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Analysis of Polymer-Dispersed Liquid Crystals by Infrared Spectroscopy

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Index Headings: FT-IR microscopy; FT-IR spectroscopy; Polymer-dispersed liquid crystals (PDLC).

INTRODUCTION

A polymer-dispersed liquid crystal is an inhomogeneous material capable of scattering light or transmitting light. The applications for PDLC technology are growing. A low-molecular-weight liquid crystal (LC) is dispersed as droplets throughout a polymer matrix. The polymer adds a dimension of flexibility and processibility. These electrically modulated films have tremendous potential, but the theory and molecular mechanics are only beginning to be understood due to the complexity of these systems.1-3

Optical performance properties such as extent of scattering, transmission, driving voltage, and response times are influenced by factors including droplet size, shape, and density, dielectric anisotropy, director configurations, elastic constants, rotational viscosity, and LC surface anchoring.4-6

Infrared spectroscopy is a tool capable of analyzing the above effects.7,8 IR microspectroscopy, in particular, is able to distinguish properties of specific areas within the sample. The molecular-structure parameters important to the PDLC can be observed.

EXPERIMENTAL

Three liquid crystals were used for these experiments: E7, 5CB, and ZLI-1957/5. E7 is a eutectic liquid crystal mixture consisting mostly of 4-pentyl-4'-cyanobiphenyl (5CB). 5CB is a single-component liquid crystal, and ZLI-1957/5 is a eutectic LC mixture of phenylcyclohexanes. All LCs were purchased from EM Industries, New York.

The thermoset PDLC system used was a 1:1:1 mixture of Epon 828, Capure 3-800, and ZLI-1957/5. The mixture was allowed to cure at room temperature for several hours.

The polymers used in the thermoplastic PDLCs were: polyvinylpyrrolidone (PVP), 40,000 g/mole, and poly(methyl methacrylate) with molecular weights of 12,000 and 30,000 g/mole. All thermoplastic PDLC samples were made by a combination of the solvent-induced phase separation (SIPS) and the thermally induced phase separation (TIPS) techniques.3,6 Solutions of LC/polymer/chloroform were mixed in the ratio of 7:3:90 to produce PDLC films of 70:30 LC/polymer ratio after solvent evaporation. After the solvent was allowed to evaporate in air for a few hours, the samples were heated to 110°C for 10 min and cooled to room temperature at an uncontrolled rate. This quick cooling rate produced relatively small droplets of <1 μm. The samples used for the droplet size experiment were subsequently cooled from 110°C at 5°C/min to obtain smaller droplets (10-15 μm in diameter) or 1°C/min for larger droplets (20-30 μm in diameter). A Mettler FP84HT/FP80HT thermal microscope cell was used to control the cooling rate. Mylar films (25 μm) were used for spacers to keep the sample thickness constant. Samples for the IR microscope were made on platinum-coated NaC1 salt plates to be conductive, and all other IR samples were made on germanium plates.

A General Radio Company AC power supply was used to apply the electric field across samples. Alternating-current power was used, instead of direct current, to decrease possible sample degradation by a direct current. The time between each maximum value of amplitude in the alternating current must be faster than the relaxation of the liquid crystal from the aligned state. The frequency for each experiment was 2 kHz. The voltage was measured on a Keithley 169 multimeter.

IR microspectra were taken on a Spectra-Tech, Inc. IRμS infrared microscope equipped with a 250 × 250 μm narrow-band MCT detector. A 32× objective combined with a 10× condenser was used to obtain transmission spectra with 50 scans at a resolution of 4 cm⁻¹. All other IR spectra were taken on a Digilab FTS-60 spectrometer with a 250 × 250 μm broad-band MCT detector. The spectra were taken in transmission with 4 cm⁻¹ resolution and 64 scans. All spectral data were processed on a Microvax III+ with the use of in-house software written in Fortran 77.

A Perkin-Elmer wire-grid polarizer was used to polarize the incident IR beam. The terms 0° and 90° polarized are used only to express the 90° difference in polarization.
PURE LIQUID CRYSTALS FOR POLC FILMS

We label 0° as polarization in the y-direction and 90° as polarization in the x-direction. The incident IR beam and the sample thickness are both parallel with the z-axis. The sample geometry is shown in Fig. 1.

