is increasing, and as the field of application expands, consumer demands are also diversifying.

Therefore, it became a key objective to realize various electro-optical characteristics of PDLC according to their purpose of applications. Further, it is essential to investigate the possible factors that determine the electro-optical properties of PDLC. The current work has been performed to investigate the effect of polymer precursors on the electro-optical properties of PDLC. PDLC films were fabricated with different properties of polymer precursors, and the trend analysis of changes in electro-optical properties was conducted.

2. Experimental work

2.1. Materials and methods

In the current work, LVUL010300-100 from Livicon's [20] is used as liquid crystals (LCs). It is a mixture of a total of 6 substances such as: 4-Isocyno-4'-pentyl-1,1'-biphenyl, 4-Hexyl-4'-isocyno-1,1'-biphenyl, 4-Isocyno-4"-pentyl-1,1':4,1"-terphenyl, 4-Hexyl-4"-isocyno-1,1':4,1"-terphenyl, 4-Isocyno-4""-pentyl-1,1':4',1":4",1""-quaterphenyl, 4-Hexyl-4""-isocyno-

,1':4',1":4',1""-quaterphenyl. The basic properties and structural formulas are mentioned in Table 1.

The polymer used in PDLC fabrication is a mixture of various monomers, oligomers, and other additives, and this mixture forms a polymer matrix through polymerization. It is assumed that as the properties of the polymer precursor mixture vary it affects the size of the liquid crystal droplet which results in differences in the electro-optical properties of the PDLCs. In this experiment, a mixture of acrylate-based oligomer, triethylene-glycol-dimethacrylate (TEGDA), and 3 precursors of different chain lengths was used (Fig. 1). The precursors were named as 2-Hydroxyethyl acrylate (HEA), 3-Hydroxypropyl acrylate (HPA), 4-Hydroxybutyl acrylate (HBA) having 2-carbon (2C), 3-carbon and 4-carbon chain length respectively. From these, a total of 3 polymer precursor mixtures were prepared. The composition of the mixture is shown in Table 2. The chain length of the monomers increases in the order of HEA → HPA → HBA.

Table 1. Basic Characteristics of LC- LVUL010300-100

Physical Characteristics	LC- (LVUL010300-100)
Clearing point (Appearance)	92 °C (Milky white)
C _p (°C) (Δn)	117.7 (0.212)
Resistivity (cm.Ω)	2.0E12

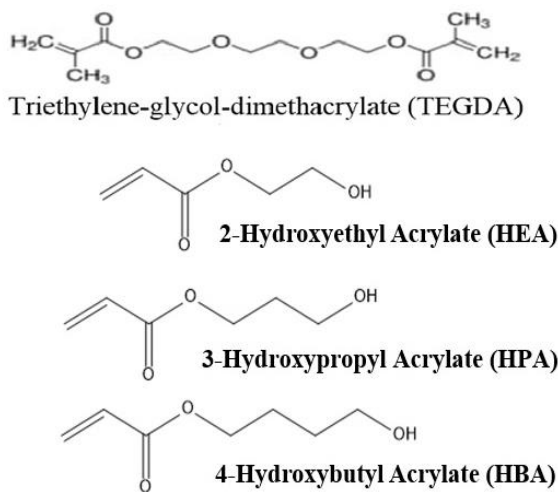


Fig. 1. The chemical structure of the used monomers constituting mixed solution of oligomers and precursors

2.2. Methodology/ PDLC film fabrication

2.2.1. Polymer precursors and LC mixture

In this experiment, the ratio of the polymer precursor and the liquid crystal (LC) mixture was all fixed at 45wt%: 55wt% to prepare a PDLC film (as mentioned in Table 3). There is no extra additive other than the polymer precursor (MA¹, MA², MA³) and liquid crystal (LVUL010300-100) were mixed, and the solution is mixed at 1000 rpm for 10 minutes using a homogenizer to make a uniform isotropic solution, and then used for PDLC production. The ratio of the mixed solution is shown in Table 3.

