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Polymer 40 (1999) 3821–3828

polymer

Fluorescence study on intermolecular complex formation between mesogenic terphenyldiimide moieties of a thermotropic liquid-crystalline polyimide

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Received 25 May 1998; received in revised form 29 July 1998; accepted 10 August 1998

Abstract

Intermolecular complex formation between mesogenic terphenyldiimide moieties of a thermotropic liquid-crystalline (LC) polyimide (P-11TPE) was studied by steady-state fluorescence and fluorescence lifetime measurements together with differential scanning calorimetry (d.s.c.) and wide-angle X-ray diffraction (WAXD). The P-11TPE shows various highly-ordered crystalline phases and a smectic phase during heating, according to the d.s.c. and WAXD results. By comparing the fluorescence spectra and fluorescence lifetimes between P-11TPE and its model compound (*N*,*N′*-diundecylter-phenyldiimide), the fluorescing complex at 438 nm of P-11TPE is confirmed to be an intermolecular ground-state complex between two terphenyldiimide moieties. The fluorescence peak wavelength of this intermolecular complex shifts slightly to shorter wavelength below the glass transition temperature and shifts abruptly to longer wavelength around crystallization, then shifts gradually to shorter wavelength again from various crystalline phases until the isotropic phase. The changes in fluorescence intensity and fluorescence lifetime around phase transition temperatures are also observed. These apparent changes in fluorescence behaviour indicate the differences in the nature and number of intermolecular complexes and radiationless deactivation processes in various phases. The characteristics of fluorescence behaviour for P-11TPE are also compared to those for various LC polyesters studied previously, and it is concluded that the red shift of fluorescnece is due to the apparent change in molecular arrangement between mesogenic moieties and the blue shift of fluorescence is due to the almost identical packing pattern with increasing thermal fluctuation during phase transition for liquid crystal polymers. By using fluorescence technique, molecular interaction between mesogenic moieties of liquid crystal polymer has been proved to show various patterns of changes during phase transition processes.

Keywords: Thermotropic liquid-crystalline polyimide; Fluorescence; Intermolecular ground-state complex

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1. Introduction

Liquid-crystalline polymers (LCPs) have attracted much attention because of scientific interest and numerous technological applications [1,2]. Molecular interaction between mesogenic moieties is well known to play an important role in determining the physical properties of LCPs. Various fluorescent species, such as monomers, excimers, and ground-state complexes, have been observed owing to the differences in the formation of molecular interaction between moieties of polymers [3–5]. Thus, the change in molecular interaction of LCPs can be studied directly by investigating the change in fluorescence behaviour of fluorescing complexes in LCPs.

Based on this concept, we introduced fluorescence technique to study the intermolecular complex formation between mesogenic moieties of various types of LCPs [6–8] and two series of LC polyesters with mesogenic biphenyl moieties [9–11]. For LC polyesters with mesogenic 4,4′-dihydroxybiphenyl moieties containing various methylene units (PB-*n*), a strong excitation wavelength dependence of fluorescence was observed for all PB-*n* and proved to be due to the formation of various intermolecular ground-state complexes corresponding to different degree of overlap between 4,4′-dihydroxybiphenyl moieties. Moreover, the fluorescence peak wavelengths of these intermolecular ground-state complexes all converge to a longer wavelength during heating to isotropic temperature [9,10]. On the contrary, for LC polyesters with mesogenic 4,4′-biphenyldicarboxylate moieties (BB-*n*) whose mesogenic moiety is only different in the sequence of oxygen in ester group

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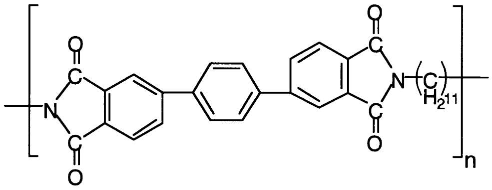
PII: S0032-3861(98)00589-8

comparing with PB-*n*, excitation wavelength dependence of fluorescence was not observed owing to the higher uniformity in molecular arrangement of BB-*n* in comparison with PB-*n*. In addition, BB-*n* shows the shift of fluorescence peak wavelength to shorter wavelength owing to the increase in thermal fluctuation during heating [11]. According to these fluorescence studies on LC polyesters with mesogenic biphenyl moieties, the change in molecular interaction between mesogenic moieties of LCPs has been proved to show two kinds of pattern during phase transition processes.

