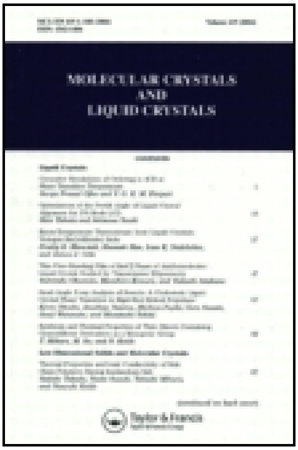

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Measurement of Degree of Order in Mixed Polarised Fluorescent Polymer Liquid Crystal Films

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Measurement of Degree of Order in Mixed Polarised Fluorescent Polymer Liquid Crystal Films

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Raman spectroscopy is used to investigate the degree of order found in *in-situ* photopolymerised films exhibiting polarised emission. Studies indicate that the mixed system shows different degrees of order for its two molecular components. The degree of order was measured in the mesophase for the mixed monomers prior to polymerisation and was found to be in close agreement with the order of the two components measured in equivalent cured films. These studies have therefore provided an insight into the nature of molecular ordering in these mixed systems and shows that the *in-situ* photopolymerisation process does not greatly change the ordering in the system.

Keywords: Raman spectroscopy; order; polarised emission

INTRODUCTION

The last few years has seen many advances in the field of organic optoelectronics, specifically, light emitting devices using polymers and other smaller molecules [1]. The performance of such devices has improved

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considerably due to optimisation of material interfaces, improvement of quantum yield and a better understanding of charge transport and degradation processes in amorphous organic systems.

The point has now been reached where more sophisticated devices such as organic microcavity structures [2] and polarised emitters [3] are beginning to be reported. Fabrication of polarised emitting films has employed a number of different alignment techniques [4–6]. These techniques have been applied with varying degrees of success; there are still some problems to overcome. All of the techniques have so far failed to produce particularly high degrees of linear polarisation.

The approach which we have used in an attempt to overcome some of these problems is *in-situ* photopolymerisation of functionalised oriented liquid crystals to produce highly aligned chromophore networks. This technique has been studied for a number of years [7] for potential application in solid state liquid crystal display devices. Its exploitation in other areas is still however limited.

To produce these oriented polymer networks, *in-situ* photopolymerisation of macroscopically oriented mixtures of liquid crystal (LC) diacrylates was used. Figure 1 depicts the photopolymerisation process in the liquid crystal phase. This technique involves the macroscopic alignment of the LC diacrylates and the 'freezing-in' of the orientation by photopolymerisation. Previous work has invariably employed molecules where the saturated

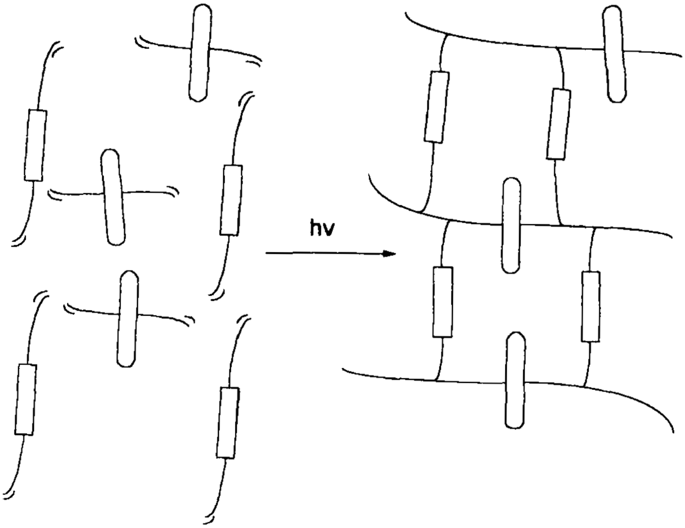


FIGURE 1 Schematic of *in-situ* photopolymerisation.

carbon chains are positioned at either end of the long axis of the liquid crystal core [7]. In our case however, the alkyl chains are bonded across the short axis of the core (see Fig. 1). Networks obtained by this method are highly cross-linked and well ordered. This high degree of orientation is both thermally and temporally stable.

