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Fluorescence study of a thermotropic liquid crystal: bis(*p*-hexyloxyphenyl)terephthalate

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The microstructure of the low molecular weight thermotropic liquid crystal, bis(*p*-hexyloxyphenyl)terephthalate (PP6), was analysed by fluorescence. The material has an emission around 400 nm in its various liquid crystalline phases, but this emission disappears in the isotropic phase. The emission was attributed to fluorescence from an intermolecular ground state complex between two different chromophores of PP6 based on fluorescence experiments of model compounds and dilute PP6 solutions. No peak shifts were observed on changing temperature, while the fluorescence intensity decreased as the temperature was increased. The fluorescence intensity changed dramatically at the phase transitions. An abrupt change in the fluorescence intensity was observed on changing depending on the temperature especially at the smectic–nematic transition temperature. Thus, the intermolecular fluorescence of the liquid crystal is greatly affected by the phase structure and the order of liquid crystalline phase.

1. Introduction

There have been a large number of reports concerning the preparation and physical properties of low molecular weight and polymeric liquid crystals. The phase behaviour of thermotropic liquid crystals is usually measured by DSC and polarizing microscopy, and the phase structure analysed by X-ray diffraction. Recently their conformations have been clarified by solid state ^{13}C NMR [1–3]. These methods can attain a great success in the individual cases. There have been, however, few studies on the intermolecular aggregation in the liquid crystalline state, although various intermolecular interactions such as dipole–dipole, hydrogen bonding [4–7], and the charge transfer interaction [8–10], are considered to be important as driving forces for organizing the liquid crystalline structure. Hence, a new method is needed in order to elucidate the intermolecular aggregation and the microenvironment in the liquid crystalline states over a wide temperature range.

Recently, we have shown that the fluorescence measurement is a powerful tool in understanding the intra- and intermolecular aggregation state of aromatic polymers both in solid [11, 12] and liquid crystalline phases [13–15]. The advantage of this technique lies in the fact that it is sensitive to the interactions between neighbouring chromophores. This technique gives some information about the spatial geometry of these chromophores. Sone *et al.* [14], have studied rigid-rod polyesters with flexible side chains based on 1,4-dialkyl esters of pyromellitic acid and 4,4′-biphenol, which form thermotropic liquid crystalline phases. These liquid crystal polymers were known to have layered structures (from X-ray diffraction measurements), but the fluorescence study has also clarified how the aromatic main chains are arranged inside each layer. They found that this liquid crystal polymer emits charge-transfer (CT) fluorescence between the pyromellitic and biphenyl groups, showing that these two moieties at adjacent main chains are aligned alternately across the main chains in the rigid-rod layer. In this way, the intermolecular interactions or microenvironment of the molecules in the liquid crystalline state, which could not be determined by X-ray studies, can be detected sensitively by using the fluorescence method.

The present paper deals with the first observation of fluorescence, over a very wide temperature range (27–208°C), of low molecular weight thermotropic liquid crystals as a model of liquid crystal polymers, because their phase structure changes more remarkably with temperature than that of liquid crystal polymers. The fluorescence from the intermolecular ground-state complex between the two different chromophores of the

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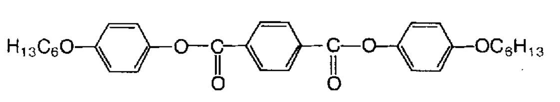
liquid crystalline molecule studied showed a marked change in intensity at the smectic–nematic phase transition temperature.

2. Experimental

2.1. *Materials*

We prepared a low molecular weight liquid crystal, bis(*p*-hexyloxyphenyl)terephthalate (PP6), from terephthaloyl dichloride and *p*-hexyloxyphenol [16]. Telephthaloyl dichloride is a commercial product. *p*-Hexyloxyphenol was prepared from hydroquinone and 1-bromohexane according to the method of Samulski *et al.* [17]. A solution of *p*-hexyloxyphenol and terephthaloyl dichloride in 30 ml pyridine was stirred for 24 h at room temperature and then poured into dilute hydrochloric acid. The precipitate was filtered off, washed with sodium bicarbonate solution and water, and then recrystallized from ethyl acetate.