Aromatic polyimides have been well known for many years as high temperature and high performance polymers, and have found many applications in aerospace, electronics, and other industries [12,13]. The outstanding thermal stability and other physical properties of aromatic polyimides are closely associated with the rigidity of polymer chains and strong charge-transfer intermolecular complex formed between imide (acceptor) moieties and aromatic (donor) moieties [12,13]. Thus, LC polyimide seems to be more appropriate than LC polyester to study the change in molecular interaction between mesogenic moieties, since the strong charge-transfer intermolecular complex of LC polyimide may reflect the change in molecular interaction more sensitively than the not-so-strong intermolecular complex of LC polyester does. Recently, Inoue et al. synthesized the first example of a high crystallinity thermotropic LC polyimide with mesogenic terphenyldiimide moieties (P-11TPE) [14]. The repeating units of this LC polyimide can be represented as follows.



P-11TPE

According to the differential scanning calorimetry (d.s.c.) and wide-angle X-ray diffraction (WAXD) results of P-11TPE [14,15], P-11TPE shows two highly-ordered crystalline phases and a smectic phase during heating. For the cooling process, nematic and smectic phases were observed but only one crystalline phase was shown. More recently, the synthesis of this LC polyimide series containing 6–12 methylene units was made, and their LC behaviour was also studied in detail [15].

In this article, to clarify the pattern of the change in molecular interaction of LCP during phase transition by using fluorescence method together with d.s.c. and WAXD, we investigate the intermolecular complex formation of P-11TPE and its change in steady-state fluorescence behaviour during phase transition process. In addition, the characteristic change in its fluorescence lifetime during phase transition is studied in detail.

2. Experimental

2.1. Materials

The LC polyimide, P-11TPE, was synthesized by high-pressure thermal polycondensation from its salt monomer, as was described elsewhere [14] in detail. In an effort to provide a common thermal prehistory, all the samples were placed on a quartz plate, annealed at 260°C for 5 min, and then cooled to room temperature before fluorescence measurements.

A model compound, *N*,*N*′-diundecylterphenyldiimide (11TPI), was synthesized from 4,4″-terphenyltetracarboxylic dianhydride and aminoundecane in nitrogen atmosphere at 300°C overnight, then a chloroform/methanol mixture solvent was used for recrystallization. 4,4″-Terphenylte-tracarboxylic dianhydride and aminoundecane were purified by sublimation and distillation under vacuum before use. Chloroform and acetonitrile (spectroscopic grade) were purchased from Wako Pure Chemical Industries, Ltd, and used directly without purification.

2.2. Measurements

D.s.c. measurements were performed with a Perkin-Elmer DSC II. Samples of about 10 mg were examined at a scanning rate of 10°C/min under a flow of dry nitrogen.

Ultraviolet–visible (UV-vis) absorption spectra were measured with a Jasco UV-vis V-570 spectrophotometer.

Steady-state fluorescence spectra were measured with a Hitachi 850 fluorescence spectrophotometer equipped with a 30 kV xenon lamp. The band passes were 5 nm for both excitation and emission monochromators. The fluorescence and its excitation spectra for 1.11×10^{-6} M 11TPI acetonitrile solution were measured by using a 1-cm quartz cell in side-face detection. For the 1.39×10^{-2} M 11TPI chloroform solution, the fluorescence and its excitation spectra were measured at the surface of a 1-cm quartz cell. The 11TPI crystal and P-11TPE films were sandwiched between two quartz plates and their fluorescence was measured in a front-face arrangement to minimize the self-absorption. The temperature of P-11TPE for fluorescence spectrum measurements during heating was controlled by means of an Alpha Engineering thermostat coupled with a temperature-controlling unit.

Fluorescence lifetime measurements were performed with a Hamamatsu C4780 sub-nanosecond single-photon counting system. A nitrogen laser (Laser Photonics Ltd, LN120C) was used as an excitation pulse source (337.1 nm) with a pulse width of 300 ps (fwhm). The excitation pulse was directed to the sample through optical fiber, and the emitted light was also guided through optical fiber to a Hamamatsu C4334 streak scope then transformed to streak images. The delay time was controlled by a Hamamatsu C4792 trigger unit. The instrument response function of the whole system was about 1.4–1.8 ns (fwhm). Probably

