## Liquid Crystals

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# Polarized infrared study of a polymer network deformation in a nematic liquid crystal host

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Using polarized infrared (IR) spectroscopy we have observed deformation of a polymer network in a liquid crystal host during the reorientation of the liquid crystal by an external electric field. In the system studied, containing 2% BMBB-6 polymerized at zero applied field in the host nematic liquid crystal 6CB, the observed deformation angle was between 20° and 40° ± 10°. These experimental results provide some of the first conclusive experimental evidence that the polymer network elastically deforms as a direct result of the reorientation of the liquid crystal host.

## 1. Introduction

The discovery of polymer dispersed liquid crystals (PDLCs) [1]; formed by polymerization induced phase separation, suggested various novel electro-optic applications. Subsequently, interest in liquid crystalline materials confined to various geometries has been intensified better to understand the interaction between the liquid crystal and polymer. A new system called polymer stabilized liquid crystal (PSLC) was recently proposed [2–4] for application to conventional liquid crystal display devices. In a PSLC system, liquid crystal is mixed with a monomer and then polymerized. However, unlike the PDLC systems, the monomer concentration is very low—often less than 5%. Polymer networks in PSLC systems have been shown significantly to improve the electro-optic performances of several different types of liquid crystal display [5–10].

Preliminary investigation of the influence of polymer networks in nematic liquid crystal have been performed and a reasonable agreement between experimental and calculated results has been demonstrated [11]. However, the elastic deformation of the polymer network was not separated from other factors affecting the strength of the polymer–liquid crystal interactions. In this work we have adopted IR spectroscopy as a tool to investigate the orientational changes of the mesogenic moieties of the polymer networks [12] resulting from polymer–liquid crystal interactions.

## 2. Experimental

Samples were prepared by dissolving 1.8 wt % of monomer 4,4′-bis{4-[6-(methacryloyloxy)hexyloxy]-benzoyloxy}-1,1′-biphenylene (BMBB-6, see figure 1 for structure) and ∼ 0.2 wt % of the photoinitiator benzoin methyl ether (BME) in the nematic liquid crystal 4-hexyl-4′-cyanobiphenyl (6CB, see figure 2 for structure). The nematic–isotropic (N–I) transition temperature $T_{\text{N-I}}$ of bulk 6CB is 28°C, the crystalline–nematic transition is at 13.5°C. 6CB was chosen because one can easily identify the polymer networks, which contain ester groups, from the 6CB background by IR spectroscopy.

The mixture was briefly homogenized at 50°C. Salt (sodium chloride crystal) slides were first coated with indium tin oxide (ITO) of thickness 600 Å, and were then spin coated with polyimide alignment layer Nissan 1180, thinned 3 : 1, at 4000 rpm. The polyimide coated salt slides were baked at 80°C for 60 min and then at 120°C for 60 min. The polyimide was hand-rubbed and,

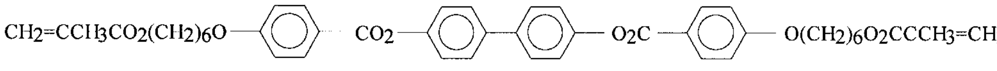

Figure 1. Structure of monomer BMBB-6.

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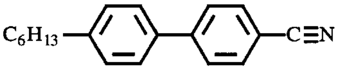

Figure 2. Structure of 6CB.

based on the manufacturer's data sheet, we expected to obtain a low pretilt of about 1°. Salt slides with rub directions antiparallel to each other and separated by mylar spacers of nominal thickness 12.5 µm were cemented with a five-minute epoxy on two opposite sides. In this type of cell the director field, in the absence of an applied electric field, will be uniformly aligned without any distortion. One cell was filled with the liquid crystal and monomer mixture at ambient temperature. It was then heated to above the clearing temperature and slowly cooled back to room temperature to achieve a texture-free and uniform alignment. Lastly, the cell was exposed to a UV light source to polymerize the monomers. Light scattering due to phase separation between the polymer network and liquid crystal occurred as shown in figure 3. A second cell was prepared and then filled with pure 6CB for comparison purposes. To perform the measurements, an IR polarizer was mounted on a holder in the sample chamber of the infrared spectroscopy system (Nicolet Magna-IR spectrometer 550). The cells were then placed in another holder such that the rubbing direction was parallel to the polarization direction of the infrared polarizer.