(PP6)

2.2. *Measurements*

Liquid crystalline textures were observed with an Olympus BH-2 polarizing optical microscope equipped with a Mettler FP-80 hot stage. DSC measurements were performed with a Perkin–Elmer DSCII calorimeter at a scanning rate of 10°C min^{-1}. Smectic phase tilt angles were measured by X-ray diffraction. Fluorescence spectra were measured with a Hitachi 850 fluorescence spectrometer whilst changing temperature over the phase transition temperature ranges. When spectra were measured at high temperatures, the sample was put into a 1 mm thick quartz cell as a bulk or placed between two quartz plates with a transparent polymer support. The temperature of the sample was controlled with a temperature-controlling unit.

3. Results and discussion

3.1. *Thermotropic phase behaviour of PP6*

Figure 1 shows the DSC second heating thermogram of PP6 with five exothermic peaks. The textures observed under polarizing optical microscopy are shown in figure 2. The compound has the following phase sequence:

$$\mathrm{Cr_1} \xleftrightarrow{134^\circ\mathrm{C}} \mathrm{Cr_2} \xleftrightarrow{162^\circ\mathrm{C}} \mathrm{S_C} \xleftrightarrow{176^\circ\mathrm{C}} \mathrm{S_A} \xleftrightarrow{182^\circ\mathrm{C}} \mathrm{N} \xleftrightarrow{206^\circ\mathrm{C}} \mathrm{I}$$

where $\mathrm{Cr_1}$ and $\mathrm{Cr_2}$ are crystals. These temperatures agree well with those previously reported [17].

Figure 3 gives the results of the X-ray diffraction measurements. The tilt angle in the smectic phase decreases with increasing temperature and disappears in the temperature range of the smectic A phase. This temperature dependence of the tilt angle is characteristic of the smectic C phase.

3.2. *Fluorescence measurements of PP6*

Figure 4 shows the fluorescence spectra of PP6 when the sample was placed between two quartz plates coated with an ethylene–propylene copolymer. When the sample was put into the quartz cell, however, the scattered light was very strong in crystalline state and the fluorescence spectra were covered by the tail of the