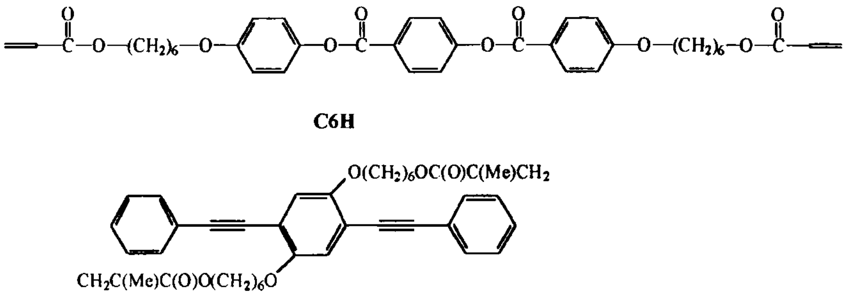
Polarisation dependent absorption and fluorescence has already been studied in these films [8] and not unusually, absorption and fluorescence measurements imply different degrees of order. To study the degree of order on the molecular scale, we undertook the polarisation dependent Raman studies described herein in an attempt to obtain a better understanding of the organisation on a molecular scale.

RESULTS AND DISCUSSION

In this study, we sought to utilise the long range ordering characteristics of liquid crystals to produce a thin film which would preferentially emit light in a particular polarisation and would exhibit good thermal stability properties. We therefore set out to design and synthesise a liquid crystal with an emissive functional core and cross-linkable side-groups. Our aim was to utilise such a liquid crystal in an ordered thin film form.

Phase Transition Studies

In order to produce oriented films with linearly polarised emission characteristics, a chromophore with a blue/violet emissive core and acrylate functionalities (FLLC) was synthesised (Fig. 2) [8].



C6H

FLLC

FIGURE 2 Chemical structure of **FLLC** and **C6H**.

The phase transitions of **FLLC** were studied using differential scanning calorimetry (DSC) and polarising microscopy. The material is crystalline at room temperature and on heating shows a phase transition at 38°C to an unidentified intermediate phase. The transition from this intermediate phase to the isotropic phase has an onset temperature of 67°C and peak is at 80°C. The sample exhibits no phase transitions when it is cooled from the isotropic phase until below 30°C where it crystallises.

Long Range Ordering

A mixture of **FLLC**, 2% mol. of photoinitiator (CIBA-Irgacure^{TM} 651) and 0.1 mole percent of thermal inhibitor (4-methoxyphenol) was prepared.

A glass cell was filled with the mixture in molten form by capillary action. The sample was cooled overnight to allow recrystallisation. The sample was heated to its intermediate state (50°C) and any ordering in the film was observed through cross-polarisers under a microscope. Unfortunately no long range ordering was observed in this intermediate phase.

In order to produce a low viscosity nematic phase, 5% by weight of **FLLC** was mixed with 1,4-phenylene bis{4-[6-(acryloyl-oxy)hexyloxy]benzoate} (**C6H**), a previously studied cross-linkable nematic liquid crystal [9]. The structure of **C6H** is shown in Figure 2. The same proportion of photoinitiator and thermal inhibitor as before was then added. This new mixture exhibits a crystalline–nematic phase transition at 116°C and a nematic to isotropic transition at 150°C. Glass cells containing this mixture were found to exhibit long range in the nematic phase. It is possible to 'freeze-in' this long range ordering by photopolymerisation. This procedure was found to be effective for loadings of up to 15% by weight of **FLLC**.

Films prepared in this manner were previously studied for optical absorption and emission anisotropy [8]. It was found that the two different experiments implied different degrees of order. We have therefore employed Raman spectroscopy to determine the nature of order on the molecular scale in these films.

Raman Anisotropy Studies

In an attempt to gain greater insight into the degree and nature of ordering in these systems, we undertook Raman anisotropy studies.

