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# Investigation of thiolene based polymer matrix crosslinked with polyoxamer in Polymer dispersed liquid crystal display

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This study is performed to explore the alteration of flexibility and solubility of polymer matrix in polymer dispersed liquid crystal (PDLC) films via electrically-optically variations and change in glass transitions temperatures. Following PDLC cell is formed by photo induced phase separation method, in which a mixture of thiolene-isocyanate-ether based monomer is crosslinked with polyoxamer with various weight ratios. The characteristics of resulting PDLC devices have been determined through latest techniques. The droplet size variations have been determined through scanning electron microscope (SEM) and exhibited an increase with rise in polyoxamer ratio. Current electro optical studies revealed a decrease in threshold voltage and increase in the contrast ratio with higher contents of polyoxamer. Beside this, the optimal electro optical properties, a decrease in glass transition temperature for thiolene based polymer matrix has been observed with growth in amount of polyoxamer. This behavior was due to hydrophobic characteristics of polyoxamer material which showed less attractions towards the thiolene polymer matrix. Thus, it gave a competent degree of phase separation, and boosted the flexibility of polymer matrix that resulted into rise of free volume. Consequently, such findings suggest the usage of this material which enhances PDLC electro optical performance with scrupulous concentrations.

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*Keywords:* Thiolene monomer, Glass transition temperature, Polymer dispersed liquid crystal, Electro-optical properties

## 1. Introduction

Polymer disperse liquid crystals (PDLCs) films are highly scattered at zero voltage and show transmittance on applying the small external voltage. In PDLC films, the micron size nematic liquid crystal (LC) droplets are embedded in polymer matrix. These have been the subject of interest related to light control applications and electronic displays devices for the last few decades [1]. In the previous findings the priority was given to the study of morphology and electro-optical properties of PDLC display with various mixtures i.e. LCs, monomers, dye [2-5], curing conditions such as temperature, UV irradiation [6-7], and on chemical structures of the materials [8-9].

Earlier it has been evaluated; the special interactions among the LCs with the polymer matrix and as well as with the glass substrate have highly impact on the PDLC morphology and electro optical properties [1-8]. These special types of interactions on the surfaces and among the molecules are considered as the anchoring energies. Formerly in emulsion industry to control the surface energies, the amphiphilic block copolymers, polymers, and surfactants have been widely used as a surface-active agent to reduce the following interactions [10-12].

Norland Optical Adhesives (NOA65) is well known as commercial material [13,15] and this product is made of thiol-ene molecules containing the $SH_2$- group and multifunctional groups insuring cross-linking and network formation in addition to a photo-initiator. The product is widely used as an efficient non-toxic adhesive and in research as a network forming system with a high cross-linking density under UV-irradiation [13-15]. While polyoxamer are known as potential polymers in medicine [16] and in emulsion, and in detergent industry as self-aggregating hydrophobic materials [17-18]. Moreover, in PDLCs they have been used as potential elements to control the rate of phase separation and related electro optical and morphological properties [19].

The aim of this work is to explore the insertion of polyoxamer in the thiolene based PDLC. In order to investigate the polymer matrix inter-molecular interactions, flexibility, thermal properties and further its effect on morphological and electro optical variations in following PDLC system. For this study, different weight ratios of thiolene-polyoxamer were used while the compositions of liquid crystals remained fixed. The effect of addition of the polyoxamer in thiolene based PDLCs was investigated by morphologically, electro optically and variations in glass transitions temperature of thiolene polymer matrix.