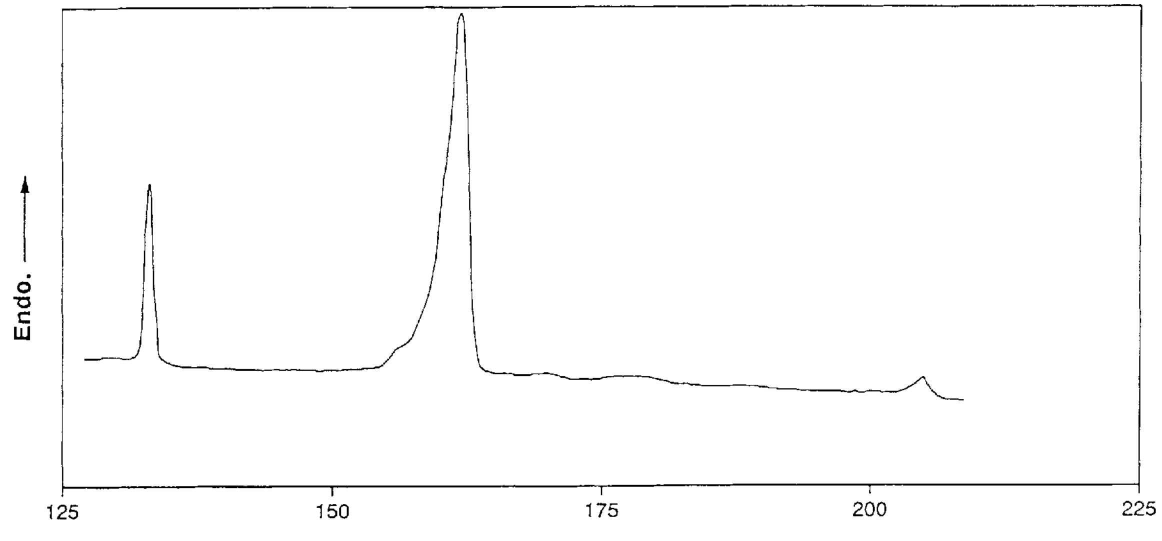
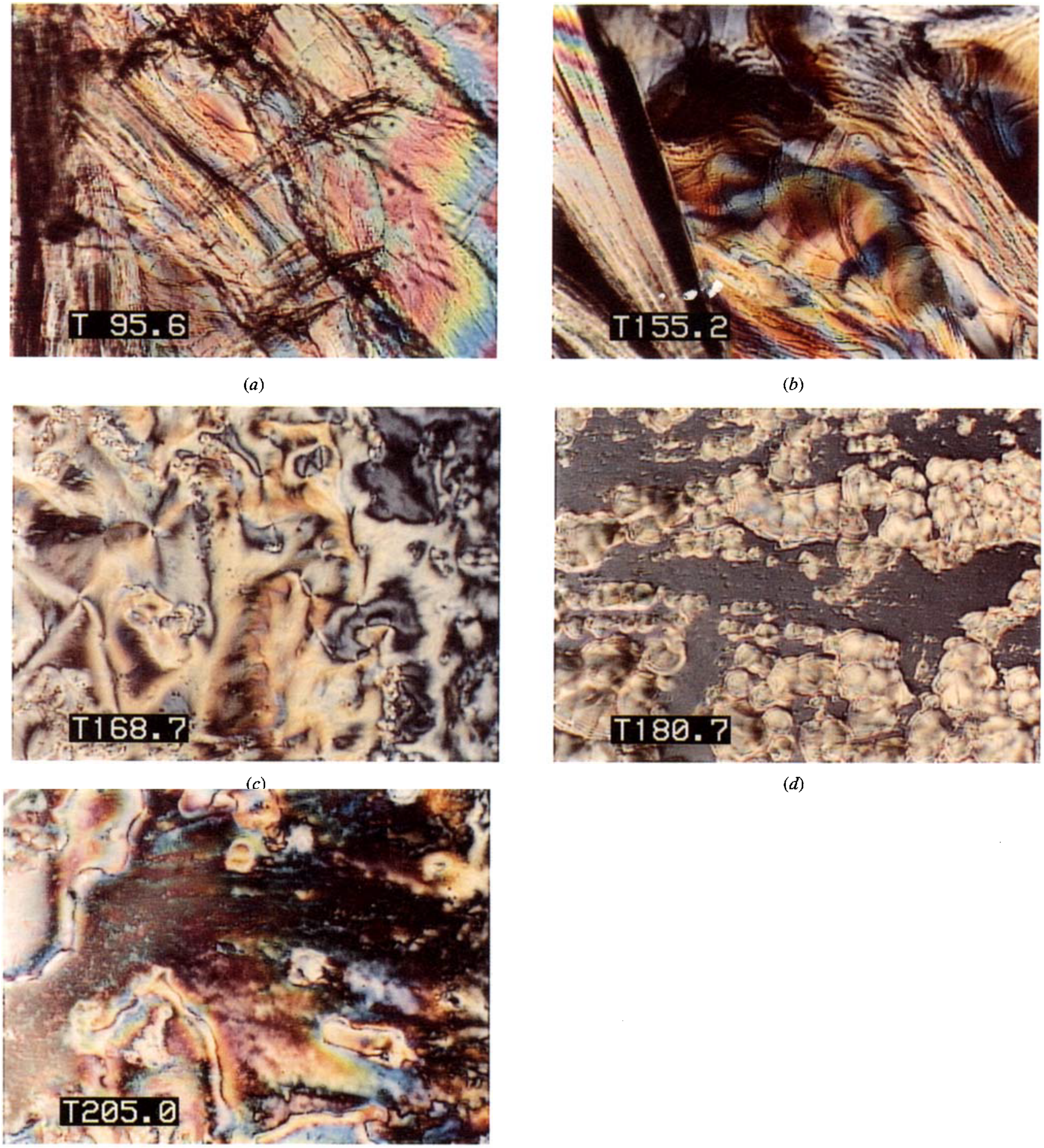


Figure 1. Second DSC heating thermogram of PP6 at a scanning rate of 10°C min^{-1}.