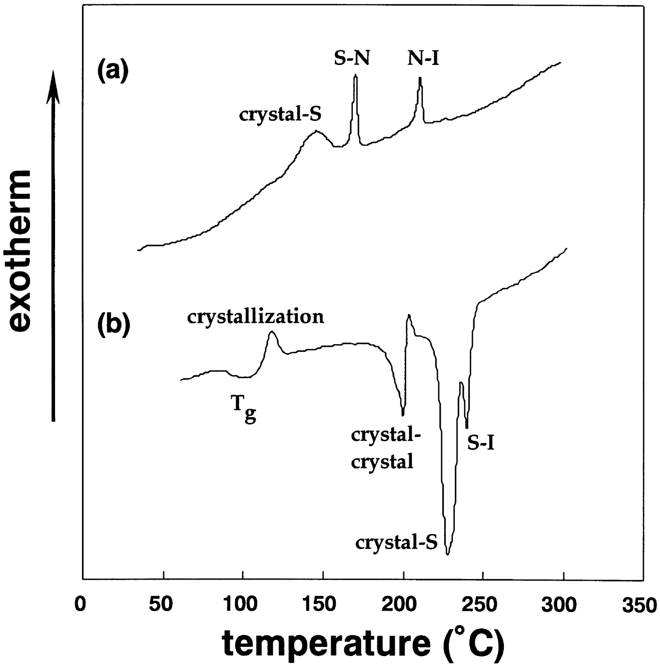


Fig. 1. D.s.c. first cooling (a) and second heating (b) thermograms for P11TPE at a rate of 10°C/min after initially being heated to isotropic phase.

due to the characteristics of terphenyldiimide chromophore, $I_f(t)$ can be best fitted with a double exponential function:

$$I_f(t) = A_1 \times \exp(-t/\tau_1) + A_2 \times \exp(-t/\tau_2)$$

where $I_f(t)$ is the fluorescence intensity at time t, A_1 the pre-exponential factor for the component with much longer lifetime, τ_1 the lifetime for the component with much longer lifetime, A_2 the pre-exponential factor for the component with shorter lifetime, and τ_2 the lifetime for the component with shorter lifetime. Since the ratio of the component with much longer lifetime $(A_1\tau_1/(A_1\tau_1 + A_2\tau_2))$ is over 0.85 and c^2 is around 1.09–1.66, we adopt the component with much longer lifetime and neglect the component with shorter lifetime as in previous works [7,8]. The temperature of P-11TPE for fluorescence lifetime measurements during heating was controlled by a Linkam THMS 600 hot stage with a LK-600PM central processor. Steady-state fluorescence and fluorescence lifetime measurements during heating were kept standing for about 30 min for each measurement to equilibrate the temperature.

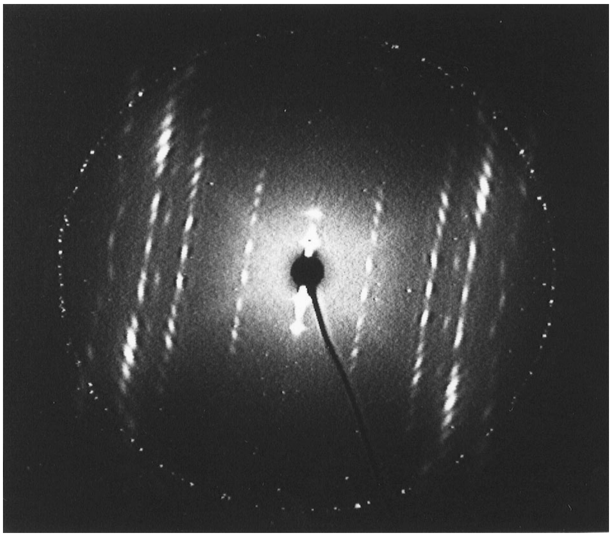


Fig. 2. X-ray diffraction pattern of P-11TPE at 190°C.

3. Results and discussion

3.1. Thermal properties

Fig. 1 shows the first cooling (a) and second heating (b) d.s.c. thermograms for P-11TPE after initially heated to isotropic phase. By comparing with our previous d.s.c. results [14,15] for heating process (b), one can observe the glass transition and crystallization around 89°C and 117°C, respectively. One can also observe an obvious endothermic peak around 200°C, which can be regarded as crystal–crystal transition. Moreover, one can observe crystal–smectic (S) and smectic–isotropic (I) transition at 228°C and 240°C, respectively. Upon the cooling process (a), P-11TPE shows isotropic–nematic (N) (210°C), nematic–smectic (169°C), and smectic–crystal (144°C) transitions as reported in the previous papers [14,15]. However, because of the high crystallinity and high viscosity of P-11TPE, LC phases can only be observed for a short-period time and will be crystallized during a long-period time of cooling process. Thus, the change in fluorescence behaviour was studied principally during the heating

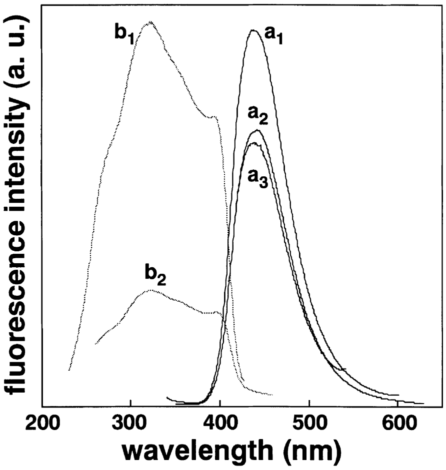


Fig. 3. Fluorescence (black curves) and its excitation spectra (gray curves) of P-11TPE cooled from 260°C and measured at 18°C. a_1, a_2, and a_3 are the fluorescence spectra excited at 320 nm, 400 nm, and 280 nm, respectively. b_1 and b_2 are the fluorescence excitation spectra monitored at 438 nm and 500 nm, respectively.

process, owing to the formation of crystallization during a long-period time for temperature equilibrium of the cooling process.

