The Absorption of Block Copolymer: Block Copolymer based Polymer Dispersed Liquid Crystal (PDLC) Film

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In this work the properties of PDLC film based on block copolymer film are presented. The FTIR; phase transition temperature properties are studied in order to see the absorption of block copolymer with the LC. Optical microscopic work showed the increase in droplet size with the increase in block copolymer contents. It is found absorption of block copolymer does not increase linearly with the increase in its contents. Moreover a decrease in refractive index is observed with the increase in block copolymer contents. The decrease in refractive index of block copolymer with temperature is interesting for thermo-optical and electro-optical devices simultaneously.

Keywords: Polymer Dispersed Liquid Crystal (PDLC); Phase separation; Liquid Crystal (LC): FTIR spectroscopy

Polymer-dispersed liquid crystal (PDLC) films are heterogeneous composite structures in which smaller sized (ranges from micrometer to nanometers) LC droplets are surrounded by solid polymer matrix (1,2). Due to unique properties of LC and PDLC structure it exhibit distinctive electro optical properties [3]. PDLC displays are interesting from an application point of view due to their simple technology, low cost, large apertures and high durability; which fascinate it over the respective LC displays [4, 6]. The very first applications of PDLC displays have been the smart windows [7], light modulators [8, 9] and fiber optic devices [10] have been developed.

The microscopic interactions of polymer and LC played a crucial role on the morphology and electro optical properties of PDLC films. The nematic fluid in contact with a solid substrate, adopts a preferred alignment; that is referred as anchoring which is dominated by the microscopic interactions at the interfaces between the LC and the polymer matrix [11, 13]. Microscopic interactions are considered to control the electro optical properties of PDLC films by adjusting the polyacrylate branched or straight side chain length, the composition of amphiphilic group, and by deposition of surfactants and self-assembled monolayers [13, 17].

Here in this discussion the block copolymer is studied with the liquid crystal in order to understand the anchoring properties as the absorption of block copolymer with the LC and phase separation of PDLC mixture. For the purpose PDLC films morphologies and thermo-optical properties are studied by using the FTIR spectroscopy, polarized optical microscopy and by monitoring the phase transition temperature of LC. This work have been made in order to see the potential application of block copolymer in the PDLC films for good thermo-optical as well as for electro-optical properties.

Experimental work

Materials and methods

To study the thermo and electro-optical properties of block copolymer based PDLC film; an amphiphilic block copolymer the polystyrene-b-polyethylene oxide (PSPEO) is selected. The molecular mass and block ratio for ethylene oxide and styrene block for PSPEO has been found as 1.62 X 10^4 g/mol and 1:2.2 respectively [18]. The liquid crystal used for these experiments is E7 (Sigma), which is an eutectic liquid crystal mixture consisting mostly of 4-pentyl-4'-cyanobiphenyl (5CB). This LC is chosen instead of the single-component 5CB because 5CB does not phase separate easily to form droplets [19]. The PSPEO and E7 contents are varied from 1:1; 1:2; 1:4 and 1:6 wt % (as 10wt%, 20wt%, 33wt% and 50wt for PSPEO). Next to this 7 wt % of the total 3 wt % EHA (2-Ethylhexyl Acrylate; Sigma) is mixed as hardener for PDLC film. Following this less than 0.1wt % UV initiator (HMPP; Sigma) is added in it.

The any change in block copolymer morphology generated *in situ* due to interactions and absorption PSPEO ratio at scattering state (off state) and the change in phase transition temperature of LC; have been studied by mean of polarized optical microscopy (POM) (Olympus Model BX-60) fitted with charge-coupling device on digital camera interfaced and also equipped with a hot stage. An IR spectroscope (Nicolet Magna IR 760) is used to investigate the diffusion of LC into block copolymer matrix. Refractive index is measured on Abbe refractometer (ATAGO 41 Japan). These measurements are reported after taking the averages of three runs.

Results and discussions

FTIR analysis

The properties of block copolymer polystyrene-polyethylene oxide (PSPEO) based PDLC films are performed by FTIR spectroscopy. Former the PSPEO is characterized as amphiphilic block copolymer in aqueous and organic media [12]. The PSPEO has been observed as surface active on the aqueous/organic bulk under 0.1 g/dL concentration at 25^{0}C.