RESULTS

The pure spectra of the various liquid crystals and polymers, along with the structures, are shown in Figs. 2 and 3. A very useful region in the spectra is between 2300 and 1500 cm⁻¹. In this region, the LC and polymer each have at least one unique, nonoverlapping peak. Except for the epoxy PDLCs, the broad LC peaks between approximately 900 and 800 cm⁻¹ are useful. They arise from the overlap of the C-H aliphatic and aromatic bending modes and belong only to the liquid crystal molecules. The peak assignments for the E7 liquid crystal mixture are shown in Table I.

IR Microspectroscopy. For PDLC films with fairly large droplets (> 50 μm diameter) and a low droplet density (> 50 μm apart), spectra of isolated regions of the polymer matrix and the LC droplet could be taken. The different spectra obtained for the ZLI/epoxy and E7/PVP PDLCs are shown in Figs. 4 and 5. In the ZLI/epoxy set of spectra, there is LC dissolved in the polymer matrix, as revealed by the small LC peaks at 2229 cm⁻¹ and 1736 cm⁻¹. The LC C=N and C=O peaks present in the LC contribute to the ZLI spectrum. The E7 film spectrum in Fig. 5 shows a much smaller C=O peak at 1736 cm⁻¹ as a shoulder on the broad polymer peak.

TABLE I. Peak assignments for E7 nematic liquid crystal mixture of 51% 5CB, 25% 7CB, 16% 8OCB, and 8% 5CT.

<table>
<thead>
<tr>
<th>Peak (cm⁻¹)</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>3072 w</td>
<td>ν CH aromatic</td>
</tr>
<tr>
<td>3053 w</td>
<td>ν CH aromatic</td>
</tr>
<tr>
<td>3041 w</td>
<td>ν CH aromatic</td>
</tr>
<tr>
<td>3029 w</td>
<td>ν CH aromatic</td>
</tr>
<tr>
<td>2956 ms</td>
<td>ν CH₂ asym</td>
</tr>
<tr>
<td>2929 s</td>
<td>ν CH₂ sym</td>
</tr>
<tr>
<td>2871 m, sh</td>
<td>ν CH₃ sym</td>
</tr>
<tr>
<td>2858 ms</td>
<td>ν CH₂ sym</td>
</tr>
<tr>
<td>2226 ms</td>
<td>ν C=N</td>
</tr>
<tr>
<td>1514 w</td>
<td>Combination band</td>
</tr>
<tr>
<td>1407 ms</td>
<td>ν C=O phenyl ring</td>
</tr>
<tr>
<td>1456 ms</td>
<td>ν C=O phenyl ring</td>
</tr>
<tr>
<td>1408 m, sh</td>
<td>ν C=O phenyl ring, δ CH₂, and δ CH₃</td>
</tr>
<tr>
<td>1399 mw</td>
<td>C-H chain deformation</td>
</tr>
<tr>
<td>1380 w, sh</td>
<td>δ sym CH₃</td>
</tr>
<tr>
<td>1314 vw, sh</td>
<td>(CH₂)₃, in-phase twist</td>
</tr>
<tr>
<td>1291 w</td>
<td>ν C-C-biphenyl</td>
</tr>
<tr>
<td>1268 vw, sh</td>
<td>Peaks unique to E7, not in 5CB</td>
</tr>
<tr>
<td>1252 mw</td>
<td>ν asym C-O-C from 8OCB</td>
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<tr>
<td>1181 mw</td>
<td>δ C-H aromatic in-plane</td>
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<tr>
<td>1120 w, br</td>
<td>δ C-H aromatic in-plane</td>
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<tr>
<td>1007 w</td>
<td>δ C-H aromatic in-plane</td>
</tr>
<tr>
<td>968 vw</td>
<td>ν terminal CH₃</td>
</tr>
<tr>
<td>853 mw, sh</td>
<td>C-H aliphatic chain</td>
</tr>
<tr>
<td>822 ms</td>
<td>C-H aliphatic chain</td>
</tr>
<tr>
<td>814 ms</td>
<td>ω C-H aromatic out-of-plane, para</td>
</tr>
<tr>
<td>723 w</td>
<td>(CH₂)₃, in-phase rocking</td>
</tr>
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</table>

polymer area decrease by 64% and 83%, respectively, when the droplet and polymer regions are compared. The same is true for the polymer C=O peak in the E7/PVP PDLC, which decreases by 96%. However, the LC C=N peak decreases only by 14% between the E7 and PVP areas.