3.2. Highly-ordered crystalline phase

According to the WAXD patterns of P-11TPE in the previous paper, P-11TPE shows a highly-ordered orthorhombic crystalline phase at 160°C with $a = 12.48$ Å, $b = 4.56$ Å, and $c = 47.4$ Å, and hence the corresponding density is 1.28 g/mL [14]. P-11TPE also shows a well-ordered crystalline phase at 205°C, but the crystal structure is difficult to determine owing to the coexistence of several similar crystalline phases [14]. A d.s.c. thermogram of P-11TPE (Fig. 1) also shows a complicated crystal–crystal transition around 200°C. This may indicate the formation of another kind of crystalline phase around 200°C. Fig. 2 shows the WAXD pattern of P-11TPE at 190°C. This WAXD pattern shows a highly-ordered pattern similar to the crystalline phase at 160°C as reported in the previous paper [14]. The unit cell of this crystal is also orthorombic with $a = 11.58$ Å, $b = 5.03$ Å, and $c = 47.4$ Å. The c repeat distance is consistent with twice the length of repeating unit of P-11TPE, and the unit cell volume, $V = 2760$ Å^3, requires four repeating units per unit cell; the corresponding density is then 1.25 g/mL, which is slightly lower than the density of the crystalline phase at 160°C (1.28 g/mL). This suggests the formation of a different crystalline phase around 190°C and indicates that the density of P-11TPE decreases gradually during heating.

3.3. Origin of the fluorescing complex of P-11TPE

Fig. 3 shows the fluorescence and its excitation spectra of P-11TPE cooled from 260°C and measured at 18°C. As can be seen in Fig. 3, in spite of the excitation at 320 nm (a_1), 400 nm (a_2), and 280 nm (a_3), P-11TPE shows fluorescence only at 438 nm, thus the excitation wavelength dependence of fluorescence which has been demonstrated for PB-*n* is not observed for P-11TPE. This is due to the much higher uniformity in crystalline structure of P-11TPE proved from the highly-ordered WAXD pattern in comparison with the case of PB-*n*.

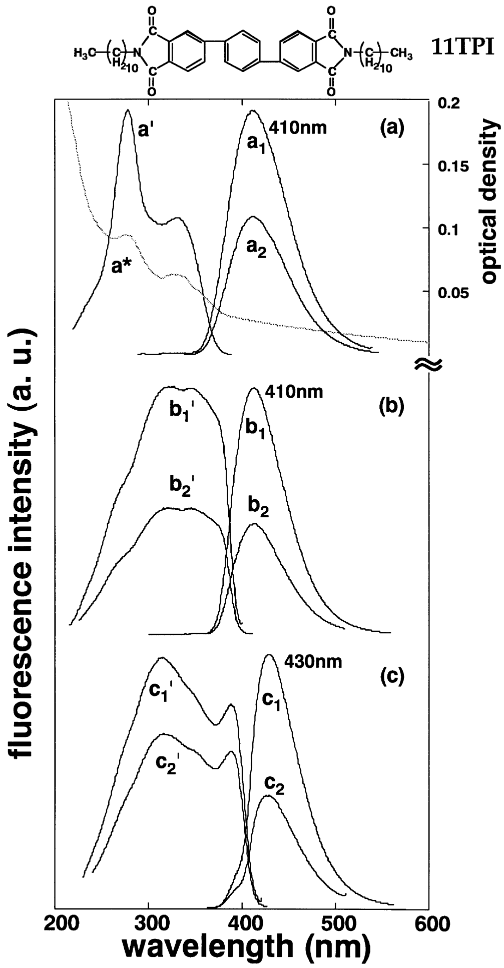


Fig. 4. Absorption (a^*; gray lines), fluorescence and its excitation spectra of 11TPI in 1.11×10^{-6} M acetonitrile solution (a), 1.39×10^{-2} M chloroform solution (b), and crystal (c). (a) a_1 and a_2 are the fluorescence spectra excited at 280 nm and 330 nm, respectively; a' is the fluorescence excitation spectra monitored at 420 nm. (b) b_1 and b_2 are the fluorescence spectra excited at 320 nm and 260 nm, respectively; b_1' and b_2' are the fluorescence excitation spectra monitored at 410 nm and 450 nm, respectively. (c) c_1 and c_2 are the fluorescence spectra excited at 320 nm and 260 nm, respectively; c_1' and c_2' are the fluorescence excitation spectra monitored at 430 nm and 450 nm, respectively.