Table 2. Mixing ratio of polymer precursor MA¹, MA², and MA³

Polymer precursor	Added Monomer	Monomer (wt%)
MA ¹	TEGDA:HEA	9:1
MA ²	TEGDA:HPA	9:1
MA ³	TEGDA:HBA	9:1

Table 3. Mixing ratio of polymer precursor with the liquid crystal

Polymer precursor	Liquid Crystal (LVUL010300-100)
MA ¹ 45wt %	55wt %
MA ² 45wt %	55wt %
MA ³ 45wt %	55wt %

2.3. PDLC samples fabrication

Fig. 2 shows the PDLC film production method. First, an appropriate amount of liquid crystal and polymer precursor mixture is dropped on the ITO side of the PET film (which contained a resistance of 150 Ω/sq) coated with ITO (Indium Tin Oxide) (Fig. 3-a). Then it was covered with the ITO side facing (Fig. 2-b).

The gap of the PDLC film, that is, the cell gap, is controlled using the roll gap of the laminator (Fig. 2-c). At this time, the thickness of the cell gap is 15 μm. Finally, the film is placed under the UV lamp (λ=365 nm) and irradiated for 210 seconds to be cured (Fig.2-d). The intensity of UV was kept as 5.2 mW/cm², and such intensity was measured using EIT's UV POWER PUCK II. All manufacturing processes were carried out at room temperature, and ITO PET film was used without additional treatment. In the current work, all of the PDLCs films were prepared by polymer induced phase separation (PIPS) methods.

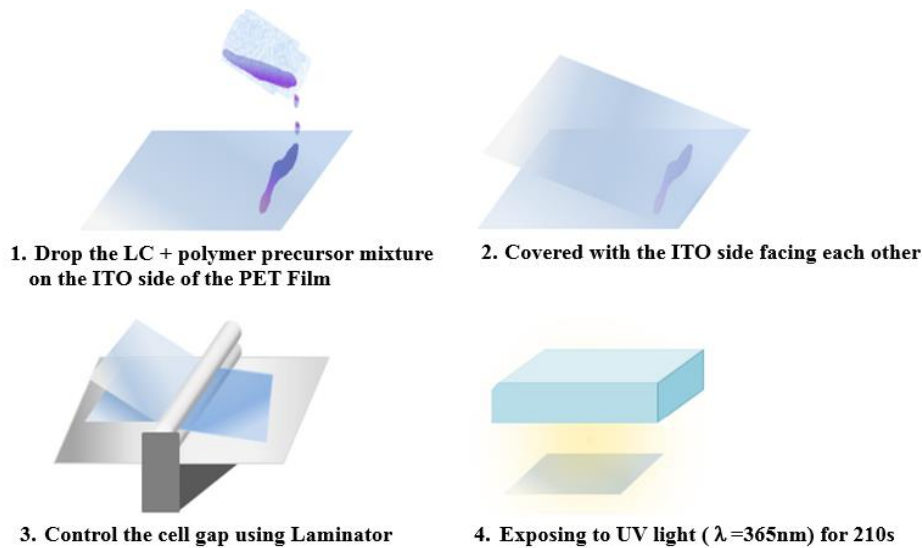


Fig. 2. A snapshot of the PDLC film production method (color online)

2.4. PDLC analysis technique

2.4.1. EO Properties

Transmittance and haze were measured while applying a voltage from 0V to 40V using a TH-100 Haze meter from CHN Spec. To check the threshold voltage of PDLC, transmittance and haze were measured at 1V intervals from 0V to 25V, and then at 5V intervals from 25V to 40V.

3. Morphology measurements

In order to estimate the liquid crystal (LC) droplet size and the thickness of the polymer matrix, the PDLC film was peeled off and the surface of the PDLC was observed. It was observed at $\times 2000$ magnification using a Flex SEM 1000 manufactured by Hitachi High-Tech, a scanning electron microscope.

4. Results and discussion

4.1. PDLC according to the chain length of the monomer changes in electro-optical properties

Fig. 3 shows transmittance measurements of PDLCs made using polymer precursors MA¹, MA², and MA³. The chain length of the monomer added to the polymer precursor increases in the order of MA¹ \rightarrow MA² \rightarrow MA³. From 0V to 25V, the threshold voltage was measured in units of 1V, and from 25V to 40V was measured in units of 5V. At 0V, where no voltage is applied, the transmittance values of PDLC using MA¹, MA², and MA³ are 15%, 17%, and 22%, respectively, showing a tendency to increase as the chain length of the monomer increases.