A visual image and two corresponding IR functional group images of a ZLI-1957/5 droplet (~180 μm diameter) in the epoxy matrix are shown in Fig. 6. The image in Fig. 6A is taken with crossed polarization. The contour maps on the bottom are based on the absorptions of the C=N stretching mode of the LC (Fig. 6C), and the O-H stretching mode of the epoxy (Fig. 6D). The two irregular points associated with the bipolar configuration, referred to as boojums, can be seen in Fig. 6A, revealed by the two sharp black points near the top and the bottom of the droplet.

There are two areas of higher intensity in the IR functional group image based on the LC C=N stretching mode. These areas correspond to the two white areas in quadrants I and III of the droplet in the visual image. Notice that the image based on the epoxy peak does not show any regions indicative of the droplet configuration.

In Fig. 7, IR images based on the LC C=N absorption demonstrate the effect of IR polarization. The droplet in Fig. 7 is not the same droplet in Fig. 6. Both images are of the same droplet, but the IR beam was polarized in either the yz-plane (0°) or in the xz-plane (90°). The high-intensity points appear in different positions when the polarization is changed.

Finally, the IR images of an LC droplet under the influence of an electric field are shown in Fig. 8. Again, the droplet in Fig. 8 is not the same as in Fig. 6 or 7, but the images within Fig. 8 are of the same droplet. Although the spatial resolution is low, changes within the droplet due to alignment with the applied field can be seen.

IR Spectroscopy. Figures 9–11 demonstrate the influence of droplet size on the nature of the switching of the E7/PVP PDLC films. The baseline-corrected intensities of three stretching modes arising from the absorption of 90° polarized IR radiation are plotted as a function of wave numbers.
FIG. 6. Different images of the same ZLI-1957/5 droplet in an epoxy matrix. (A) A visual image with a 20 × glass objective under crossed polars. (B) A schematic diagram of a bipolar droplet (also see Fig. 1B). (C–D) Two IR functional group images of the same droplet in A based on the LC C≡N (C) and the epoxy O-H (D) stretching modes.

applied ac voltage. The LC C≡N peak shows a completely switched sample by 8 V for the larger droplets and by 12 V for the smaller droplets. The LC phenyl C=C peak at 1605 cm⁻¹ shows completely switched droplets by 11 V for the larger droplets, but does not indicate any change with voltage for the smaller droplets. Finally, the LC CH₃ symmetric stretching mode reveals that the larger droplets switch by 9 V, and the smaller droplets by 11 V. In all three cases, the smaller droplets require a higher voltage in order to switch. Also, the smaller droplets produce much broader curves in the regions between where the droplets start to switch and where they are completely switched.

The hysteresis effect is obvious in Figs. 9–11 in the curves of absorbance as a function of voltage. The voltage was increased manually from zero volts to about forty volts, then decreased in the same manner. Between each voltage change, the sample was allowed to equilibrate for approximately 10 min.

Another parameter which shows a hysteresis effect is temperature. The temperature was increased quickly between each temperature point for a ZLI/epoxy PDLC
film and allowed to equilibrate for 10 to 15 min before the spectra were taken. At the end of the temperature program the same path was followed for the decreasing temperature steps. As shown in Fig. 12, the absorbance with temperature exhibits a slightly larger amount of hysteresis after the nematic-isotropic transition at 85°C.