In order to investigate the intermolecular complex formation of P-11TPE during heating, it is necessary to clarify the origin of the fluorescing complex at 438 nm of P-11TPE. We used 11TPI as a model compound to study the formation of this fluorescing complex of P-11TPE. Fig. 4 shows the absorption, fluorescence, and fluorescence excitation spectra of 11TPI in various concentrations (*a*, *b*) and crystal state (*c*). At first, we refer to the absorption (a^*), fluorescence (a_1,

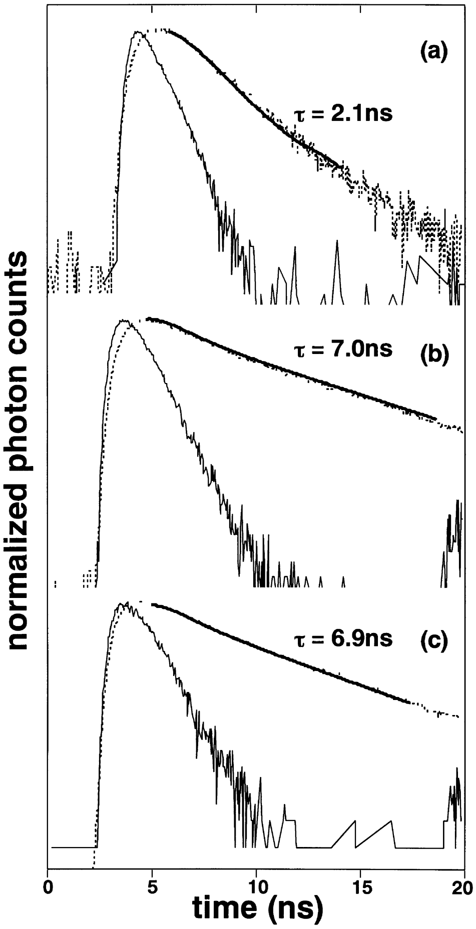


Fig. 5. Fluorescence decay profiles for L1TPI in 1.11×10^{-6} M acetonitrile solution (a), 11TPI crystal (b), and P-11TPE (c) at 400–460 nm. Solid curves are excitation pulses, dotted curves are the decay profile of the samples, and bold curves are the convoluted decay profile.

a_2), and fluorescence excitation spectrum (a') of a dilute solution (1.11×10^{-6} M) in Fig. 4a. The UV-vis absorption spectrum (a^*) shows absorption around 280 nm and 330 nm, which is in agreement with the peak of fluorescence excitation spectrum (a'). Hence the fluorescence at 410nm (a_1, a_2) is demonstrated to be due to a usual monomer emission. Similarly, the 11TPI solution with a higher concentration (1.39×10^{-2} M) also shows monomer fluorescence at 410 nm (b_1, b_2) as in Fig. 4b. The 11TPI crystal in Fig. 4c shows a longer fluorescence peak wavelength at 430 nm (c_1, c_2) than that of monomer, and its fluorescence excitation spectra (c_1', c_2') show an obvious shoulder around 390 nm, while this shoulder is not shown in the fluorescence excitation spectra of 11TPI solution (a', b_1', b_2'). Correspondingly, the shoulder around 390 nm of fluorescence excitation spectra is also observed in those of P-11TPE in Fig. 3. This may indicate that the fluorescing complex at 438 nm of P-11TPE is due to the formation of an intermolecular ground-state complex, but not a monomer or an excimer. To confirm the origin of fluorescing complex of P-11TPE, we measured the fluorescnece lifetime of 11TPI in dilute solution (a), 11TPI crystal (b), and P-11TPE (c), as shown in Fig. 5. According to the analysis of the fluorescence decay profile for 11TPI dilute solution (a), it implies that the fluorescence lifetime of monomer is 2.1 ns. On the contrary, according to the analysis of fluorescence decay profiles for 11TPI crystal (b) and P-11TPE (c), the fluorescence lifetimes of fluorescing complex of 11TPI crystal (7.0 ns) and P-11TPE (6.9 ns) are almost in accord with each other and are both much larger than that of monomer. This confirms that the fluorescing complexes of both P-11TPE and 11TPI crystal originated from an identical intermolecular complex. Consequently, we conclude that the fluorescing complex at 438 nm of P-11TPE is formed by an intermolecular ground-state complex between two mesogenic terphenyldiimide moieties.