Due to the low monomer concentration (~ 2 wt %), the mixture of liquid crystal and monomer is homogeneous and in the liquid crystalline phase at room temperature. When the monomers are being photopolymerized the surface alignment layers control the orientation of the liquid crystal and, consequently, the orientation of mesogenic units of the polymer networks. The polymer network formed in this way has been previously shown to be anisotropic [13–15]. An a.c. (1 kHz) electric field applied to the sample causes the liquid crystal molecules, because of their positive dielectric anisotropy ($\Delta\varepsilon > 0$), to align preferentially parallel to the field direction. The infrared absorption changes of C–O and C=O in the ester groups on the mesogenic units of the polymer networks were monitored as a function of the electric field strength, to observe how the polymer network is influenced by the reorientation of the surrounding liquid crystal host. Three different absorption peaks were monitored to provide information specific to either the liquid crystal or polymer (see the table).

## 3. Results

Figure 4 illustrates the absorbance vs. wavenumber with the solid curve corresponding to the sample with polymer networks, and the dotted curve corresponding to the sample filled with only the liquid crystal 6CB. The absorbance is defined by:

$$A = \int_{\text{bandwidth}} \ln\left(\frac{1}{\%T}\right) \mathrm{d}\nu \qquad (1)$$

where $\%T = I/I_0$.

The C–O band in aryl conjugated esters, such as in the monomer used in this experiment, usually absorbs strongly in the infrared near 1280 cm$^{-1}$. However, due to its low concentration (~ 2 wt %), only a weak absorption peak was observed in this study. Because of their location in the core region of the mesogenic unit of the polymer networks, any systematic change in the ester C–O absorbance can be taken as a direct indication that the polymer networks were undergoing reorientation. Another factor that could affect the degree of absorption

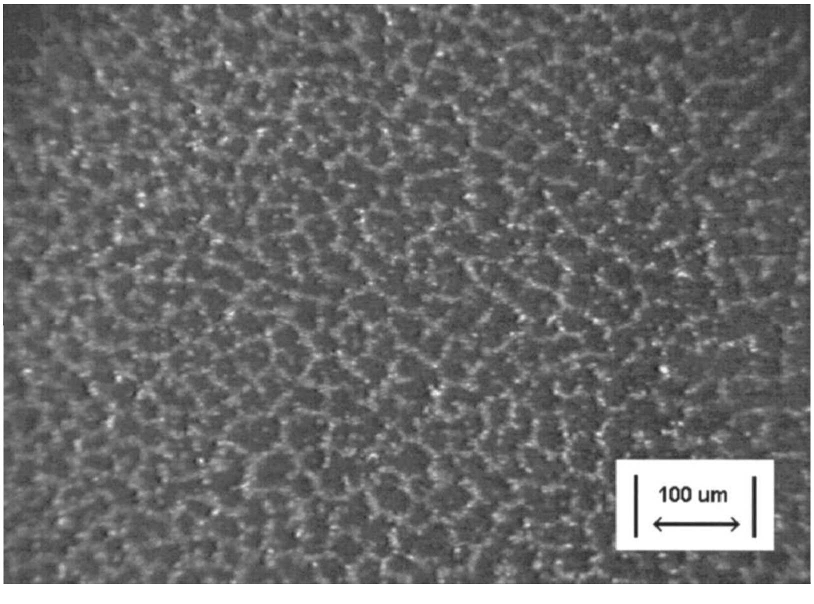

Figure 3. Image of the polymer stabilized 6CB sample taken between crossed polarizers with the optic axis of the liquid crystal aligned with one of the polarizers. The bright spots appear to be phase separated polymer rich regions.

