Polarised photoluminescence from oriented polymer liquid crystal films

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Optical anisotropy in a new form of crosslinked liquid crystal network incorporating a fluorescent chromophore has been demonstrated. Linearly polarised absorption and fluorescence is observed in oriented thin films. From measurement of absorption and fluorescence anisotropy, the order parameter was found to be 0.65 and 0.80, respectively. Temperature dependent birefringence measurements reveal that there is no appreciable loss of alignment up to 200 °C.

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 considerably due to optimisation of material interfaces, improvement of quantum yield and a better understanding of charge transport 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. In any study of new systems, the starting point is characterisation of the optical (absorption and photoluminescent) properties. This paper therefore presents the optical characterisation of a new method of inducing polarised photoluminescence by the use of aligned, crosslinked liquid crystal networks.

To date, work in this area has employed a number of different alignment techniques designed to induce polarised emission. The first technique is controlled chemical vapour deposition (CVD) which has been used to produce polycrystalline thin films of small conjugated organic molecules.[4] The second technique is Langmuir–Blodgett film deposition, which was used to fabricate polarised polymer light emitting diodes.[5] Finally, polarised luminescent films have been produced from functionalised polymer liquid crystals by substrate rubbing-induced alignment in the liquid crystal phase.[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. Fig. 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 photo-polymerisation. Previous work has invariably employed molecules where the saturated 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 crosslinked and well ordered. This high degree of orientation is both thermally and temporally stable.

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 crosslinkable side-groups. Our aim was to utilise such a liquid crystal in an ordered thin film form.

Synthesis and characterisation

In order to produce oriented films with linearly polarised emission characteristics, a chromophore with a blue–violet emissive core and acrylate functionalities (**3**) was synthesised. The synthetic route to **3** is depicted in Scheme 1. A similar molecule without any functionalities at the end of the alkyl tails has been previously synthesised[8] and the same general method was used to prepare **2**. Compound **3** was characterised by IR, ^{1}H NMR, ^{13}C DEPT NMR and UV–visible spectroscopy.

Differential scanning calorimetry (DSC) showed that **3** exhibits a small enthalpy phase transition at 36 °C and a larger transition (to the isotropic phase) at 80 °C on the heating cycle. On the cooling cycle, however, no phase transitions could be observed. This is possibly due to slow recrystallisation, since on cooling overnight the phase transitions had returned.

Compound **3** exhibits strong blue–violet fluorescence in dilute chloroform solutions. Fig. 2 shows the electronic absorption and fluorescence spectra of the compound in dilute toluene solution. The quantum yield of fluorescence in chloroform was determined by a comparative method[9] and was found to be 60% in dilute solutions of cyclohexane.

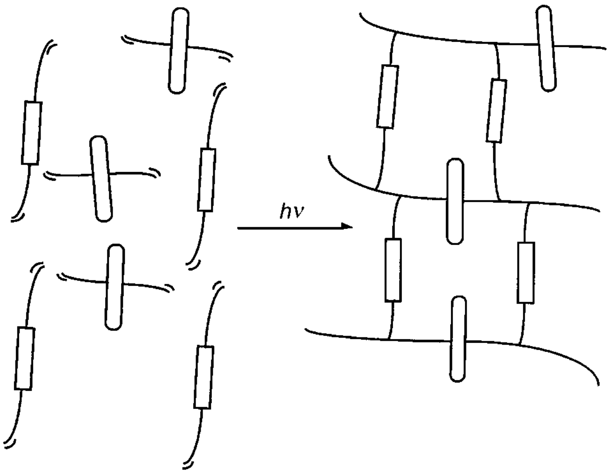
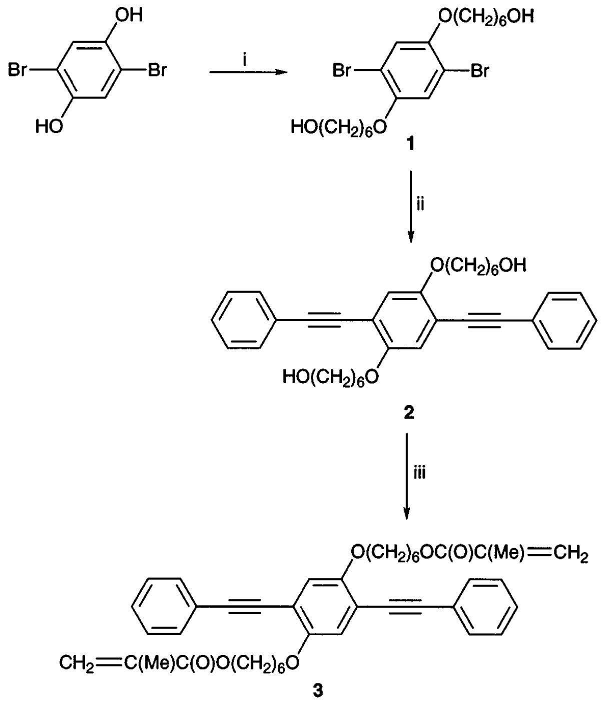