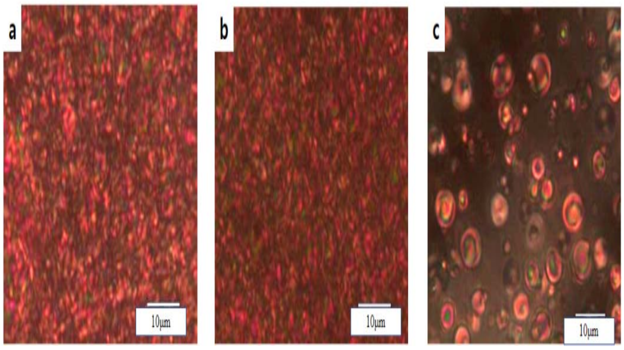

*Fig. 1. Surface morphology of PDLC as viewed by polarized optical microscope*

## 2. Experimental work

### 2.1. Materials

In a complex polymeric matrix to investigate the inter molecular interactions, free volume space via polymer dispersed liquid crystal films (PDLC) a UV curable monomer NOA65 ((Norland Products Co., Merck-Korea) is used as thiolene monomer. This Norland Optical Adhesive 65 (NOA65) is a clear, colorless, liquid photopolymer, when exposed to ultraviolet light it become 100% solids. It showed at -60°C the glass transition temperature that showed the high rigidity of the polymer film [13]. Its further characteristics are shown in Table 1. In the following complex matrix study, a polyoxamer (PO) was chosen as second polymer. This is amphiphilic (mostly behaved as hydrophobic) Poly(ethyleneoxide)-b-poly(propyleneoxide) Pluronic® F-68 (Mw= 8350) (Sigma-Aldrich chemical). To make the PDLC devices from the following polymer materials a mixture of nematic liquid crystals BL-001 (Merck-Korea) were utilized. BL-001 has a composition of 51% n-pentyl-cyanobiphenyl (5CB), 25% n-heptylcyanobiphenyl (7CB), 16% n-octyloxy-cyanobiphenyl (8OCB), and 8% n-pentyl-cyanoterphenyl (5CT) with a clearing point of TNI = 61 °C and ordinary refractive index of 1.5216.

*Table 1. Chemical properties of NOA65*

| | |
|---|---|
| **Solid** | **100%** |
| **Viscosity at 25℃** | **1200cps** |
| **Refractive index** | **1.524** |
| **Modulus of Elasticity(psi)** | **20,000** |
| **Tensile Strength(psi)** | **1500** |

### 2.2. PDLC preparation

The PDLC mixture consist of different compositions of thiolene, polyoxamer (PO) while BL-001 ratio was remained fixed. The contents of thiolene and PO were varied from 0-15wt% while amount of LC were selected as 60 wt%. Following compositions in weight ratios are shown in Table 2. These were vigorously stirred over night at room temperature conditions to make a homogenized isotropic mixture. Further, the PDLC devices were prepared by using polymer-induced phase separation method with UV light photo-initiated polymerization technique. Subsequently this mixture was sandwiched between two cleaned conductive indium tin oxide (ITO) glass plates. To control the film thickness, the micro bead spacer with 20 μm of diameter (Sekisui chemicals, Japan) was dispersed over the ITO glass prior to disperse the PDLC mixture. Afterwards, this was UV cured by irradiation of 365 nm wavelength (λ) of light at room temperature conditions. After preparations of following PDLC devices various properties were studied by using different analyzing techniques.

*Table 2. Compositions of polymer dispersed liquid crystal film*

| **WEIGHT RATIOS OF MATERIALS** | |
|---|---|
| THIOLENE: POLYOXAMER (WT%) RATIO | LIQUID CRSYTAL (WT%) RATIO |
| 1 : 0 | 60 wt% |
| 7 : 1 | |
| 3: 1 | |
| 1.16 : 1 | |

### 2.3. Experimental measurements

To investigate the inter-molecular interactions, flexibility and free volume space among the polymer matrix and with the LC molecules initially the conventional technique was used. At first to observe surface morphology of the PDLC films, it was viewed by polarized optical microscope (POM) (Olympus Model BX-60) at 10X magnification fitted with charge coupling device and a digital camera interfaced with computer. Afterward, the electro optical properties were determined by using the UV-vis spectrophotometer Minolta (Japan) (model UV-3500d) and a manually operated volt meter to control the voltage. Later on, to investigate the droplet size and extant of phase separation the following devices were viewed by SEM Scanning Electron Microscope (Japan, JOEL Co. JSM5200) at an x1500 magnification. For such studies initially the PDLC cells were immersed in ethanol for 20 hours to remove the liquid crystals. To evaluate the glass transition temperature (Tg) of polymer matrix and solubility of block copolymer with LCs molecules, the glass transitions temperatures have been estimated by Diamond DSC of Perkin Elmer pyris series of USA. To investigate the change of glass transition temperature according to the ratio of the polymers supporting PDLC, 0.03 g of the PDLC mixture were placed on the DSC stage with selective weight ratios of the materials. The heating rate was increased from -65 ° C to 65 ° C at 2 ° C / min rate. After holding at 65 ° C for 3 minutes, the temperature was cooled to 20 ° C / min. This process was repeated twice.