(a) (b) (c) (d) (e)

Figure 2. Photographs of textures of PP6 through a polarized microscope: (a) crystalline state (Cr_1), (b) crystalline state (Cr_2), (c) smectic C phase (S_C), (d) smectic A phase (S_A) and (e) nematic phase (N).

scattered light. We had to, therefore, give up measuring the sample in bulk form. The emission band was observed at around 400 nm when the sample was excited at 360 nm, while the excitation peak was observed at 370 nm. The emission intensity decreased as the temperature increased, but no peak wavelength shifts were

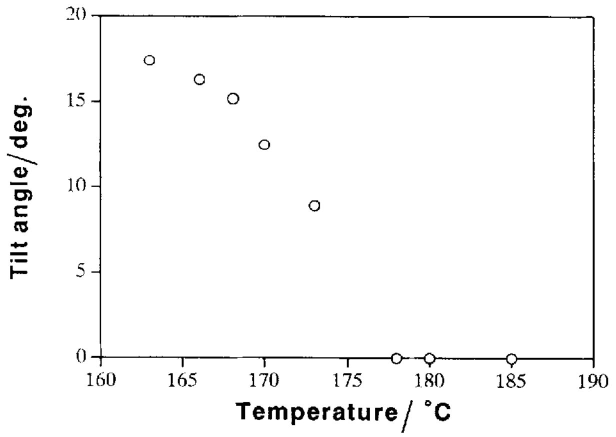


Figure 3. Smectic C tilt angle as a function of the temperature from X-ray diffraction measurements.

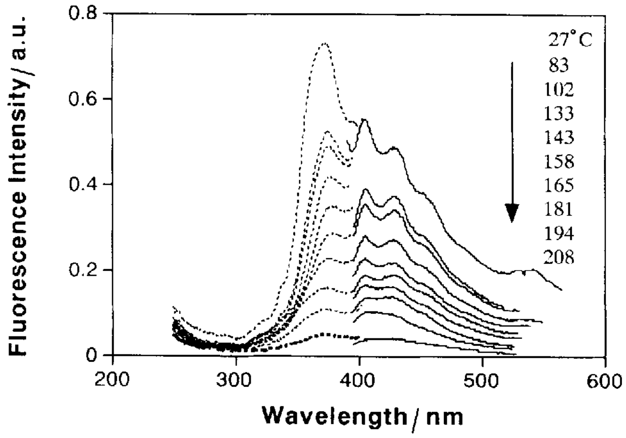


Figure 4. Fluorescence spectra of PP6 over the temperature range 27°C to 208°C (solid lines: emission spectra excited at 360 nm; dotted lines: excitation spectra monitored at 430 nm).

observed. In the case of fluorescence from an intermolecular exciplex or ground-state complex, peak wavelength shifts generally mean that the distance or degree of overlapping between chromophores changes. The decrease in fluorescence intensity is usually attributed to the effect of the increase in the non-radiative deactivation rate from the excited state with increasing temperature and/or the change in the number of chromophore pairs due to the change in microstructure. The emission at around 400–420 nm is composed of two peaks with a shoulder at the low temperature range. As the temperature increases, these emission peaks cannot be distinguished from each other and it almost appears to be one peak at high temperature. Splitting into two peaks in the low temperature region may reflect the microstructure of the phase, but we do not know enough about it to be able to discuss details.