Actually the monomer functionality and their chain length have considerable role to alter the transmittance, saturation volt, threshold voltage via controlling the morphologies of the PDLC films. The reason here, for increase in transmittance at zero voltage is due to the increase of monomer chain length, which is linked with the morphologies of the PDLC films [14].

The maximum transmittance at 40V when voltage was applied was measured to be 83.8%, 84.0%, and 84.3%, respectively. Further as in 0V, the transmittance tends to increase as the chain length of the monomer increases. Checking the threshold voltage, the transmittance change using MA¹ fabricated PDLC, by MA² fabricated PDLC and, with MA³ fabricated PDLC, an increase of 10.05%, 10.50% and 14% was observed, respectively between 4V and 5V. Similarly using the MA¹ fabricated PDLC the transmittance increased by 7.0% between 3V and 4V. With the MA² fabricated PDLC and by the MA³ fabricated PDLC, the transmittance increased by 9% and 5%, respectively between the 3 V and 4 V.

Although it is a small difference, it reacts sensitively at a lower voltage in the order of MA¹ \rightarrow MA² \rightarrow MA³ that is, the longer the chain length of the monomer added to the polymer precursor increases. Therefore, it can be seen that the longer the chain length of the monomer, the lower the threshold voltage of PDLC.

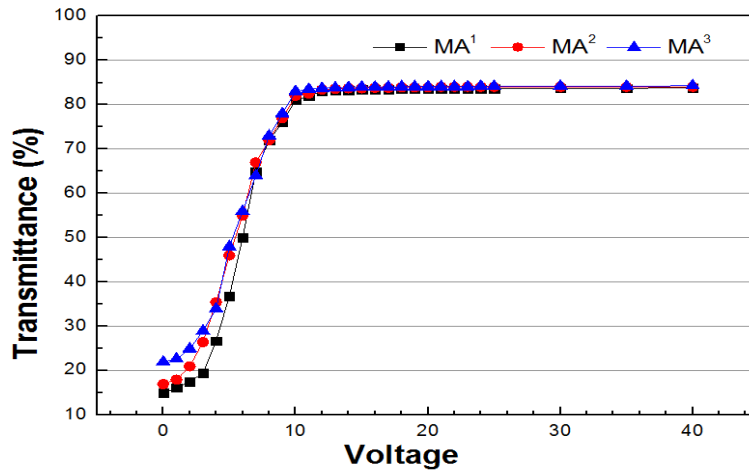


Fig. 3. Voltage Vs Transmittance curve of PDLC using MA¹, MA², and MA³ (color online)

4.2. Contrast ratio (CR)

The contrast ratio (CR) ($CR = T_{on}/T_{off}$) [21-22] was measured using the transmittance value at 40V, and the transmittance value at 0V. The contrast ratios of PDLC using MA¹, MA², and MA³ are 5.58, 4.94, and 3.83, respectively, and are shown in Fig. 4 for the comparison. The contrast ratio was calculated using the transmittance measurement.

From the CR response (as shown in Fig. 4) it is clear that as the chain length of the monomer increases, the

contrast ratio tends to decrease. The V-T curve increased overall, but the contrast ratio decreased, indicating that the transmittance increase rate in the ON state was lower than the transmittance increase rate in the OFF state. PDLC basically exhibits a high light blocking rate in the OFF state, that is, low transmittance and high transmittance in the ON state, so that it can be evaluated that the efficiency is good when it has a high contrast ratio.

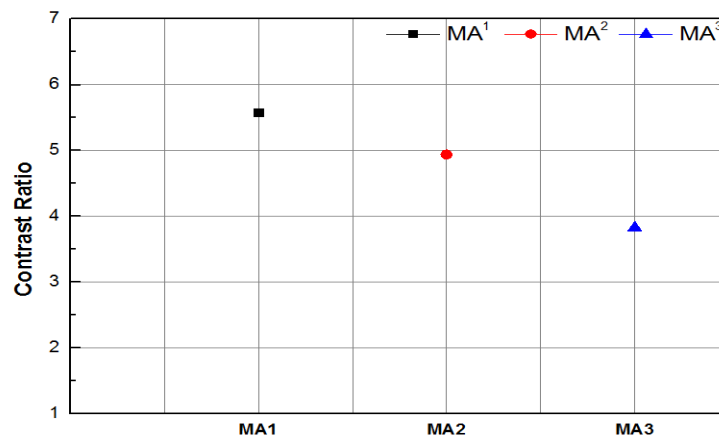


Fig. 4. Contrast ratio of PDLC using MA¹, MA², and MA³ (color online)