## 3. Results and discussions

### 3.1. Morphologies

Initially to study the complex polymer interactions inside the PDLC the surface morphology of the PDLC devise have been observed. The investigation of surface morphologies of thiolene with polyoxamer based PDLCs were initially considered by conventional method Polarized Optical Microscopy (POM) at 10x lens magnification with 90 angle of polarizer film at zero applied voltage. The following PDLC device images are shown in Fig. 1 with respect to variation in percentage ratios contents of thiolene ratios to PO i.e. 7:1, 3:1 and 1.6:1 wt%. The liquid crystal contents were remained fixed in the fabrication of following devices. Fig. 1(a,b,c) represents two states (dark/colored state Fig. 1(a,b)) and these deformities in images under the POM, basically which establish the random orientation of nematic LCs in all directions [20]. Fig. 1(c) showed dark/colored images of nematic liquid crystals, possibly owing the larger droplet size. Apparently, these droplets are of different in sizes from 2 to 10 mm. It is considered earlier at azimuthal angle close to 0° the concentric LC configuration circles were perpendicular to the bottom polarizer. Hence the droplet exhibited a minimum optical retardation effect and the texture was dim (dark) [21]. Deep study of following Fig. 1(c), showed that it has characteristic bipolar eye like texture [1].

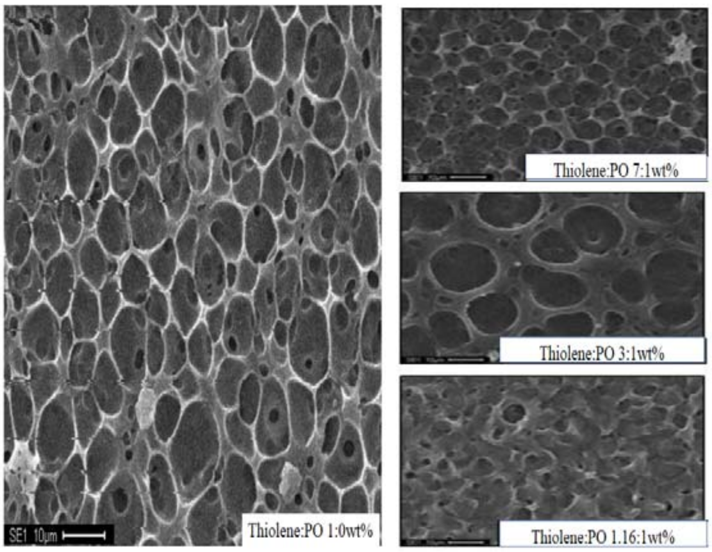

*Fig. 2. SEM images of PDLC*

For further analysis the SEM images were taken for the following devices. For the purpose to understand the variations in droplet formation and sizes with the insertion of thiolene- polyoxamer (PO) matrix. In this direction, initially the LCs are extracted out from the devices by dipping them in the ethanol/isopropyl 1:1 mixture for 10 days. Next to this these devices were dried to evaporate all solvent at vacuum $60^{o}$C temperature. Afterwards, the surface images from SEM were taken for small pieces of devices. These images are displayed in Fig. 2(a,b,c). Fig. 2a displayed that with insertion of zero weight percent of polyoxamer PO the PDLC device fabricated with thiolene polymer showed droplet morphology having larger sized droplets imbedded in matrix. Droplets were ranges in sizes from 2-10μm. The thiolene reaction uses allyl-functionalized monomers to form monomer chains while thiol compounds are crosslinked with each other [1]. Once the ethylene oxide polymer was inserted of 7:1-3:1wt ratios of thiolene compound a variation in droplet size and shape was observed (Fig. 2c-d). It was viewed as a decrease in droplet size and regularities in droplet size and shape for 7:1 wt ratios of PO with thiolene. However, a distortion in LC droplets size was observed for increase in PO (3:1wt%) matrix. Moreover, droplet morphology tending to polymer ball morphology as the PO is extended to 1.16:1 wt% for thiolene. The polymer balls were relatively small in sized remained under the 10 μm. The variation in droplet size is tableted in Table 3. This variations in droplet morphology reveals the variation in emulsion composition, polymerization rate, flexibility and inter molecular interactions of following matrix as other conditions were remained fixed. The variations in morphology expose the varying electro optical behavior for following devices. It was essential to find factors behind the variations in morphology and electro optical properties related to each other.