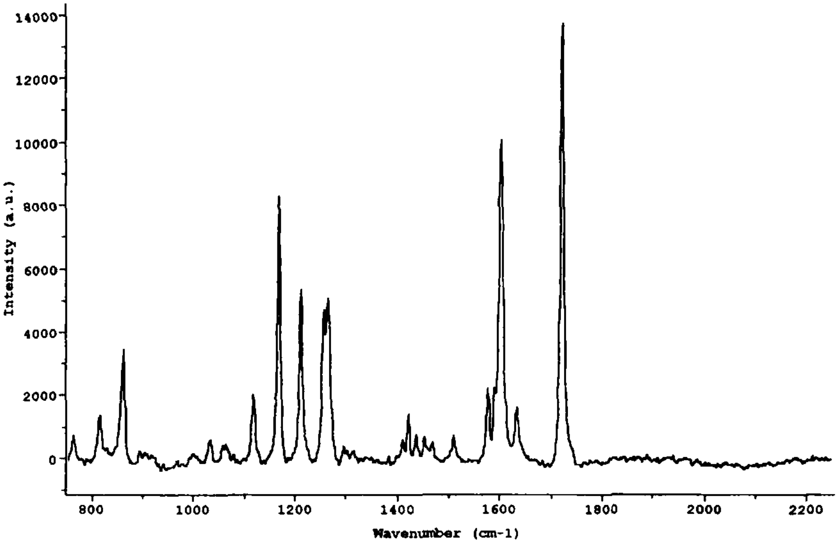
Raman spectroscopy was chosen specifically because it was found that the carbon–carbon triple bond stretch from **FLLC** was too weak to be observed in the IR spectrum of cured films. The thin film form of the samples makes them much easier to measure using Raman spectroscopy than infrared. It was also found that the Raman spectra contains far fewer peaks and it is therefore simpler to interpret spectra and measure absolute peak intensities.

The studies were designed to probe the chemical nature of ordering in these systems. This was achieved by measuring the polarisation dependence of Raman peaks which may be assigned discreetly to modes exhibited by either the **C6H** or the **FLLC** moiety in the mixed, photopolymerised films.

In order to study order in the films, pump polarisation dependent Raman spectra were recorded. To distinguish between modes associated with the host and fluorescent guest, the Raman spectra of the two monomers in powder form were first recorded (Figs. 3a and 3b).

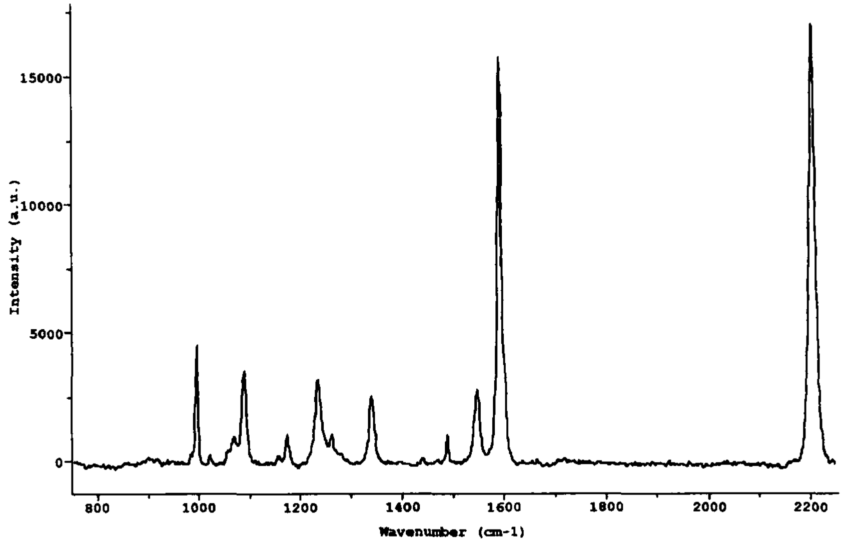
The spectral region of interest here is from 1585 to 2250 cm^{-1} since here there are peaks which may be unambiguously assigned to either **C6H** or **FLLC** molecular cores. For **FLLC**, the peaks at 1590 and 2200 cm^{-1} are of interest. These are assigned to a phenyl mode and a carbon – carbon triple bond mode respectively. For **C6H**, the peaks at 1600 cm^{-1} and 1730 cm^{-1} are assigned as phenyl ring and carbonyl modes respectively.

It is interesting to note the absence of a peak at around 1730 cm^{-1} in the spectrum of **FLLC** (which also contains carbonyl bonds in the acrylate



3a: **C6H**

FIGURE 3 Raman spectra of the monomers **C6H** and **FLLC**.



3b: **FLLC**

FIGURE 3 (Continued).

functionalities). The presence of this peak in the spectrum of **C6H** is therefore probably from the ester linkages and not from the acrylate end groups.

Equivalent peaks to these at practically identical frequencies were found in cured film mixtures and thus it is assumed that the *in-situ* photopolymerisation process has no effect on the positioning of these peaks. Initial investigations showed that all four peaks shared a similar polarisation dependent intensity variation.