3.4. Change in fluorescence peak wavelength and fluorescence intensity during heating

The fluorescence (right) and its excitation spectra (left) of P-11TPE during heating are depicted in Fig. 6. The fluorescence peak wavelength of intermolecular ground-state complex shifts slightly to a shorter wavelength before glass transition (18–80°C) and shifts abruptly to a longer wavelength around the crystallization temperature (121°C), then shifts gradually to shorter wavelength again from various crystalline phases to the isotropic phase (121–246°C). Moreover, in spite of the distortion due to monomer self-absorption and multiscattering effects, the shoulder around 390 nm of fluorescence excitation spectra (left) becomes a much stronger peak at high temperatures (121–246°C). This indicates that the change in fluorescence peak wavelength is not only due to the change in the excited state but also due to the change in the ground state, and implies that the species of intermolecular ground-state complex has changed during heating.

In order to study the change in fluorescence peak wavelength in detail, the tempearture dependence of the fluorescence peak wavelength during heating is presented in Fig. 7. From room temperature to glass transition temperature (18–89°C), because of the increase in local mobility of mesogenic moieties towards glass transition, the interaction of intermolecular ground-state complex becomes weaker and near to the monomer state, thus the fluorescence peak wavelength shifts slightly to a shorter wavelength (438–433 nm). During crystallization transition (117°C), the fluorescence peak wavelength shifts abruptly to a longer wavelength (433–460 nm). This is because the terphenyldiimide moieties rearrange to form a highly-ordered crystalline structure and make the electronic distribution between two terphenyldiimide moieties change to form a more stable state at a lower energy level, then emit fluorescence at a longer wavelength. This kind of red shift in fluorescence peak, caused by the difference in molecular arrangement during phase transition, has also been reported for LC polyesters [7,9,10]. During the phase transition from several

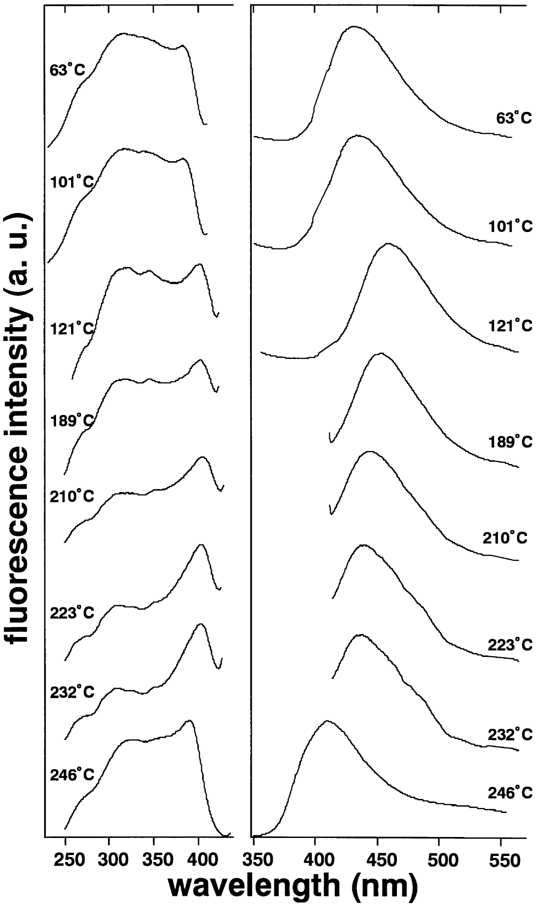


Fig. 6. Fluorescence (right) and its excitation spectra (left) of P-1ITPE during heating. Fluorescence spectra are all excited at 320 nm and excitation spectra are all monitored at 450 nm.

similar orthorombic crystalline phases to smectic phase (117–240°C), the fluorescence peak wavelength shifts gradually to a shorter wavelength (460–438 nm). This is because the temperature effect makes thermal fluctuation become stronger with increasing temperature and induces the decrease in molecular interaction between two terphenyldiimide moieties. The intermolecular ground-state complex with strong interaction changes gradually to the one with weak interaction, which is near to the monomer state, and thus emits fluorescence at a shorter wavelength as has been reported for BB-*n* [11]. Correspondingly, this is in good agreement with the decrease in density with increasing temperature during several similar orthorombic crystalline phases, as is discussed in Section 3.2. Above isotropic transition temperature (240–268°C), the fluorescence peak wavelength shifts abruptly to a shorter wavelength and remains at about 410 nm, which is the wavelength corresponding to monomer fluorescence. This is reasonable because the intermolecular ground-state complex formed between two terphenyldiimide moieties cannot interact with each other in a highly mobile isotropic phase, and thus emit the fluorescence of an independent terphenyldiimide moiety. To sum up, as can be seen in Fig. 7, the temperature dependence of the fluorescence peak wavelength during heating shows breaks around phase transition temperatures, which is also similar to the change in fluorescence behaviour during phase trsansitions of other LCPs [7–11]. This indicates that the temperature dependence of the change in molecular ineraction for various phases are also different for P-11TPE.