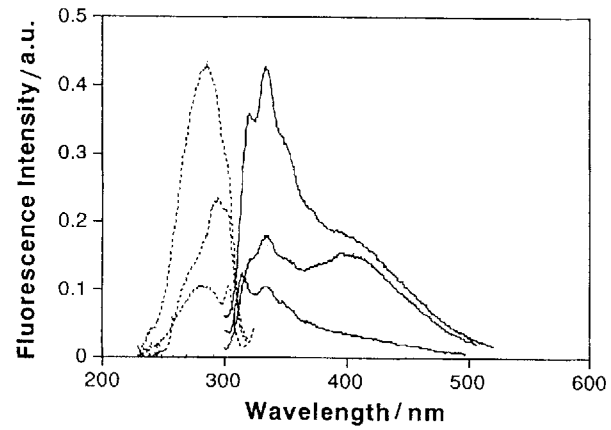


Figure 5. Fluorescence spectra of dilute dichloromethane solution of PP6 excited at 285 nm (solid lines: emission spectra excited at 285 nm; dotted lines: excitation spectra monitored at 335 nm, at a concentration of $1{\cdot}0 \times 10^{-6}$ M, $1{\cdot}0 \times 10^{-4}$ M and $1{\cdot}0 \times 10^{-5}$ M, respectively, from the bottom).

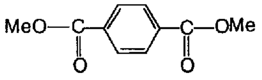
To clarify the origin of the emission around 400 nm, we measured the fluorescence spectra of a dilute solution of PP6 in dichrolomethane (see figure 5). The spectrum of a $1{\cdot}0 \times 10^{-6}$ M solution, which has an emission maximum around 335 nm when excited at 280 nm, is thought to be attributed to the fluorescence from isolated molecules, the solution being very dilute. As the concentration of the solution was increased ($1{\cdot}0 \times 10^{-5}$ M, $1{\cdot}0 \times 10^{-4}$ M), a new emission peak appeared around 400 nm. The same excitation spectrum with a peak at 290 nm was observed for the 400 nm emission as for the monomer emission at 335 nm. Thus the new peak at 400 nm is attributed to an intermolecular excimer or exciplex between chromophores formed during the excited-state lifetime in solution.

However, the excitation peak wavelength of 370 nm for the 400 nm emission of PP6 in the condensed state is quite different from that of 290 nm for the 400 nm emission of the $1{\cdot}0 \times 10^{-4}$ M solution. Therefore, it leads us to conclude that PP6 forms intermolecular ground-state complex in the condensed state.

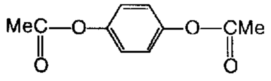
The emission at 400 nm disappeared in the isotropic phase above 206°C. In this phase, molecules move quite randomly and there is no order. Taking into account that this emission is derived from the intermolecular interaction, it is quite reasonable that it cannot be observed.

3.3. *Fluorescence measurements of model compounds*

In order to investigate which part of the molecule emits the fluoresces the fluorescence of two model compounds of PP6, i.e., dimethyl terephthalate (DMT) and 1,4-diacetoxybenzene (DAB) in dichloromethane solutions was measured (see figure 6). In the case of DMT, when excited at 300 nm, a monomeric emission was observed at around 320 nm, and a new emission peak at around 380 nm appeared with increasing concentration of the solution, as shown in figure 6 (*a*). This new emission band has been assigned to an excimer emission. On the other hand, DAB showed only a monomeric emission at 325 nm when excited at 285 nm (see figure 6 (*b*)). At the emission band wavelengths obtained here, there is no emission in the condensed state of PP6.



(DMT)



(DAB)

Moreover, fluorescence for an equimolar mixture of DMT and DAB in each $1{\cdot}0 \times 10^{-1}$ M dichloromethane solution (see figure 6 (*c*)) shows an emission peak at around 410 nm, which is different from the DMT excimer emission band and, of course, from each monomeric emission band. Therefore, this emission band is ascribed to an exciplex between DMT and DAB. The wavelength of the emission peak coincides with that of the emission band of PP6 in the condensed state. To sum up, the emission around 400 nm is derived from intermolecular interaction of the two different moieties in PP6, which form a ground-state complex in the condensed state.