The FTIR study is used to monitor change in absorption of PSPEO and LC by varying the block copolymer composition in the form of solution and during phase separation. For the purpose the spectrums of pure block

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copolymer [12], E7 and mixture of these are observed after Phase separation. The various peaks are assigned for pure PSPEO and for E7 are explained elsewhere [12, 18]. Block copolymer showed a wide strong absorption characteristic ether peak for -COC linkage at 1102 cm^{-1}. For E7 liquid crystal the characteristic peak for -CN stretching band [18] is assigned at 2227 cm^{-1}. Moreover to manipulate the any change the absorption spectra for E7/PSPEO solutions and its PDLCs are shown in figures 1 and 2 respectively. Comparison with spectra of the pure components shows that there are no peaks unique to the PDLC system. All peaks in the spectra of the PDLC films arise from either the liquid crystal or the block copolymer. The change in peak shape is observed as the block copolymer and E7 contents are varied (fig. 1 and 2). This change is calculated as the difference between the full widths at half-maximum (DWM) for the PDLCs at solution and at PDLC formation for the -Ca≅N and -COC specific peaks for E7 and block copolymer respectively (fig. 3). It is observed that the -CN peak does not exhibit as much of a change in shape like as the alkyene peak.

It is observed that the -COC (1680-1780cm^{-1}) peak broadens with increase in E7 contents after curing the PDLCs (fig. 2), indicated as the DWM values (fig. 3). Also, as the concentration of block copolymer in the PDLC increases, the amount of broadening of the alkyene peak is reduced. The similar trend found for the nitrile peak with increasing liquid crystal content; the nitrile peaks narrow with the increase in liquid crystal concentration. Thoroughly observation of spectra for block copolymer PDLC series as a function of concentration, the absorbance of a few peaks does not correspond to the changes in concentrations. Moreover the LC nitrile peak for all E7 contents exhibits a much smaller amount of change and, in contrast to the -CO peak, becomes broader with higher E7 ratios.

The broadening of the polymer peak may be due to the fact that, as the LC phase separates from the polymer matrix, the polymer becomes more solid-like or less plasticized by the liquid crystal. Likewise, the more of the LC molecules are in the bulk LC, as opposed to being dissolved in the polymer. They are in a more liquid-like state, which gives rise to a narrower peak.

Extent of phase separation

These changes are studied as degree of phase separation of block copolymer and LC. According to expression [12, 20, 21] the absorption of –CN band as cure and uncure state are recorded. figure 4, 5 and 6 demonstrate this phenomenon by showing the E7 nitrile (CN) absorbance at uncure and CN absorbance for cure and ratio of absorbance of (CN_{uncure}-CN_{cure}/CN_{uncure}); which corresponds to extent of phase separation. This is calculated by following the equation 1 and 2 [12, 20, 21].

$$A_{CN.uncured} = \Phi A_I \quad (1)$$

$$\alpha = \left(\frac{A_{CN.uncured} - A_{CN.cured}}{A_{CN.uncured}}\right)\left(\frac{A_I - A_N}{A_I}\right)^{-1} \quad (2)$$

Consider A_I be the absorbance of the liquid-crystal-specific band in its isotropic state and A_N be the absorbance of the liquid-crystal-specific band in its nematic state. Further, let ϕ be the fraction of liquid crystal in the initial homogeneous mixture with the matrix precursor. For a constant cell thickness, the absorbance of the liquid crystal-specific band is given simply by equation 1. If (α) is the fraction of liquid crystal which phase separates during the polymerization process, then the total fraction of the liquid