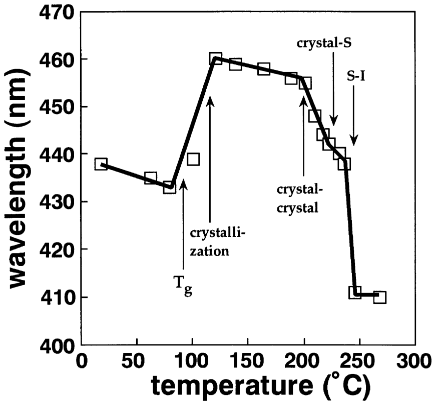


Fig. 7. Temperature dependence of the fluorescence peak wavelength excited at 320 nm during heating.

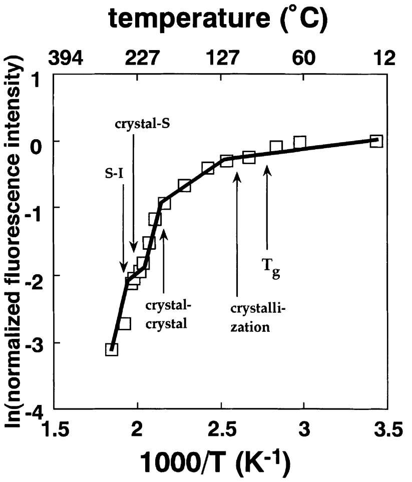


Fig. 8. Arrhenius-type plots for the change in fluorescence intensity of P11TPE excited at 320 nm during heating.

In order to investigate the deactivation process of the excited singlet state of P-11TPE during heating, we present in Fig. 8 Arrhenius-type plot for the change in fluorescence intensity during heating. In general, the fluorescence intensity decreases with increasing temperature owing to the increase in radiationless transition. Moreover, the Arrhenius-type plots of fluorescence intensity show breaks around phase transition temperatures in accord with the change in fluorescence peak wavelength shown in Fig. 7, which is also observed for the change in fluorescence intensity of other LCPs during phase transition process [9–11]. This suggests that the deactivation processes of intermolecular ground-state complexes are also different in various phases for P-11TPE.

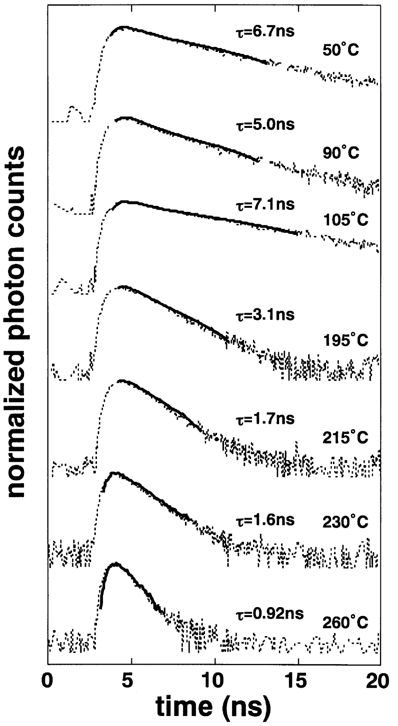


Fig. 9. Fluorescence decay profiles of P-11TPE at 400–480 nm during heating. Dotted curves are the decay profile of the sample and bold curves are the convoluted decay profile.

3.5. Change in fluorescence lifetime during heating

In order to study the change in fluorescence emission process of the intermolecular ground-state complex during heating, the fluorescence decay profiles of P-11TPE during heating are presented in Fig. 9. As can be seen in Fig. 9, the fluorescence lifetime decreases from 6.7 ns to 5.0 ns around glass transition (90°C) and increases abruptly to 7.1 ns around crystallization (105°C), then decreases gradually again from various crystalline phases to the isotropic phase. Corresponding to the change in fluorescence peak wavelength during heating, this implies that the fluorescence emission processes of intermolecular ground-state complexes are different in various phases, and confirms the formation of various intermolecular ground-state complexes in different phases.