Fig. 1 Schematic of *in situ* photopolymerisation



Scheme 1 *Reagents and conditions*: i, $HO(CH_2)_6Br$ (2 equiv.), butanone, K_2CO_3, heat; ii, PhC≡CH (2 equiv.), piperidine, $Pd(PPh_3)_4$, CuI, 90 °C, 36 h; iii, $CH_2{=}CMeCOCl$ (2 equiv.), CH_2Cl_2, Et_3N

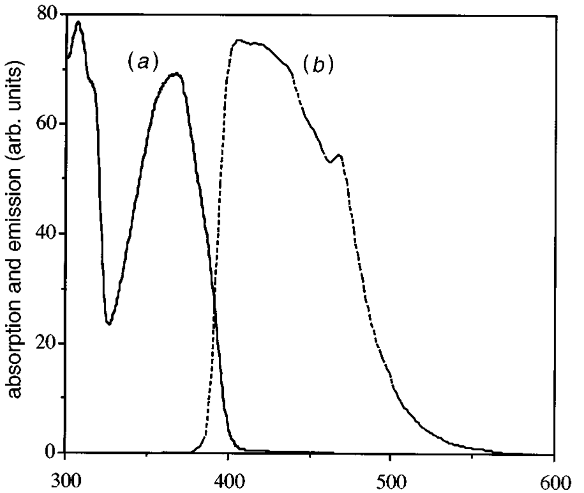


Fig. 2 (*a*) Absorption and (*b*) fluorescence spectra of a toluene solution of **3**

Phase transition studies

The phase transitions of compound **3** were studied using DSC and polarising microscopy. The material is crystalline at room temperature and on heating shows a phase transition at 36 °C to an unidentified intermediate phase. The transition from this intermediate phase to the isotropic phase has an onset temperature of 69 °C and the 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 **3**, photoinitiator (2 mol%; CIBA-Irgacure® 651) and thermal inhibitor (4-methoxyphenol; 0.1 mol%) was prepared. A glass cell was filled with the mixture in molten form by capillary action, and 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.

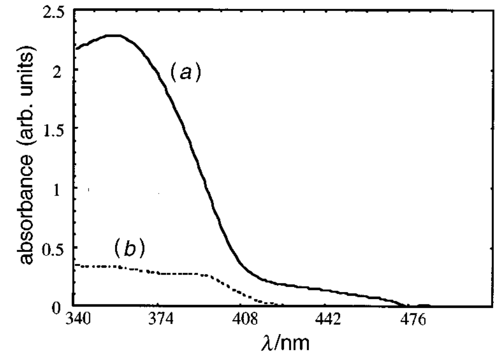


Fig. 3 Linear polarisation dependence of optical absorption (*a*) parallel and (*b*) perpendicular to the director

In order to produce a low viscosity nematic phase, 5% by weight of **3** was mixed with 1,4-phenylenebis{4-[6-(acryloyloxy)hexyloxy]benzoate}, a previously studied crosslinkable nematic liquid crystal.[10] The same proportion of photoinitiator and thermal inhibitor as before was then added. This new mixture exhibited a crystalline–nematic phase transition at 116 °C and a nematic–isotropic transition at 150 °C. Glass cells containing this mixture were found to exhibit long range ordering in the nematic phase. It was 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 **3**.

Polarised absorption and emission studies

In order to measure optical anisotropy in the film, polarisation dependent UV–visible absorption spectra were recorded. Spectra recorded for polarisations perpendicular and parallel to the director and normalised for the polariser absorption are shown in Fig. 3.