The angular dependence of Raman scattering intensity was therefore investigated for these four peaks in a 10% **FLLC**; 90% **C6H** *in-situ* cured film. Raman spectra were recorded for various angles with respect to the orientation direction and the integrated intensity dependence for the four peaks is shown in Figures 4a and 4b. Figure 4a shows the angular dependence of intensity for the two peaks associated with **FLLC** and Figure 4b shows those for **C6H**.

As expected, all of the peaks show a symmetrical, periodic variation of intensity with angle. This demonstrates ordering of both the guest and host in these films.

In order to compare the degree of order of **C6H** and **FLLC** in the films, the order parameter (S) was determined from the measurements.

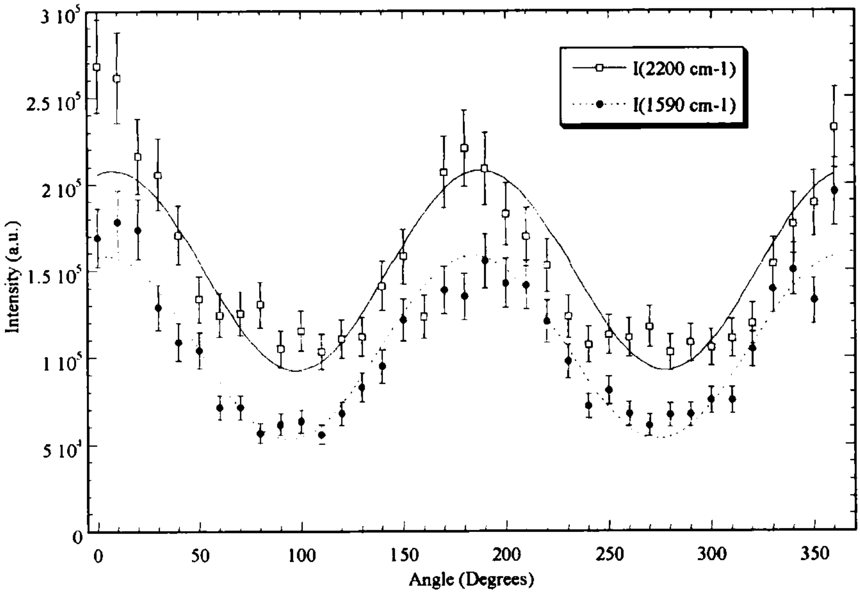


FIGURE 4a Angular dependence of intensity for peaks associated with **FLLC** (lines depict fits to Eq. (2)).

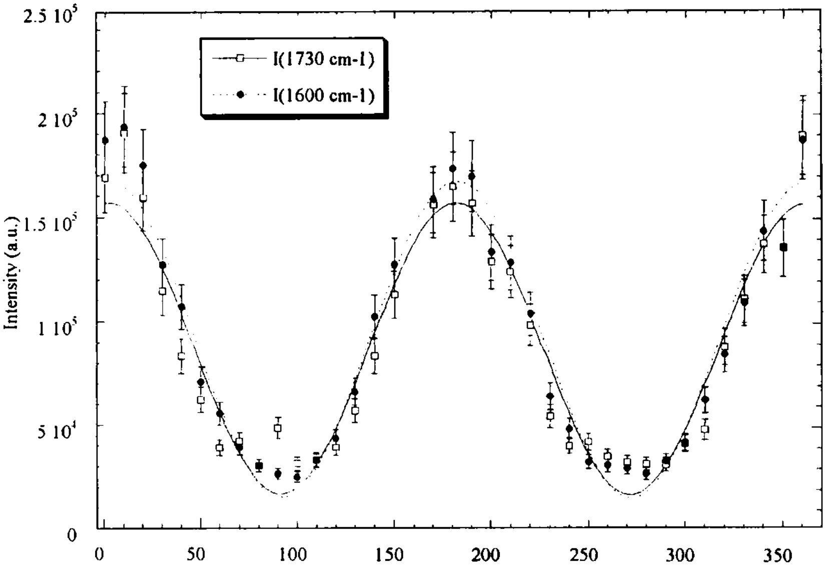


FIGURE 4b Angular dependence of intensity for peaks associated with **C6H** (lines depict fits to Eq. (2)).

S is defined here as:

$$S = \frac{I_{\text{pa}} - I_{\text{pe}}}{I_{\text{pa}} + 2I_{\text{pe}}} \tag{1}$$

where I_{pa} and I_{pe} are respectively the peak intensities parallel and perpendicular to the orientation direction.