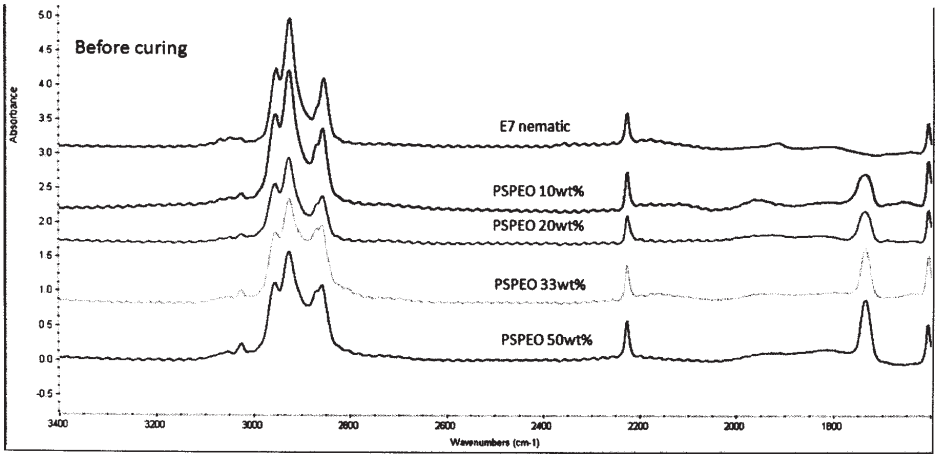

Fig. 1. FTIR spectrum of block copolymer based PDLC solution mixtures

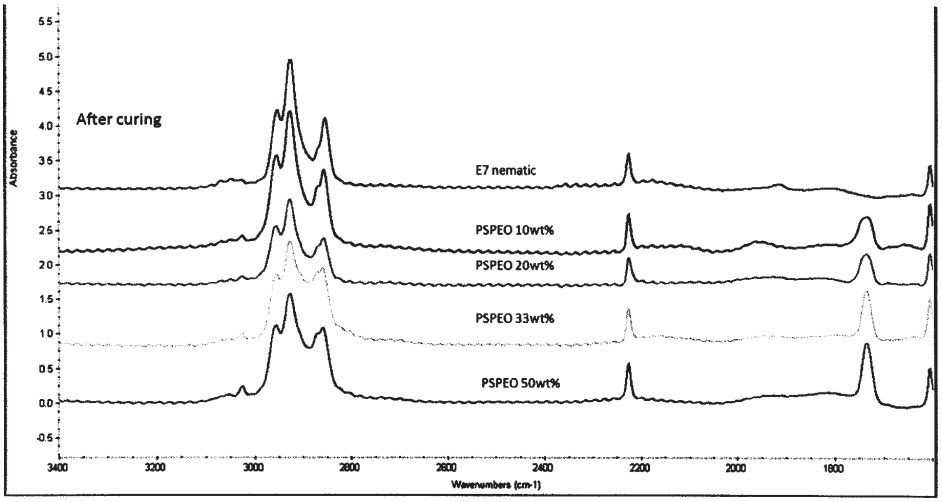

Fig. 2. FTIR spectrum of block copolymer based PDLC at cure state

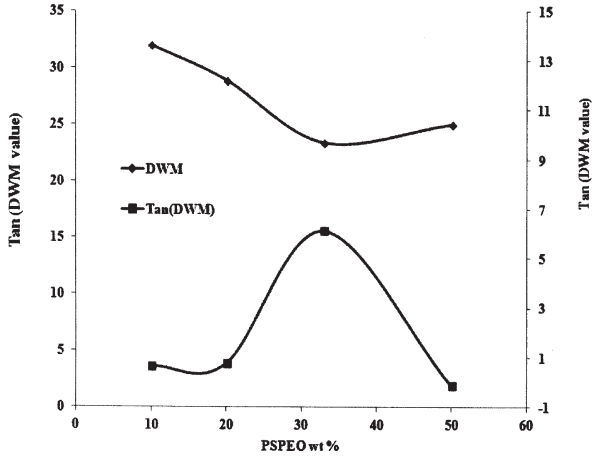

Fig. 3. DWM values for carbon-carbon double bond of PSPEO for PDLC mixtures

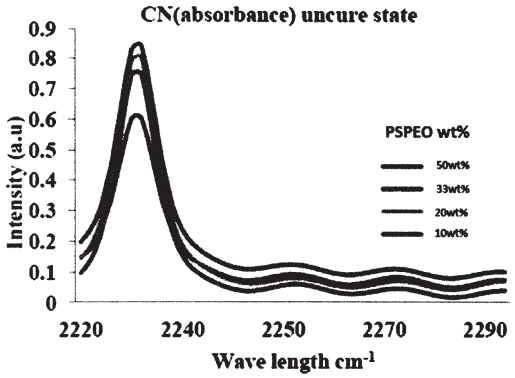

Fig. 4. Change in absorbance of CN bond for PSPEO doped un-cure solution

crystal in the droplets is ($\alpha\phi$) . Further on eliminating (ϕ); it gives liquid crystal fractions (α) as given in equation 2.