From the CR response (as shown in Fig. 4) it is clear that as the chain length of the monomer increases, the contrast ratio tends to decrease. The V-T curve increased overall, but the contrast ratio decreased, indicating that the transmittance increase rate in the ON state was lower than the transmittance increase rate in the OFF state [14,24], indicating that the efficiency of PDLC decreased. PDLC basically exhibits a high light blocking rate in the OFF state, that is, low transmittance and high transmittance in the ON state, so that it can be evaluated that the efficiency is good when it has a high contrast ratio.

4.3. Haze measurement

The optical haze is known as the fast decay of transmission at large viewing angles [19]. Usually the haze is caused by the effective increase in the refractive index of the liquid crystal [23]. The haze measurement [15-16, 19] values according to the applied voltage of the PDLC using MA¹, MA², and MA³ were evaluated like the transmittance Vs applied voltage technique. The initial haze of PDLC using MA¹, MA², and MA³ were all 100%, and the change in haze started at 5V. The haze at 5V was 99.1% for MA¹, 93.1% for MA², and

93% for MA³ and the haze changed steeply in the order of MA¹ → MA² → MA³. As in the permeability, it can be seen that the higher the chain length of the monomer, the steeper the haze change at low voltage, so that the threshold voltage is lowered. Haze showed a sharp decrease from 5V to 15V, and then the decrease became very narrow after 16V. However, it showed a steady decrease up to 100V, and the values of the final haze were measured to be 2.45% for MA¹, 2.39% for MA², and 2.3% for MA³. These are characteristics haze properties of the PDLC and it was expected from PDLCs having good performance.

The haze Vs voltage response of PDLC using MA¹, MA², and MA³ can be seen in Fig. 5. The curve overall had very little difference, and the beginning and end of the curve seemed to coincide. A closer view of the Fig. 6, reveals that haze rapidly decreases, it can be seen that the haze decreases more steeply at lower voltages in the order of MA¹ → MA² → MA³. The beginning and end of the curve are almost identical, but the steeper the curve, the more the PDLC saturates the haze at lower voltages. Therefore, it can be interpreted that the longer the chain length of the monomer, the lower the threshold voltage of PDLC. The threshold voltage can be related to the size of the liquid crystal droplet.

When the size of the liquid crystal droplet is formed large, the anchoring energy on the surface of the liquid crystal droplet decreases, and the liquid crystal molecules constituting the liquid crystal droplet are relatively less affected by the polymer, so a delicate and sensitive reaction is possible at low voltage. Therefore, it can be expected that the larger the size of the liquid crystal droplet, the lower the threshold voltage of the PDLC, and the increase in the chain length of the monomer would lead to the formation of a larger liquid crystal droplet.

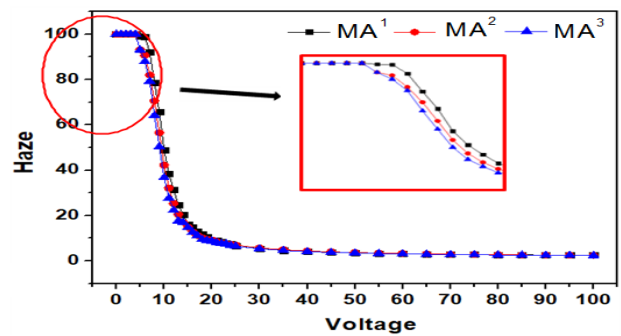


Fig. 5. H-T curve of PDLC using MA¹, MA², and MA³ (color online)

4.4. Surface morphology of PDLC (i.e., SEM analysis)

In order to investigate the crosslinking behavior and according to the chain length of the monomer the droplet sizes were observed at a magnification of $\times 2000$ using SEM. Fig. 6 shows the morphology of PDLC using MA¹, MA², and MA³. If you look at the image, it can be seen that the size of the liquid crystal drops increases in the order of MA³ → MA² → MA¹ and the interval between the liquid crystal drops, that is, the tendency of the thickness of the polymer matrix to thicken. Among the liquid crystal droplets observed by SEM were randomly selected and measured, and the average was calculated.