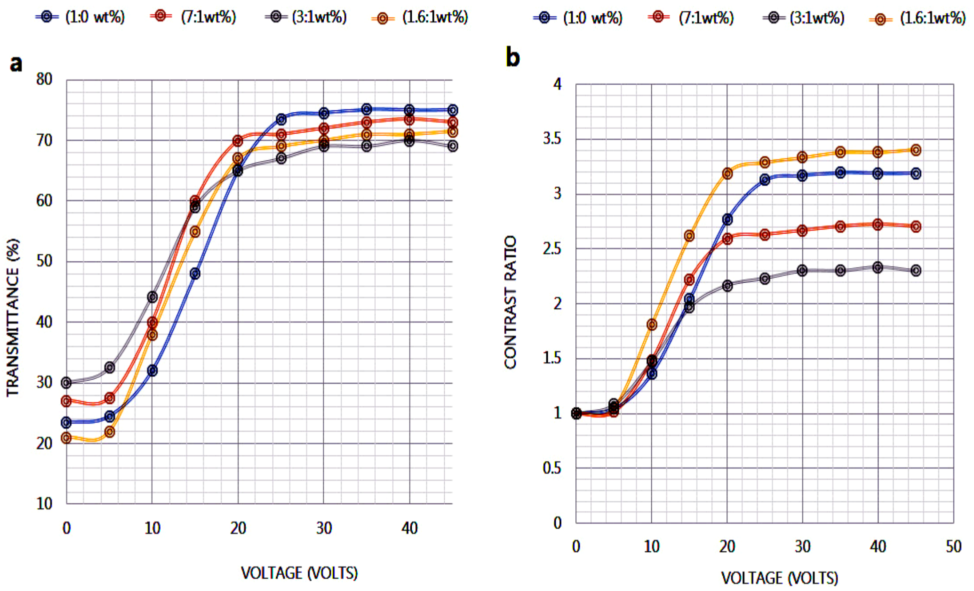

*Fig. 3. Electro optical properties of PDLC*

### 3.2. Electro-optical properties

Morphological studies tell the variations in droplet morphology as lead by variations in PDLC emulsion compositions. The electro optical properties of the following devices were calculated and plotted in Fig. 3. The percent transmittance of incident light at zero angle through PDLC devices was measured by using UV-visible spectrophotometer at various voltages. A familiar transmittance-voltage curve of PDLC display can be seen in Fig. 3. It was showed that transmittance- and CR-curves against voltages increased with various trends. Since, the study of surface morphology anticipated the variations in electro optical properties with varying surface morphologies. Transmittance vs voltage curves plotted in Fig. 3a showed that it increases with voltages. However, three curves with distinguished slopes reveled the dependency of EO properties on emulsion composition that is controlled by physio chemical changes during fabrication process. Fig. 3a showed a decent increase in off scattering of PDLC device that is fabricated with emulsion having 7:1 weight ratios of polyoxamer -thiolene group as compared to 1:0 wt% of thiolene. Other devices showed that device fabricated with 1.16:1 wt% ratios of following group showed a decrease in off scattering. However, ON transmittance seems independent of emulsions compositions or showed little effect on this property. The contrast ratio (CR) calculated for these devices are shown in Fig. 3b, that enlighten the importance of following material. It is observed from Figure 3b, that CR of device fabricated with 1:0 wt. ratios of polyoxamer -thiolene mixture have highest contrast 2.04 CR at 15 volts and further it crossed the highest level 3.2 CR at 30 volts. However, the PDLC device fabricated with 1.16:1 wt% of thiolene (or max PO group) showed max scattering at 0 voltage and showed max transmittance at max volts ON state i.e 3.4. This exposed the importance of PO group in thiolene mixture to make optimal properties PDLC device. The plot for the threshold voltages (Vth) and saturation voltages (Vsat) is shown in Fig. 4(a,b).