3.4. *Fluorescence intensity change*

A peak shift was not observed during a temperature change in the present system. Let us now, therefore, discuss the fluorescence intensity changes related to the phase transition of the liquid crystal. The fluorescence intensity for PP6 is plotted in figure 7 as a function of the reciprocal of absolute temperature. As mentioned above, the fluorescence intensity decreases with increasing temperature. It is clearly seen that an abrupt change in the temperature dependence of the fluorescence intensity is observed at a temperature close to the smectic–nematic (S–N) phase transition. This result suggests that the mode of molecular motion, phase structure, fluidity of each phase and hence the number of intermolecular complexes are quite different between smectic and nematic phases. There is also a break in this figure at a temperature close to the crystal–crystal phase transition temperature. At this temperature, the crystal structure seems to change; we cannot however, discuss the crystal–crystal phase transition further because of the unknown detailed crystal structure. The smectic A–smectic C phase transition could not be determined from this figure. This may indicate that the average molecular motion in both the smectic A and smectic C phases of this liquid crystal is not so different, or that there is so little difference in the structures of these

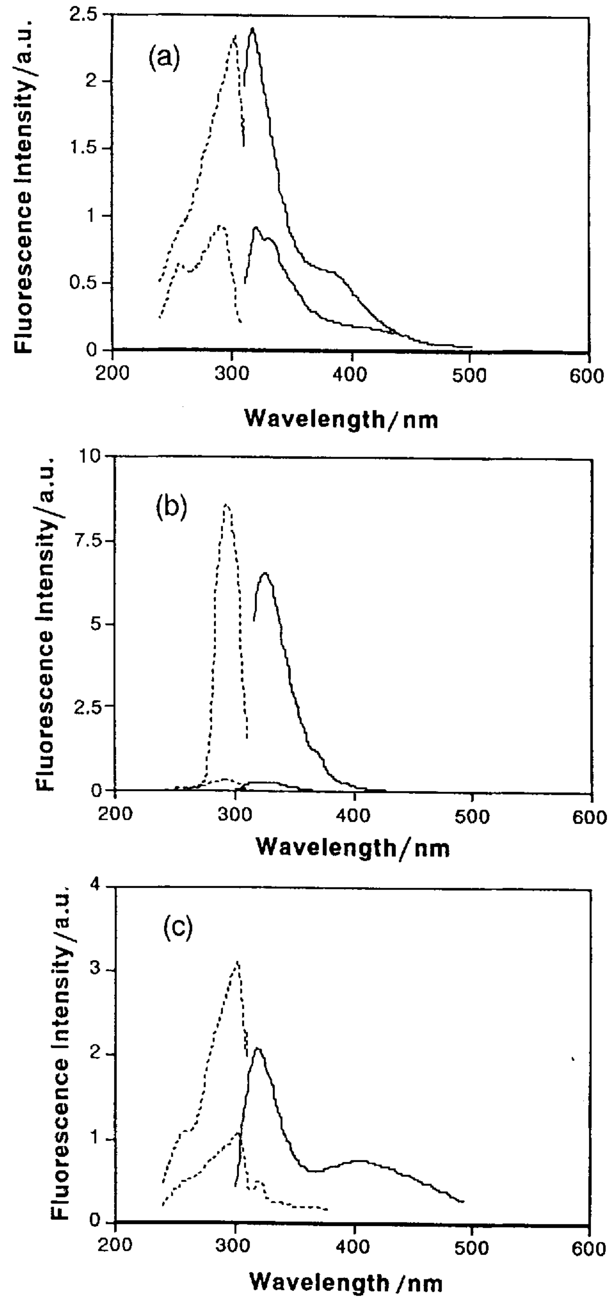


Figure 6. Fluorescence spectra of model compounds in dichloromethane: (*a*) DMT; solid lines (upper and lower): emission spectra excited at 300 nm dotted lines (upper and lower): excitation spectra monitored at 320 nm, at $1{\cdot}0 \times 10^{-1}$ M and $1{\cdot}0 \times 10^{-4}$ M, respectively. (*b*) DAB; solid lines (upper and lower): emission spectra excited at 285 nm, dotted lines (upper and lower): excitation spectra monitored at 325 nm, at $1{\cdot}0 \times 10^{-1}$ M and $1{\cdot}0 \times 10^{-3}$ M, respectively. (*c*) equimolar mixture of DMT and DAB (each $1{\cdot}0 \times 10^{-1}$ M); solid line: emission spectrum excited at 280 nm, dotted lines (upper and lower): excitation spectra monitored at 320 nm and 410 nm, respectively.

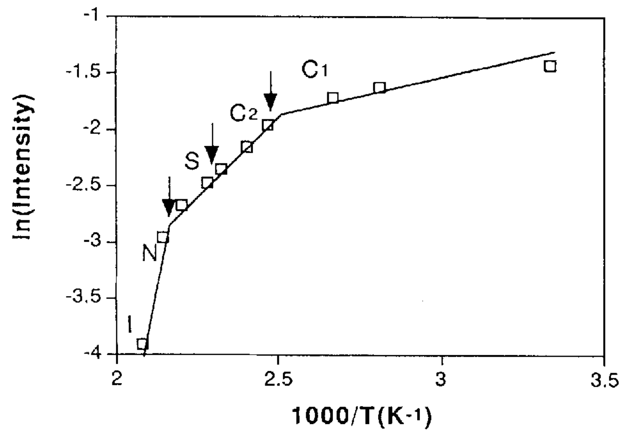


Figure 7. Arrhenius plot of the fluorescence intensity of PP6 (the phase transition temperature is indicated by arrows).