Each absorbance values are obtained from the spectrum of the PDLC film at un-cure and cure state of formation. For the PSPEO PDLCs, the absorption peak for the E7 ratio increased with block copolymer contents; whereas in solution form this absorption further decreases with the increase of block copolymer contents. While the difference and ratios of the un-cure and cure increased with the LC contents. Both of the above ratios are obtained with the use of LC peaks only.

In the liquid state, molecular motions are faster than in the solid state, so the molecular motion which is able to be detected is an average of all the motions, which lead to the narrow peak. In other words, the overall mobility of the liquid crystal, as indicated by the shape of the IR peak, is increased when the liquid crystal molecules reside within the droplet of a PDLC film. The magnitude of the change in the peak shape over the concentration for both the LC and the block copolymer; it decreases as the percentage of block co-polymer in the PDLC increases. With less LC present in the PDLC film, the droplets are smaller. Also, at higher polymer concentration, the droplets do not combine or coalesce. Therefore, the amount of bulk LC is less, leading to a smaller change in the peak shape.

Droplet morphologies

In order to see correlation between PSPEO and LC absorption; droplet size and morphology is examined by polarized optical microscope. A general trend with the increase in liquid crystal contents increase in droplet size is observed. Deep analysis of the figure .7 showed that very small size LC droplets have well bipolar shape. While as the LC contents are increased LC droplets increased in

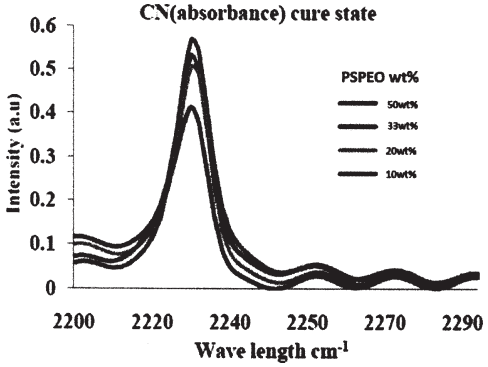

Fig. 5. Change in absorbance of CN bond for PSPEO doped PDLCs at cure state

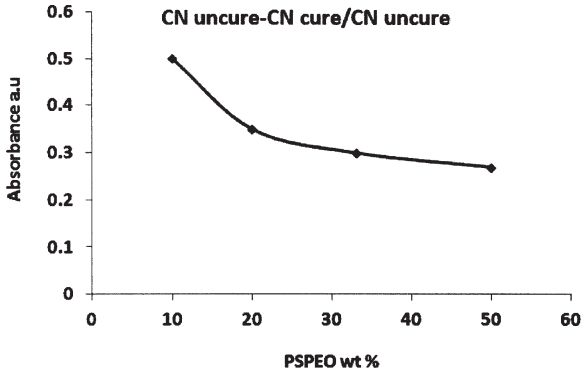

Fig. 6. Extent of phase separation of PSPEO and E7 based PDLC

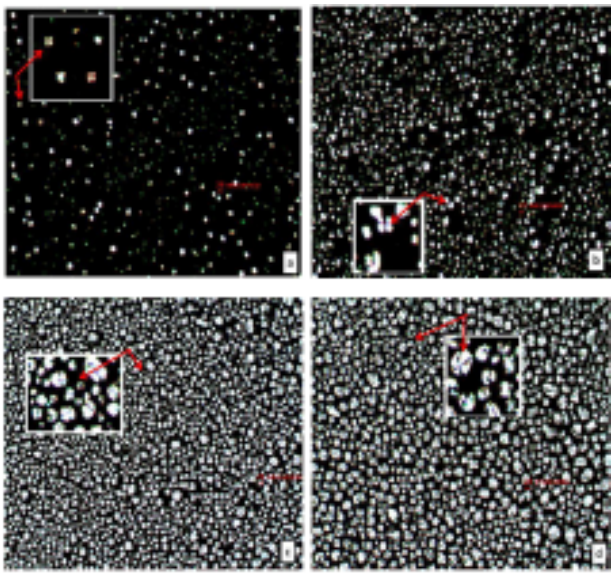

Fig.7. POM images of PDLC: [PSPEO wt %] a (50 wt %), b (33 wt %), c (20 wt %), d (10 wt %)