Table. The two absorption peaks investigated. The C≡N stretch peak is only from the liquid crystal 6CB; the C–O stretch peak is only from the polymer networks. We define the integrated absorbance as the area of the absorption peak with baseline correction considered.

| Observed Peaks/cm$^{-1}$ | Assignments [16] | Integrated absorbance, zero applied voltage | Integrated absorbance, at 8 Vrms (1 khz) | Relative absorbance change/% $(A_8 - A_0)/A_0$ |
|---|---|---|---|---|
| 2229 | C≡N stretch<br>(no polymer) | 17.402<br>(2200–2255 cm$^{-1}$) | 7.493<br>(2200–2255 cm$^{-1}$) | – 56% |
| 2229 | C≡N stretch<br>(polymer stab.) | 18.007<br>(2200–2255 cm$^{-1}$) | 9.215<br>(2200–2255 cm$^{-1}$) | – 49% |
| 1254 | C–O stretch<br>(polymer stab.) | 2.002<br>(1225–1275 cm$^{-1}$) | 1.721<br>(1225–1275 cm$^{-1}$) | – 14% |
| 1730 | C=O stretch<br>(polymer stab.) | 2.181<br>(1700–1775 cm$^{-1}$) | 2.364<br>(1700–1775 cm$^{-1}$) | 8% |

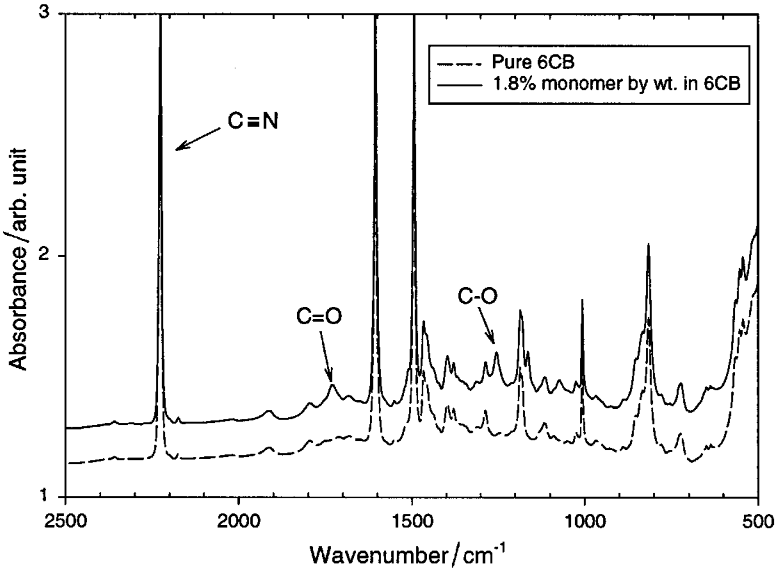

Figure 4. Infrared absorbance vs. wavenumber for a pure 6CB filled cell (dotted curve) and for a cell that contains both 6CB and polymer network. Three absorption peaks have been labelled. The ester C–O and C=O absorption peaks are missing for the pure 6CB cell.

is the variation in the local field caused by the reorientation of the liquid crystal host, however this has been estimated to affect the absorption by only a few % [17].

Figure 5 illustrates the absorbance changes $(A_{8\,\mathrm{Vrms}} - A_{\mathrm{zero\text{-}field}})$ vs. wavenumber (the absorbance at 8 V minus the absorbance at zero field). From the data listed in the table we find that, for the liquid crystal host in the sample with no polymer network, the relative absorbance change of C≡N stretching is $100\% \times (A_{8\,\mathrm{Vrms}} - A_{\mathrm{zero\text{-}field}})/A_{\mathrm{zero\text{-}field}} \approx -56\%$; whereas the liquid crystal host in the polymer stabilized sample shows a relative change of $\approx -49\%$. For the polymer network itself, the relative absorbance change of ester C–O stretching is $100\% \times (A_{8\,\mathrm{Vrms}} - A_{\mathrm{zero\text{-}field}})/A_{\mathrm{zero\text{-}field}} \approx -14\%$, whereas a relative absorbance change of 8% was calculated for the C=O stretch.