phases that they cannot be differentiated with this fluorescence technique. No change in the slope was observed for the crystal–smectic (Cr_2–S_C) phase transition, which might suggest that the local configuration of chromophores in these phases is not so different from each other. In the DSC measurements, we obtained a strong endothermic peak for this Cr_2–S_C transition, but only a very weak peak was observed for the smectic–nematic (S–N) phase transition (see figure 1). This suggests that in determining the configuration of chromophores, fluorescence measurements would be a more powerful technique than DSC, because the emission of the intermolecular complex is sensitive to the molecular order and motion of chromophores. From these results, the differences between various phases, especially the smectic and nematic phases, would be understood by using the fluorescence method.

In the present work we initially expected that these series of compounds would form intermolecular CT complexes between the DMT and DAB moieties, and strong CT fluorescence would be observed in the smectic C (S_C) phase. This is because, in the S_C phase with a tilt angle, molecules are thought to be most stable when the donor and acceptor moieties approach intermolecularly to each other. In the present experiments, a strong fluorescence of the ground state complex between DMT and DAB moieties in PP6 have been observed for the crystal and smectic stages, but the fluorescence of the S_C phase was not so special compared to the other phases. Crystal–crystal and smectic–nematic phase transitions could be detected from the Arrhenius plots of the fluorescence intensity. Thus, by using the fluorescence method, we may estimate the microstructure and configuration of chromophore mesogens from the wavelengths of the spectra, and the order and number of chromophore complexes in each liquid crystalline phase from their intensity. By considering that PP6 forms a ground-state complex not only in the crystalline state but also in the liquid crystalline state, we may think of intermolecular interactions as a driving force responsible for the organization of liquid crystalline structure. Thus it is suggested that fluorescence can be an effective technique in understanding further the microstructure of liquid crystals, when it is used in conjunction with NMR or X-ray diffraction.

4. Conclusions

The phase transition behaviour of liquid crystals can be detected by the fluorescence technique. Fluorescence spectra over a wide temperature range have provided detailed information about the intermolecular aggregation structure of chromophores and the molecular motion in the liquid crystalline state. It is suggested in the present study that the formation of the intermolecular complex between the terephthalate and oxyphenylene moieties with a fluorescence peak at 400 nm is correlated to the molecular order of the various liquid crystalline states.

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