Figure 13 shows the spectra for the E7/PVP samples resulting from different cooling rates from an initial temperature of 110°C. The cooling rates of 5°C/min and 1°C/min produce droplets with diameters of 10–15 μm and 20–30 μm, respectively. The spectra are markedly different. The LC C-H peaks at 2874 and 2852 cm⁻¹ are...
virtually gone from the sample with larger droplets. The other peaks marked in Fig. 13 are 1269/1250, 970, and 812 cm⁻¹ and correspond to liquid crystal peaks. Also, two peaks belonging to the polymer which experience a difference with droplet size are at 1667 and 1423 cm⁻¹. The carbonyl peak at 1667 cm⁻¹ has a higher wavenumber for the smaller droplets.

By observation of the peaks which distinctly belong to the liquid crystal, the effect of the polymer on the LC can be monitored. Likewise the effect of the liquid crystal on the polymer can be observed. A sample of these effects is shown in Fig. 14. As the polymer matrix is changed, the LC peak between 900 and 800 cm⁻¹ changes. The PVP matrix causes the sharpest 814-cm⁻¹ peak, which belongs to the C-H aliphatic chain. On the other hand, the LC also affects the polymer C=O peak. In all cases shown, the PDLC C=O peak is broader than the C=O peak for the pure polymer.

Orientation, as measured by the dichroic ratio, R, can be seen in Fig. 15 as a function of voltage. Pure E7 aligns with the electric field, so the polarization spectra decrease with voltage. While the 0° and 90° polarizations measure absorbances in the y- and x-planes, the LC is orienting with the z-, or thickness, direction. As expected from geometry considerations, the peak for the C=N stretching mode decreases with voltage. However, the same peak in a PDLC sample increases with voltage. Also, the dichroic ratio is relatively constant with voltage.

DISCUSSION

IR Microspectroscopy. Examination of the single spectra in the ZLI/epoxy and E7/PVP PDLCs (Figs. 4 and 5) shows a distinct spectrum for each phase. The ZLI/
Fig. 13. E7/PVP PDLCs at two cooling rates: 5°C/min for 10–15 μm droplets and 1°C/min for 20–30 μm droplets. The sinusoidal peaks surrounding the C=N peak at 2226 cm⁻¹ are interference fringes due to the uniform sample thickness between the Ge substrates.

epoxy sample shows a decrease in all LC peaks when the microscope is focused on the polymer matrix. However, that is not true for the E7/PVP PDLC. In the E7 region of the sample, there are traces of PVP peaks, but they are relatively weak. In the PVP region, all of the E7 peaks are present and they do not decrease as much as in the ZLI/epoxy PDLCs.

One difference between the two samples is the fact that the epoxy is a thermoset, while the PVP is a thermoplastic. Two possible explanations describe the above phenomenon: (1) The LC dissolved in the thermoplastic may be different enough from the LC in the droplet for a decrease in the peaks to be noticed. In the thermoplastic, the LC which is present in the polymer matrix may be in a similar orientational state as in the droplet, so a decrease in the LC absorption is not observed. (2) Perhaps the thermoplastic matrix contains a much higher percentage of LC dissolved in the polymer compared to the amount of LC dissolved in the thermoset. The thermoset may experience a more complete phase separation.

The two IR functional group images in Fig. 6C and 6D show the same droplet based on two different frequencies of absorption. The image based on the epoxy peak has low absorption in the center of the droplet and has higher intensities in the area outside the droplet. The image created by the C=N peak shows two high-intensity points in the droplet which correspond to the white areas depicted in the visual image in Fig. 6A.

The white and dark areas in the visual image of the droplet in Fig. 6A depend on the orientation of the LC molecules in the droplet. Basically, the white areas arise from the LC molecules oriented perpendicular to the direction of polarization, while the dark areas are due to the LC molecules oriented parallel to the polarization. When the nematic director of a large droplet (radius ≥ film thickness) is at an angle of approximately 15° with the direction of polarization (Fig. 1B, α₀ = 15°) and when the director is oriented 90° to the incident radiation (Fig. 1B, θ = 90°), the white and dark regions of the droplet texture are nearly equal in area and are symmetrical. This is the case with the images in Fig. 6. In other words, the boojums are in the xy sample plane and are oriented 90° to the incident light. Also, the director is approximately 15° from the direction of polarization.