Clearly, the oscillator strength in absorption is concentrated along the direction of rubbing. The order parameter S was calculated by comparing peak absorption (355 nm) parallel and perpendicular to the direction of rubbing, according to eqn. (1),

$$S=\frac{A_{\mathrm{PA}}-A_{\mathrm{PE}}}{A_{\mathrm{PA}}+2A_{\mathrm{PE}}} \tag{1}$$

where A_{PA} and A_{PE} are the values of absorbance parallel and perpendicular to rubbing respectively. The value of S for absorption was thus found to be 0.65, which compares favourably with values found for similar non-fluorescent systems.[10] It is noteworthy that there appears to be an extra absorption band in the perpendicular absorption spectrum. The origin of this band is not clear, it may perhaps be a weak vibrational mode (bending mode) polarised primarily across the long axis of the fluorescent molecule. Whatever the origin of the band, its presence reduces the value of S as determined by absorption. The emission spectra (for an excitation wavelength of 350 nm) parallel and perpendicular to the rubbing direction are shown in Fig. 4. There is obviously a strong linear polarisation of the blue–violet emission. By way of comparison, the order parameter was again determined by comparing the numerically integrated emission spectra for the parallel and perpendicular directions according to eqn. (2), a modified form of eqn. (1),

$$S=\frac{\int_0^{\infty} E_{\mathrm{PA}}\,\mathrm{d}\lambda-\int_0^{\infty} E_{\mathrm{PE}}\,\mathrm{d}\lambda}{\int_0^{\infty} E_{\mathrm{PA}}\,\mathrm{d}\lambda+2\left(\int_0^{\infty} E_{\mathrm{PE}}\,\mathrm{d}\lambda\right)} \tag{2}$$

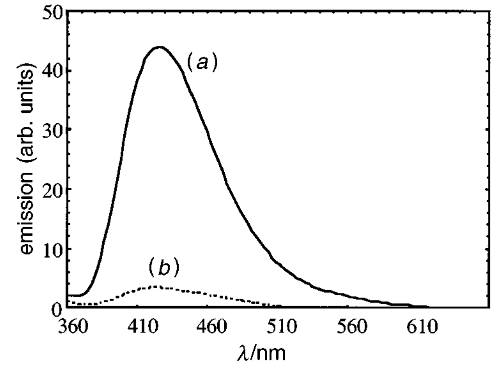


Fig. 4 Linear polarisation dependence of photoluminescence (*a*) parallel and (*b*) perpendicular to the rubbing direction

where E_{PA} and E_{PE} are the emission intensities parallel and perpendicular to orientation respectively.

In this case, S was found to 0.80, a relatively high value. The discrepancy between S determined by absorption and S found by emission probably arises either from the different measurement geometry or from the presence of the extra band in the perpendicular absorption. In the case of absorption transmitted light is monitored, whereas for fluorescence it is light scattered from the sample surface which is detected.

Variation of order with temperature

In order to monitor changes in order as a function of heating, temperature dependent birefringence was measured using a hot stage and a polarising microscope (equipped with a Leitz type M tilting compensator). This method was specifically used since thermal processes might affect the temperature dependent emission characteristics independent of order. Fig. 5 shows the variation of birefringence with temperature. There is little or no change in order as temperature increases. This is due to the very rigid nature of the crosslinked liquid crystal network. Similar characteristics to this have been observed for other acrylate functionalised liquid crystal networks.[11]

It is also interesting to note that the birefringence returns to its original value on cooling to ambient temperature, indicating that fluctuation of order is probably due to random thermal motion rather than relaxation of the order.

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.

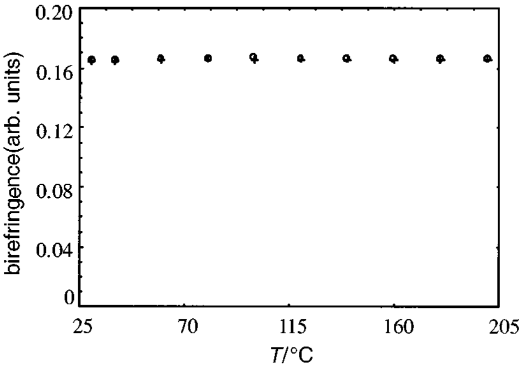


Fig. 5 Temperature dependence of birefringence: (○) heating and (+) cooling

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 **3**. Thus ordered thin films of **3** could not be produced.

Compound **3** (5% by weight) was mixed with 1,4-phenylenebis{4-[6-(acryloyloxy)hexyloxy]benzoate}. Photoinitiator (2 mol%; CIBA-Irgacure® 651) and thermal inhibitor (4-methoxyphenol; 0.1 mol%) was added. A glass cell containing the mixture was brought to 130 °C (nematic phase) and photopolymerised by irradiation for 20 min with a low intensity UV fluorescent lamp (4 W). The crosslinked film thus produced was of very good optical quality and exhibited no sign of phase separation or photodegradation. The same film was used in all subsequent studies.