In order to determine values of I_{pa} and I_{pe} for the four peaks, the data shown in Figure 4 was fitted to the following function:

$$I(\theta) = A\cos^2(\theta - B) + C \tag{2}$$

where A is an amplitude term, B is a phase correction accounting for any discrepancy between 'internal' and 'external' angle and C accounts for finite intensity at minima. Equation (1) may now be rewritten as:

$$S = \frac{A}{A + 3C} \tag{3}$$

Values of S for the four peaks were then determined from the fits (shown in Fig. 4) and are listed in Table I.

The values obtained are clearly consistent within errors. These results suggest a distinct difference in the degree of order of **C6H** and **FLLC** in the photopolymerised film. **C6H** shows a far higher degree of ordering than **FLLC** perhaps due to the fact that the flexible side chains in **FLLC** are positioned either side of the rigid core whereas in **C6H**, they are at either end of the long axis. This may limit the degree of ordering **FLLC** can achieve in the mesophase and consequently in the photopolymerised film.

It has been shown previously [9] that the temperature of photopolymerisation affects the order in **C6H** films. The polymerisation temperature is usually expressed in terms of 'reduced' temperature (T_r):

$$T_r = \frac{T_{\text{pol}}}{T_{\text{cl}}} \tag{4}$$

TABLE I Values of S for four different Raman modes

	C6H		***FLLC***	
Peak	$1600\,\text{cm}^{-1}$	$1730\,\text{cm}^{-1}$	$1590\,\text{cm}^{-1}$	$2200\,\text{cm}^{-1}$
S*	0.76 ± 0.10	0.73 ± 0.12	0.39 ± 0.05	0.29 ± 0.06

*Errors derived from fits.

Where T_{pol} is the polymerisation temperature and T_{cl} is the clearing temperature (or temperature at which transition to the isotropic phase occurs). To investigate the dependence of order on reduced temperature, Raman studies similar to those already outlined were carried out on 5% **FLLC** cured films with T_r values of 0.7, 0.8 and 0.9. For convenience, only two peaks were considered; 1730 cm^{-1} (**C6H**) and 2210 cm^{-1} (**FLLC**). The findings of these studies are summarised in Table II.

As might be expected, there appears to be a downward trend in the order of both **C6H** and **FLLC** as T_r increases (and the isotropic phase is approached). Again, it is clear that the **FLLC** is not as highly ordered as the **C6H**.

These results indicate possible reasons for the discrepancy in the previous absorption and photoluminescence measurements. Since **FLLC** and **C6H** appear to be ordered to different degrees, it might be expected that there would be variable contributions from each to the absorption and photoluminescence anisotropy.

In order to understand whether or not the order in the system changes during the polymerisation, we also studied the pre-polymerised mesophase in order to determine whether or not the order of the two monomers **C6H** and **FLLC** was similar to that found in the cured films. Molten, unpolymerised films of 5% **FLLC** content were studied using the 1730 and 2210 cm^{-1} peaks in a similar fashion to that already described. The films were mounted on a variable temperature hot plate and the temperature dependence of order was measured. Figure 5 shows the dependence of order on reduced temperature for a 5% **FLLC** content mixture. For reference, the values obtained for equivalent cured films (taken from Tab. II) are also plotted. The larger errors in the in values for the films are probably due to higher background scatter which contributes to intensity at all measurement angles and is usually a percentage error. It is clear however that there is agreement between the values for cured and uncured films. This indicates that the polymerisation process does not contribute to any change in order for either **C6H** or **FLLC**. The order found in the polymerised films is therefore the same as the order found in the pre-polymerised liquid mesophase.

TABLE II Order parameter values as a function of reduce temperature

S^*	*C6H*(1730 *cm*$^{-1}$)	*FLLC*(2210 *cm*$^{-1}$)
$T_r = 0.7$	0.85 ± 0.18	0.35 ± 0.09
$T_r = 0.8$	0.84 ± 0.18	0.32 ± 0.03
$T_r = 0.9$	0.67 ± 0.11	0.26 ± 0.08

*Errors are derived from fits.