Other evidence to support the orientational assignment comes from the rotation of the two points with polarized IR light and from the rotation of the points with the applied field. In Fig. 7, the set of points of higher intensity are rotated approximately 70° between the different IR polarizations. Looking at the diagram in Fig. 1B, we can easily see that the change of polarization would cause a new α₀ which would be the supplement of the original α₀. Therefore, the white and dark textures in the visual image change, thus moving the points of higher intensity in the IR images.

When an electric field is applied to the PDLC droplet, the points of higher intensity change both position and character, as depicted by the two IR images in Fig. 8. When the voltage is ON, the droplet director aligns with the field and θ changes from 90° to 0° (see Fig. 1B). Thus
workers studied the optical textures of oblate droplets. The infrared images coincide with their predicted visual larger than the 25-nm film thickness, so the droplets are the droplets. In Figs. 6-8 the droplet diameters are all than the smaller droplets and more LC in the bulk of shown. The larger droplets have less surface anchoring switching voltage are shown in Figs. 9-11. The larger images of the flattened droplets.

Another consideration regarding the IR functional group images shown in this work is the actual shape of the droplets. In Figs. 6-8 the droplet diameters are all larger than the 25-\(\mu\)m film thickness, so the droplets are actually discs and not spheres. Ondris-Crawford and co-workers studied the optical textures of oblate droplets. The infrared images coincide with their predicted visual images of the flattened droplets.

**IR Spectroscopy.** The effects of droplet size on the switching voltage are shown in Figs. 9-11. The larger droplets exhibit a lower switching voltage for each peak shown. The larger droplets have less surface anchoring than the smaller droplets and more LC in the bulk of the droplet. With less anchoring, the voltage required to align the droplet is less.

For the larger droplets, the C=N and CH\(_2\) peaks are completely switched at nearly the same voltage (8-9 V), while the C=C peak indicates that complete switching requires a higher voltage (11 V). This observation suggests that the C=N groups and the pentyl chain groups switch more easily than the phenyl groups. A similar trend is seen for the smaller droplets, except that the C=C peak does not show much change with voltage. Gregoriou et al. suggest that the pentyl chain reorients more rapidly than the cyanobiphenyl core in the pure 5CB component. The data here do not carry any implication of rate, but suggest that the chemical groups of the LC molecule require different energies for alignment.

The hysteresis for the absorption of the C=N and CH\(_2\) stretching modes with voltage follows opposing trends (see Figs. 9 and 11). For the large droplets, the absolute difference between the C=N absorbance at zero volts for the increasing and decreasing voltage paths (0.15 au) is less than for the small droplets (0.25 au); whereas for the CH\(_2\) peak, the PDLC with the larger droplets has a larger (0.25 au) difference at zero volts than for the small droplets (0.18 au). The pentyl tail for the larger droplets takes longer to assume its original position than is the case for the smaller drops. The LC molecules may be oriented in opposite directions for the large and the small droplets.

The polymer has a pronounced effect on the spectra of the LC molecules, as shown in Fig. 14. The peaks at approximately 853 and 822 cm\(^{-1}\) are more pronounced in the PDLC samples in comparison to the pure 5CB spectrum. These peaks correspond to the C=H aliphatic chain. The PVP has the least effect on these peaks, since PVP does not have an aliphatic chain to interact with the LC pentyl chain. However, the 814-cm\(^{-1}\) band is more pronounced in the PVP PDLC. Perhaps, the ringed side chain in the PVP interacts more with the 5CB phenyl groups.

The LC also influences the nature of the polymer peaks. The carbonyl peak for each of the three types of PDLC is broadened, reflecting the carbonyl interaction with groups of the LC molecule. The carbonyl group experiences more types of interaction when the polymer exists in the PDLC environment.