The absorbance of linearly polarized light can be written [18]:

$$A(\psi) = C\left[\frac{S}{2}\sin^2\beta + \frac{1-S}{3} + \frac{S}{2}(2 - 3\sin^2\beta)\cos^2(\psi)\right]. \tag{2}$$

It will depend on: the angle ($\beta$) of the transition moment with respect to the molecular axis, the scalar order parameter ($S$) of the molecule, and the angle ($\psi$) between the polarization axis of the incident light and the director. We can use the above expression in conjunction with the measured relative absorbance change to determine the magnitude of the molecular reorientation:

$$\Delta\psi = \arccos\left[\frac{2}{3}\,\frac{S(3\cos^2\beta - 1) + 1}{S(3\cos^2\beta - 1)}R + 1\right]^{1/2} \tag{3}$$

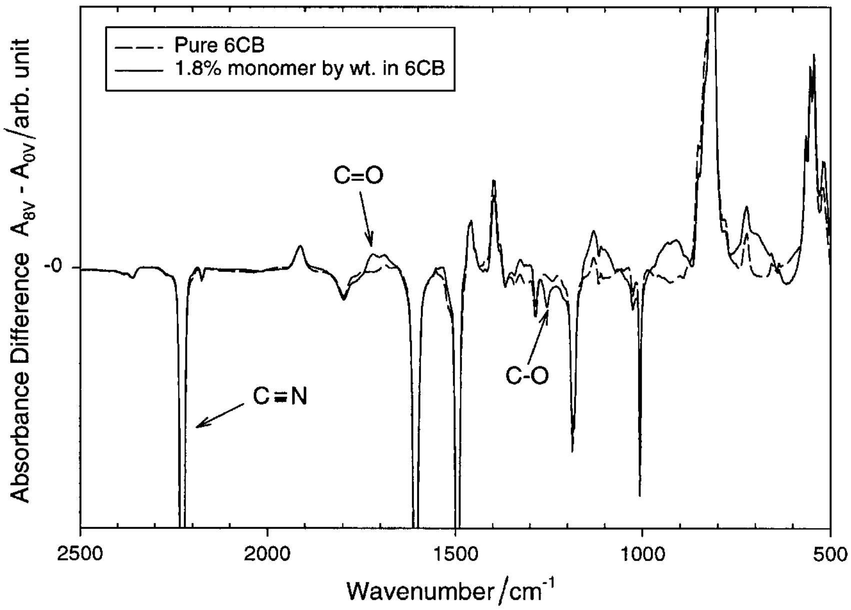

Figure 5. Infrared absorbance difference (with and without applied a.c. voltage) vs. wavenumber for a pure 6CB filled cell (dotted curve) and for a cell containing both 6CB and polymer network. As in figure 4, two absorption peaks have been labelled. The ester C–O absorption change is clearly presented, indicating that the polymer networks were deformed by the reorientation of the liquid crystal host.

where

$$R = \frac{A(\psi_{8\,\mathrm{V}}) - A(\psi_{0\,\mathrm{V}})}{A(\psi_{0\,\mathrm{V}})}. \qquad (4)$$

In our experiments the polarization vector of incident light is parallel to the director ($\psi_{0\,\mathrm{V}} = 0$). To obtain numerical results we require estimates of the angle the transition moment makes with respect to the molecular axis for the C≡N bond in 6CB, and both the C–O and C=O bonds in BMBB-6. The values were obtained by minimizing the conformational energy of the molecules. Using this technique we arrived at ≈0° and 45° for the C≡N and C–O bonds, respectively, and 75° for the C=O bond.

The negative sign of the change in the C≡N absorption tells us that, after the a.c. electric field had been applied, the liquid crystal molecules were reoriented parallel to the direction of the electric field. From figure 5, it is clear that the ester C–O absorption peak change is also negative which indicates that the mesogenic units of the polymer networks also aligned parallel to the surrounding liquid crystal molecules.

Figure 6 shows the average reorientation angle of the liquid crystal as a function of the order parameter for both the polymer stabilized and polymer free cells. The results indicate that the reorientation of the PSLC sample is ≈5°–7° less than the sample containing pure 6CB over a range of values for the liquid crystal order parameter. This difference is most likely due to the coupling between the polymer network and the liquid crystal.