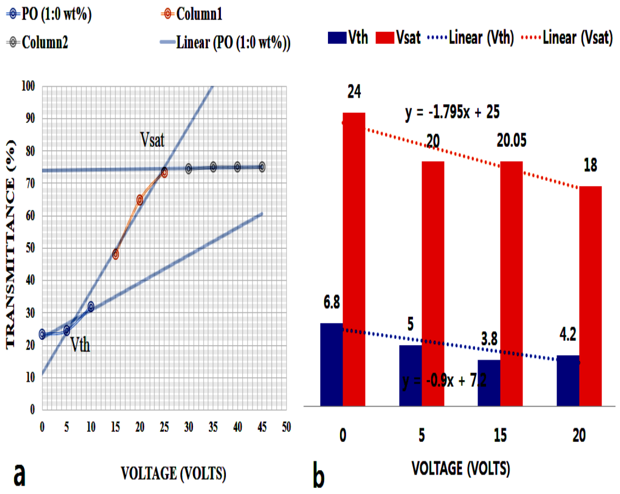

*Fig. 4. Threshold voltage and saturation voltage of PDLC*

Vth and Vsat are calculated with insertion of linear trend lines on the volt-transmittance data and crossing the two lines at maximum intersecting slopes which are shown in Fig. 4a. The data plotted in Fig. 4b displayed a decreasing trend for Vth and Vsat for increasing ratios of polyoxamer (PO) in thiolene mixture. This emphasis of insertion of external polyoxamer group in the thiolene based PDLC devices.

### 3.3. Glass transition and nematic to isotropic transition temperatures

The investigations of variations in transitions temperatures of polymer matrix (glass transition temperature (Tg) and liquid crystals (nematic to isotropic temperature (TNI)) is a successful analytical approach to find the strength of intermolecular interactions in PDLCs [22]. The study of glass transition temperature (Tg) of polymer molecules inside the PDLC is a latest method to describe the inter-molecular interactions, solubility and free volume space among the polymer with polymer molecules. It can interpret the reason for droplet size variations via the strength of polymer matrix that supporting the liquid crystals. The DSC results for the Tg of polymer matrix are written in the Table 4 according to the emulsion ratios. For such studies initially the PDLC cells were immersed in ethanol to remove liquid crystals. It was found earlier and shown in Table 4 that Tg of the NOA65 was found as -60$^{o}$C when tested alone [13]. In this work of PDLC after curing, a DSC of following polymer film without using the polyoxamer the Tg was observed at -9.86 $^{o}$C. This may represent the increase in flexibility, and less solubility of polymer matrix with the liquid crystal molecules [22]. Thus, it showed larger droplet sizes (Fig. 2a). As the 7:1wt ratio to 1.16:1 wt ratios of polyoxamer added the Tg was observed as -24.77, -15.52, and -9.87 $^{o}$C respectively. It can be observed that with the increase in weight ratio of multiple hydrogen carrying groups like polyoxamer the Tg of PDLC mixture increased. Further this reached to the pure thiolene based PDLCs. The reason at very low Tg point (-24.77 $^{o}$C) can be that at addition of small amount of polyoxamer group, the self-aggregation of such materials was disappeared at the interface among the thiolene and PO polymers. Thus, the flexibility of the polymer chain decreased and hence this exhibits a glass transition point at very low temperature (-24.77 $^{o}$C). This may result into more hard and rigid polymer matrix. However, the addition of comparatively large amount of polyoxamer group may elevate the flexibility of polymer chain thus Tg elevated to the level of thiolene group once again. The reason behind this can be the hydrophobic effect of following polyoxamer group. The hydrophobic PO polymers showed less attractions towards the hydrophilic thiolene groups thus flexibility of molecules increase and Tg decreased.

*Table 3. Droplet sizes of PDLC morphology as measured by SEM*

| THIOLENE: PO CONTENTS (WT%) | AVERAGE DROPLET SIZE (μm) |
|---|---|
| 1:0 | 6.5 |
| 7:1 | 5.1 |
| 3:1 | 7.5 |
| 1.6:1 | 5.4 |

This increase in flexibility of polymer matrix hence increases the molecular gaps that results into increase in LC droplets size. This can be exposed with SEM images and with improved electro optical properties of PDLC devices (decrease in driving voltage) with the addition of PO polymer ratios. Therefore, the amphipathic polymeric material can be used for solubility regulator, flexibility control and reduction of glass transition temperature in PDLCs.