Absorption and fluorescence measurements

Polarised absorption spectra were obtained using an ATI UV–visible absorption spectrometer and a Rowi 55 mm polariser. The polariser was placed between the spectrometer source and the film sample. The parallel absorption spectrum was recorded with the direction of polarisation parallel to the rubbing direction of the film. The polariser was rotated 90° and the perpendicular absorption spectra was recorded.

Polarised fluorescence spectra were measured using a Perkin Elmer MPF-4413 spectrophotometer. The spectrophotometer source was intrinsically polarised so no polariser was required. The parallel and perpendicular spectra were recorded by aligning the film at the appropriate angle (0 or 90°) with respect to the polarised source. The film was placed at an angle of 45° to both the excitation source and detector. The excitation wavelength was 350 nm.

Birefringence measurements

Measurements were performed using a Leitz polarising microscope and a Leitz tilting compensator (type M at 546 nm). The samples were heated using a microscope hot stage and a Eurotherm temperature controller.

Preparation of the fluorescent compound

All reactions were performed under an argon atmosphere. All solvents were dried and degassed before use. Reagents were used as supplied from the Aldrich Chemical Company. NMR spectra were recorded in $CDCl_3$ solution with an internal Me_4Si standard.

Synthesis of compound 2. Compound **1** (1 mmol) and phenylacetylene (2.1 mmol) were dissolved in 30 ml of piperidine. $Pd(PPh_3)_4$ (0.046 g, 2 mol%) and copper(I) iodide (4 mg) were then added and the mixture was stirred at 90 °C for 6 h. Following cooling, the precipitated hydrobromide salts were filtered and washed with hexane. The washings were combined with the piperidine solution and the solvents were removed under vacuum. The resulting solid was recrystallised from butanone (0.42 g, 83%); ^1H NMR: δ 0.92–1.80 [m, 8H, $(CH_2)_4$], 3.78 (t, 2H, OCH_2), 3.83 (t, 2H, $HOCH_2$), 6.81 (s, 1H, Ar-H), 7.20–7.60 (m, 5H, Ar-H); ^{13}C NMR: δ 22.5, 25.4, 29.8 and 32.0 (CH_2), 69.9 (OCH_2), 72.4 ($HOCH_2$), 86.3 and 95.0 (sp-C), 114.2 (Ar-C), 117.1 (Ar-C), 123.4 (Ar-C), 128.1 (Ar-C), 132.0 (Ar-C) and 154.0 (Ar-C).

Synthesis of compound 3. Compound **2** (0.5 mmol) was dissolved in 20 ml of THF along with hydroquinone stabiliser (3 mg) and triethylamine (1.1 mmol). The solution was heated to reflux and methacryloyl chloride (1.1 mmol) dissolved in 5 ml of CH_2Cl_2 was gradually added. Stirring was continued for 2 h before the solution was allowed to cool to room temperature. The mixture was then poured into 150 ml of water and washed with saturated sodium carbonate (3 × 20 ml), dried and the solvent evaporated *in vacuo*. The solid was recrystallised from ethanol (0.23 g, 60%); ^1H NMR: δ 1.52–1.85(m, 8H), 4.00(t, 2H), 4.18(t, 2H), 5.02(s, 3H), 5.81(d, 1H), 6.13(d, 1H), 6.80(s, 1H), 7.21–7.62(m, 5H); ^{13}C DEPT NMR: δ 25.71 (CH_2), 28.53(CH_2) 29.07(CH_2), 64.48(CH_2), 67.95(CH_2), 86.20($C{\equiv}C$), 94.87($C{\equiv}C$), 101.20(CH_3), 114.12(Ar-C), 117.24(Ar-CH), 124.16(Ar-CH), 128.32(Ar-CH), 131.24(Ar-CH), 146.59(CH), 147.20(CH_2), 153.98(ArC–O), 159.92($C{=}O$).

Conclusion

Thin films of a new oriented, crosslinked liquid crystal mixture have been shown to exhibit strongly polarised absorption and emission and large order parameter values. Furthermore, temperature dependent birefringence measurements indicate that order in the sample is largely maintained at elevated temperatures.

It was also noted that the birefringence (and hence order) returned to its original value on complete cooling. Measurement of the order parameter from absorption and emission provides large values. The discrepancy between these values is probably due to different measurement techniques or to the extra absorption feature in the perpendicular polarised absorption spectrum. Further studies on fabrication and testing of electrically driven devices are in progress with a view to producing highly polarised light emitting diodes.

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