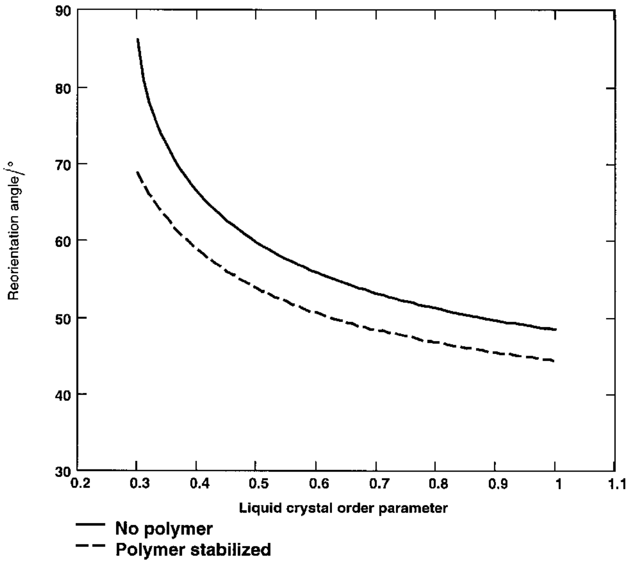

Figure 6. Comparison of the liquid crystal reorientation in two separate samples; one containing pure 6CB, the other 6CB and BMBB-6.

Figure 7 compares the measured reorientation of the liquid crystal in the polymer stabilized sample with the polymer network itself. The data indicates a substantial reorientation of the polymer network. We attempted to adjust the $\beta$ value for the C–O and C=O (keeping the sum of these equal to 120°) to make the results more consistent with each other, as we would expect both measurements to yield the same results. However, we were unable to do so for variations of ± 10° in $\beta$. The

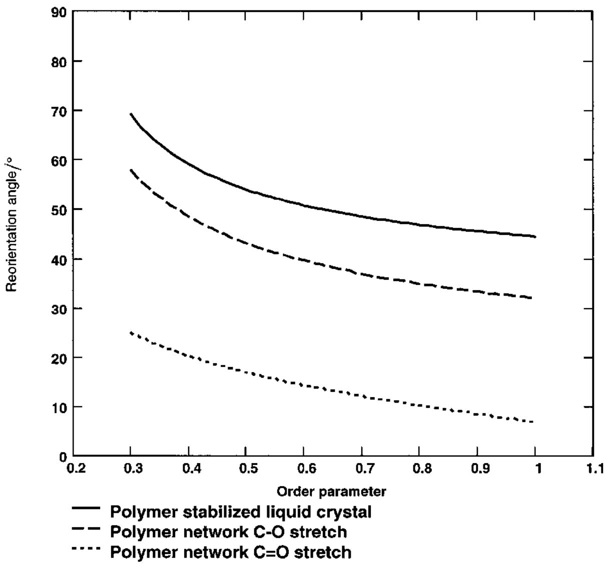

Figure 7. Calculated results of the liquid crystal and polymer reorientation.

difference is therefore attributed to spectral interfering overlays contributing to the absorbance.

## 4. Discussion

The surprisingly large absorbance change of the ester C—O stretching, that determines the magnitude of the elastic distortion, could be caused by two mechanisms. The first is orientation caused by reorientation of the surrounding liquid crystal host; the second is the interaction of the applied electric field directly coupled to the polymer network. However, it is most likely that the effect is due to the former mechanism because mesogenic units of BMBB-6 with multiple ester groups in the rigid core region typically show a negative dielectric anisotropy which favours planar alignment under an applied external electric field.

The observed reorientation is not inconsistent with that reported by Yang *et al.* [19]. They had suggested that monomers without a spacer group tend to form a rigid and densely cross-linked network when polymerized in liquid crystal, but in our experiment, the monomer BMBB-6 contains flexible spacers and is expected to form a more flexible network.

## 5. Conclusion

These experimental results provide conclusive experimental evidence that the polymer network elastically deforms as a direct result of the reorientation of the liquid crystal host in the presence of an externally applied field. The polymer network deformation is recoverable once the applied electric field is turned off; therefore this deformation is elastic in nature. In order to develop a better model for PSLC systems, similar, more detailed experiments will be pursued.

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