*Table 4. Glass transitions temperatures of PDLC as measured by DSC*

| polymers | Weight ratios | $T_g$ |
|---|---|---|
| NOA65 | 100% | -60$^{o}$C |
| Thiolene: Polyoxamer | 1:0wt% | -9.86℃ |
| | 7:1wt% | -24.77℃ |
| | 3:1wt% | -15.52℃ |
| | 1.16:1wt% | -9.87℃ |

## 4. Conclusions

In this work, a study is made for the PDLC films that are fabricated initially with familiar thiolene polymer matrix that is known as NOA65 and further a polyoxamer with hydrophobic properties has been added. This is done to explore the change in flexibility, toughness of polymer matrix that lead to change in droplet morphology and as well as electro optical properties of PDLC devices. For this purpose, the morphology, transmittance-volts, contrast ratio, Vth, Vsat, and Tg have been evaluated. Initially, the observed results have shown that with the addition of very small amount of polyoxamer the flexibility of thiolene based polymer matrix reduced and droplet size decreased. However, with the increase in hydrophobic polyoxamer polymer ratio the droplet size increased, electro optical Vth decreased and Tg reached to the flexibility point of thiolene based PDLCs. This behavior is considered as due to flat solubility of polyoxamer with the thiolene matrix and with LC molecules. Since, it is required for higher phase separation. Furthermore, the elevated values of degree of phase separation and inferior values of Tg of polyoxamer illustrate its useful properties in thiolene based PDLC display.

## References

[1] P. S. Drzaic, Liquid crystal dispersions (Singapore: World Scientific) **1**, 22 (1995).

[2] F. Ahmad, J. W. Lee, Y. J. Jeon, M. Jamil, J. Optoelectron. Adv. M. **19**(5-6), 309 (2017).

[3] F. Ahmad, M. Jamil, J. W. Lee, K. N. Lee, Y. J. Jeon, J. Mod. Optics **64**(20), 2179 (2017).

[4] J. W. Lee, J. K. Kim, F. Ahmad, M. Jamil, Y. J. Jeon, Liq. Crys. **41**(8), 1109 (2014).

[5] F. Ahmad, M. Jamil, Y. J. Jeon, L. J. Woo, J. E. Jung, J. E. Jang, G. H. Lee, J. Park, J. App. Poly. Sci. **121**(3), 1424 (2011).

[6] F. Ahmad, M. Jamil, J. W. Lee, S. R. Kim, Y. J. Jeon, Electron. Mater. Lett. **12**(5), 685 (2016).

[7] F. Ahmad, J. W. Lee, Y. J. Jeon, M. Jamil, Rev. Roum. Chim. **62**(12), 907 (2017).

[8] J. He, B. Yan, B. Yu, S. Wang, Y. Zeng, Y. Wang, Eur. Polym. J. **43**(6), 2745 (2007).

[9] H. L. Lui, H-T. Liu, F.-R. Tsai, Poly. Internl. **42**(2), 385 (1997).

[10] F. Ahmad, M. Jamil, Y. J. Jeon, Arab. J. Chem. **S339** (2017).

[11] F. Ahmad, M. Jamil, J. W. Lee, G. N. Jang, Y. J. Jeon, Liq. Cryst. **43**(2), 162 (2016).

[12] J. Lanzo, F. P. Nicoletta, G. De Filpo, G. Chidichimo, J. Appl. Phys. **92**, 4271 (2002).

[13] R-D. Benmouna, B-N. Benyoucef, J. Appl. Polym. Sci. **108**, 4072 (2008).

[14] G. W. Smith, Phys. Rev. Lett. **70**(7), 198 (1993).

[15] T. Kyu, D. Nwabunma, D. Macromolecules **34**, 9172 (2001).

[16] P. B. Shelat, L. D. Plant, J. C. Wang, E. Lee, D. J. Marks, J. Neuro. Sci. **33**(30), 12287 (2013).

[17] F. Ahmad, M. Jamil, L. J. Woo, Y. J. Jeon, Mat. Plast. **52**(2), 171 (2015).

[18] M. B. Henda, A. Gharbi, Polym. Sci. Ser. A **59**(5), 624 (2017).

[19] R. Bhargava, S. Q. Wang, J. L. Koenig, Macromolecules **32**, 8982 (1999).

[20] R. R. Guimarães, R. S. Mendes, P. R. G. Fernandes, H. Mukai, J. Phys. Condens. Matter. **25**, 404203 (2013).

[21] J. Jiang, D-K. Yang, Liq. Crys. **45**, 102 (2018).

[22] Y. H. Kir, H.-Jun Ahn, Liq. Cryst. **31**(11), 1525 (2004).

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