size similarly showed distort bipolar shape. This increase in distortion of bipolar shape pointed the decrease in anchoring energy and increase in coalescence with the decrease in block copolymer contents. This competition of droplet shape and size can be realized as block copolymer and LC molecular interactions and absorption of block copolymer with the LC.

T_{NI} change

The LC nematic to isotropic temperature can be better judged here for the block copolymer and LC interactions. The Fig. 8 shows an increase in temperature nematic to isotropic (T_{NI}) with increase in the E7 contents. This

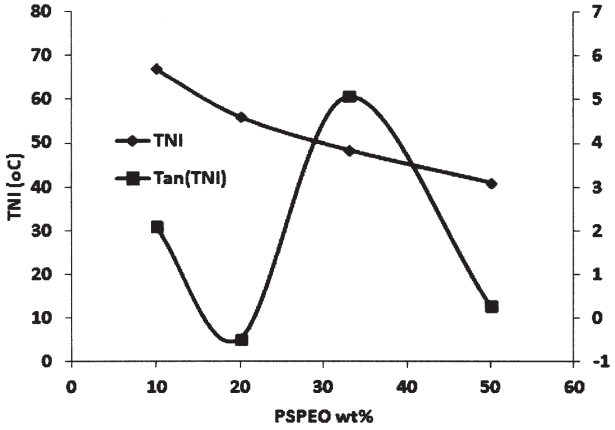

Fig. 8. Change in nematic to isotropic temperature for PSPEO doped PDLC

behavior revealed the absorption of E7 molecule over the block copolymer and it proved that the E7 molecules inhibit more absorption of the block copolymer with E7. The following data of T_{NI} is also plotted as tangent of T_{NI} representing an interesting point. The figure 8 showed a peak in the tangent T_{NI} value revealing a sharp absorption of LC molecules on block copolymer and that further decrease with the increase in LC contents. This point is considered as the optimum absorption point.

Refractive index

In order to see the solubility and absorption of LC and block copolymer; the refractive index of block copolymer and LC mixture is analysed by using the abbe refractive meter. The extraordinary refractive index of pure E7 is 1.7472. The refractice index of mixture is found minimum 1.5018 and maximum 1.5067. It can be seen from the figure 9 the refarctive index of LC/Block copolymer mixture is found increased with the increase of temperature. This pointed that the mixture at room temperatre are turbed and that reach to isotropic point as the temperature increased.

Conclusions

Block copolymer PSPEO is studied with LC as it has previously a potential history of applications in emulsions industries and has potential applications as amphiphilic molecule and as thermo-optical material. It is observed that PSPEO showed absorption with the LC due to amphiphilic characteristic. The absorption is confirmed by the TNI change and refractive index results. Further more positively it is found that a PDLC showed a good phase separation with well shaped bipolar droplets at lower LC contents. Furthermore the phase separation increased with the increase in LC contents. Whereas the LC droplets change their shape to distorted bipolar form that represent the increase in interactions of block copolymer and LC. In future due to potential applications of block copolymer PSPEO they can be further used as thermo-optical and electro-optical devices.

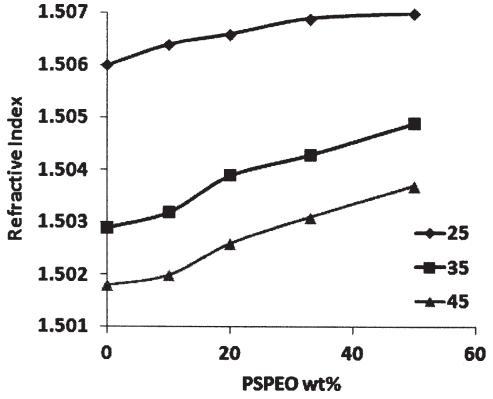

Fig. 9. Refractive index of block copolymer and LC mixture at different temperatures

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