Figure 15 compares the polarized spectral intensities for the C=N stretching mode and the dichroic ratios for the same frequency for both the pure liquid crystal and the LC in a PDLC droplet. For the pure LC, both the 0° and the 90° (y- and x-axes) polarized intensities decrease with increasing electric field. As the voltage increases, the C=N groups align parallel to the sample thickness direction (z-axis). Regardless of whether the initial average orientation was in the x-direction or the y-direction or anywhere in the xy-plane, the molecules rotate out of the xy-plane with voltage, thus lowering the C=N peak intensity (also, see Ref. 11).

However, the dichroic ratio based on the C=N absorption in the pure LC increases towards a value of 1.0 with increasing voltage. The dichroic ratio describes the difference between the parallel and perpendicular alignment of molecules with respect to the incident IR beam. When the applied electric field is absent, linear dichroism in the xy-plane exists. However, as the LC molecules align with the electric field, the nematic director of each molecule leaves the xy-plane (see Fig. 1A). Under the influence of the applied field, the C=N groups are parallel to the sample thickness or z-direction. Therefore, the 0° and the 90° polarization intensities are the same, which produces a dichroic ratio value near 1.0. Usually,
a dichroic ratio of 1.0 indicates random order because the parallel and perpendicular absorptions are equal. However in this case, the alignment in the z-direction is not accounted for by the classical two-dimensional dichroic ratio.

For a PDLC film, Fig. 15 shows that the 0° and 90° polarized intensities for the C=N stretching mode increase with increasing voltage. This is the opposite trend for the pure LC sample. When the applied electric field is absent, the droplets are oriented randomly with respect to each other. But as the voltage increases, the nematic director of each droplet aligns parallel with the electric field, due to the positive dielectric anisotropy of the LC. Since all droplets now have the same orientation relative to each other, the total number of molecules in a specific x- or y-direction increases, which causes an increase in both the 0° and 90° polarization intensities.

In other words, for the pure LC in the ON state, all molecules orient in the z-direction with the applied field, causing a decrease in absorbance. However, for the PDLC droplets in the ON state, the LC molecules at the boojums are forced to remain in the xy plane with a specific orientation, giving rise to a maximum IR absorption. Other workers also have reported the increased absorbance for the ON state for PDLC films.

Although the polarized intensities for the PDLC C=N peak increase, the dichroic ratio for a PDLC remains relatively constant with voltage. For each droplet in the PDLC, whether the droplets are aligned or oriented randomly to each other, the LC molecules within each droplet are oriented in all directions inside the spherical cavity (refer to Fig. 6B). Due to the symmetry of round droplets, there are equal amounts of molecules in the x- and y-directions. This factor leads to a dichroic ratio near unity, indicating random order.

On the basis of theoretical calculations of the dichroic ratio, $R$ is approximately equal to $\tan \theta$. Therefore, if the PDLC dichroic ratio is 1.0, then the average angle of the C=N molecules is 45° with respect to a fixed reference direction.

CONCLUSIONS

FT-IR microspectroscopy is well suited for the study of polymer-dispersed liquid crystal systems. In comparing the spectra from the polymer regions and from the droplet regions for thermoet and thermoplastic matrix PDLCs, the thermoplastic PDLC contained a higher amount of liquid crystal within the polymer regions. The thermoplastic PDLC had considerably less LC present in the polymer region of the film. IR functional group images of an approximately 180-µm droplet showed that the droplet textures observed under a visible microscope also are detectable by infrared microscopy. The textures in the IR region changed with IR polarization and with an applied electric field.

Conventional FT-IR spectroscopy was used to study bulk PDLC samples with different droplet sizes and as a function of an applied field. Smaller droplets required a higher voltage in order to switch, due to a higher amount of surface anchoring. The C=N peak and the pentyl CH2 peak required an equivalent voltage in order to switch in the IR region, but the phenyl C=C peak did not show any changes until a higher voltage was applied. This result indicates that the C=N and CH2 chain require less energy to align with the field. The hysteresis typical of PDLC films also is demonstrated in the IR region for both voltage and temperature changes. Finally, the effects of the polymer on the C-H aliphatic and aromatic peaks in the region of 900 to 800 cm⁻¹ have been discussed, as well as the considerable broadening of the polymer carbonyl peak in the PDLC compared to the pure polymer peak.

ACKNOWLEDGMENT

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