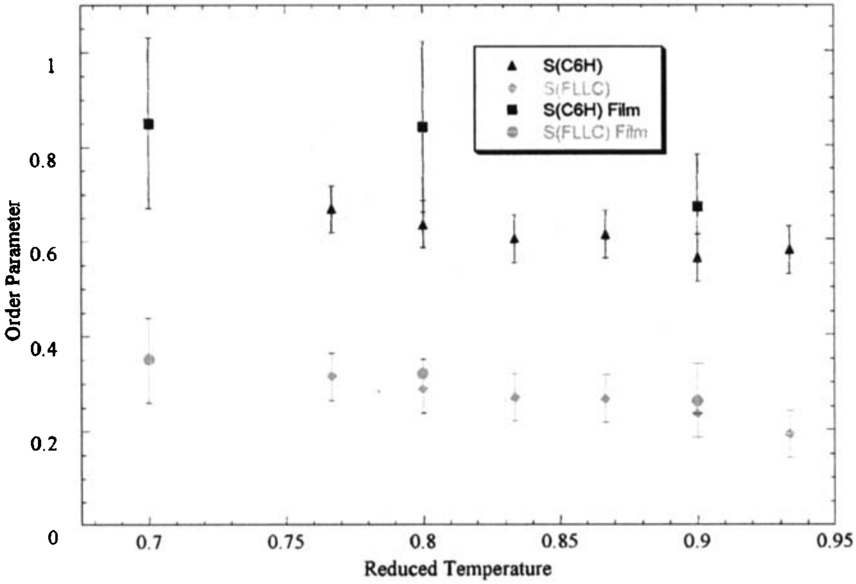


FIGURE 5 Order parameter for uncured 5% FLLC mixture as a function of temperature.

EXPERIMENTAL

Differential Scanning Calorimetry (DSC) Measurements

Measurements were performed on a Perkin Elmer DSC-4. The sample quantities were in the range of 10 mg. The heating and cooling rates were 10°C per minute, the measurements were carried out under an inert nitrogen atmosphere.

Thin Film Preparation

Oriented photopolymerised thin films were produced by an oriented rubbing method. A liquid crystal display type glass cell of 10 μm thickness was fabricated. The inside walls of the cell were coated with a thin layer (ca. 0.1 μm) of spun cast Nylon 66 which was rubbed along one direction of the film plane in order to induce alignment when the glass cell was filled with liquid crystal material. Long range ordering could not be induced in samples of compound **FLLC** alone.

Compound **FLLC** (5% by weight) was mixed with 1,4-phenylene bis {4-[6-(acryloyl-oxy)hexyloxy]benzoate}. 2% mol. of photoinitiator (CIBA-

Irgacure™ 651) and 0.1 mole percent of thermal inhibitor (4-methoxyphenol) was added.

A glass cell containing the mixture was brought to 130°C (nematic phase) and photopolymerised by irradiation for 20 minutes with a low intensity UV fluorescent lamp (4 W) lamp. The cross-linked film thus produced is of very good optical quality and exhibits no sign of phase separation or photodegradation. The same film was used in all subsequent studies.

Raman Spectroscopy Measurements

Raman spectra were recorded using an Instruments S.A. LABRAM 1B confocal microprobe system operating with a polarised Helium Neon laser at a wavelength of 632.18 nm. The polarisation extinction ratio of the laser was measured to be greater than 500:1. A 50X objective was employed, giving a nominal spot size of 1.2 μm. The power incident on the sample was 11 mW. Polarisation angle dependent spectra were recorded by rotating the sample in the plane perpendicular to the incident beam. The objective was focused before each new spectrum was recorded to ensure completely consistent incident power levels were achieved.

CONCLUSION

Measurement of order in emissive molecular films is of great current interest. In the present study, molecular order in thin films of a new oriented, cross-linked liquid crystal mixture have been probed in a new manner using Raman anisotropy measurements. These studies show that the two different molecular components in the films are ordered to different degrees. The order parameter for each component has been determined for two Raman peaks and the results are self-consistent.

The dependence of photopolymerisation temperature on order was also probed and it was found that as temperature increases, the degree of order of both molecular components decreases. This has been shown to be independent of the photopolymerisation process itself, the prepolymerised mixture showing similar order characteristics.

This method provides a more reliable measure of order parameter than UV/visible absorption or fluorescence measurements which are often conflicting. The use of Raman spectroscopy has also proven to be advantageous in situations such as this where thin film samples are the focus of study. There is also an advantage here over infrared absorption spectroscopy due to the greater Raman activity of the carbon – carbon triple bond mode and the less crowded Raman spectrum. For infrared absorption anisotropy studies, it is often difficult or impossible to completely deconvolute overlapping peaks and obtain true values of order parameter.

Further studies on fabrication and testing of electrically driven devices using this material are now in progress with a view to producing a highly polarised light emitting diodes.

Acknowledgements

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