The mean values of the droplet sizes of MA¹, MA², MA³ were 1.58 μm , 1.72 μm , and 1.86 μm , respectively, and are shown in Fig. 7. Their comparison reveals a trend like MA¹ → MA² → MA³ the size of the liquid crystal droplet was confirmed to be large. As a result, as the chain length of the monomer became longer, larger liquid crystal droplets were formed, which lowered the threshold voltage of the PDLC, and the transmittance of the PDLC was increased by forming a thick polymer matrix.

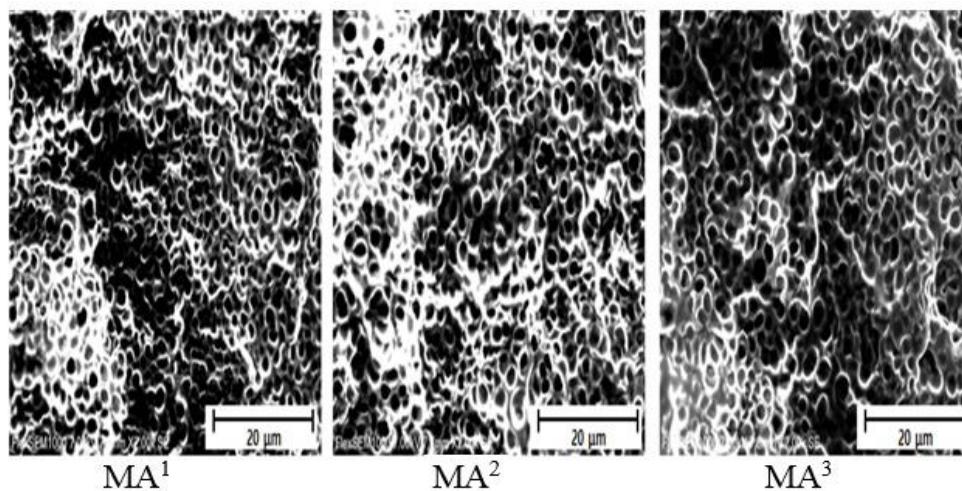


Fig. 6. Morphology of PDLC using MA¹, MA², and MA³

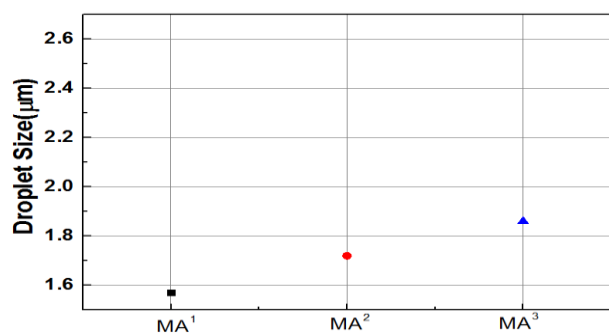


Fig. 7. Average liquid crystal droplet size of PDLC using MA¹, MA², and MA³ (color online)

5. Conclusions

In this work, the change in the electro-optical properties of PDLC was observed by changing the chain lengths of the polymer precursor. Thus the increase in the chain length away from the UV active side of the monomer is actually controlling the transmittance, CR, haze and droplet size in the process of polymerization. It is concluded that as the chain length of the monomer increases, the overall transmittance of the PDLC increases, which means that the PDLC appears more transparent at the higher chain lengths and thus CR decreases. Thus the increase in transparency of PDLC films with the increase in chain length is essentially correlated with the crosslinking behavior and intermolecular cell gaps during the polymerization process. Therefore, as the polymer matrix is formed due to larger chain lengths of monomers the transmittance of the PDLC increases. This phenomenon is confirmed by the increase in liquid crystal droplet size by SEM images with the increase in the chain length of monomers. Moreover, this behavior brings into decreased in threshold voltages. The following behavior can be validated by the contrast ratios results as well, which clearly shows decreases in CR with the increase in chain length. This work can be useful for further studies in PDLCs as the industry is growing fast and need of new monomers and LCs are essentially required to achieve useful PDLCs at the low cost.

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