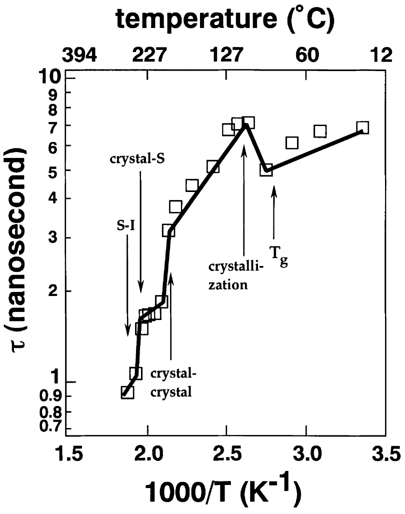


Fig. 10. Arrhenius-type plots for the change in fluorescence lifetime of P11TPE at 400–480 nm during heating.

Fluorescence lifetime (τ) can be defined by the following equation [16]:

$$\tau = (k_\mathrm{f} + k_\mathrm{d})^{-1}$$

where k_f is the rate constant for the fluorescence emission process and k_d is the rate constant for the radiationless deactivation process. This indicates that τ is affected by the fluorescing complex itself and temperature during heating in this study. Fig. 10 shows the Arrhenius-type plots for the change in fluorescence lifetime during heating. In an analogous manner, the temperature dependence of fluorescence lifetime shows breaks around phase transition temperatures, which is similar to the change in fluorescence peak wavelength shown in Fig. 7. According to Fig. 10, τ decreases slightly with increasing temperature until glass transition, owing to the increase in radiationless deactivation process, giving a larger k_d to make τ decrease. However, τ increases abruptly during crystallization around 117°C, owing to the rearrangement of molecular arrangement to form another kind of intermolecular complex with a different fluorescence emission mechanism and k_f, thus showing an abrupt increase in τ at crystallization, though the radiationless deactivation process increases with increasing temperature. However, from various crystalline phases to the isotropic phase, τ decreases gradually again with increasing temperature, which is also due to the increase in k_d. This seems to imply that the τ is mainly dominated by the factor of radiationless deactivation process above the crystallization around 117°C, but is related slightly to the intermolecular complex itself. This may be because the molecular arrangements among various crystalline phases are similar to each other as discussed in WAXD part, and hence the radiationless deactivation process becomes the dominating factor at high temperatures. Accordingly, the obvious breaks of temperature dependence of τ around phase transition temperatures indicate that the radiationless deactivation processes are different in various phases.

3.6. Characteristics of fluorescence behaviour for P-11TPE compared to various LC polyesters

Based on the previous fluorescence studies for various LC polyesters [7–11], fluorescence peak wavelength of a typical LC polyester (PET40/OBA60, where PET is polyethylene terephthalate and OBA is oxybenzoate) shifts to a longer wavelength from the glass transition temperature (T_g) to the LC phase transition temperature. This is because the obvious increase in parallel alignment between terephthalate and OBA moieties induces the electronic distribution to be more polarized [7]. For LC polyesters with mesogenic 4,4′-dihydroxybiphenyl moieties (PB-*n*), fluorescence peak wavelengths of PB-*n* also shift to longer wavelengths during heating. This is because the abrupt decrease in layer spacing from crystalline phase to LC phase also induces the obvious decrease in degree of overlap between mesogenic biphenyl moieties from a fully-overlapping one to a partially-overlapping one with increasing interaction between aromatic and ester moieties [9,10]. On the other hand, fluorescence peak wavelengths of LC polyesters with mesogenic 4,4′-biphenyldicarboxylate moieties (BB-*n*, $n = 5,6$) shift to shorter wavelengths during heating. The BB-6 shows crystal–crystal transition at 212°C, where the crystalline phases show the same herring-bone packing pattern, and the high-temperature crystalline phase shows lower density and a looser packing than the low-temperature crystalline phase does, leading to the shift of fluorescence to a shorter wavelength [11]. Therefore, the shift of fluorescence to a shorter wavelength was demonstrated to be due to the increase in thermal fluctuation with increasing temperature for the system with the same packing pattern. However, in this study, fluorescence peak wavelength of an LC polyimide (P-11TPE) with strong charge-transfer interaction shifts slightly to a shorter wavelength below T_g and shifts abruptly to a longer wavelength around crystallization (an obvious change in molecular arrangement between mesogenic moieties as in PET40/OBA60 and PB-*n*), then shifts gradually to shorter wavelength again during the change in several similar orthorombic crystalline phases and the LC phase (phase transitions of several crystalline phases as in BB-*n*). This shows that the fluorescence peak wavelengths of intermolecular complexes of these LCPs shift to longer wavelengths in the case of obvious change in molecular arrangement and shift to shorter wavelengths in the case of almost identical packing pattern with increasing thermal fluctuation.

For the change in fluorescence intensity of various LC polyesters (PET40/OBA60, PB-*n*, and BB-*n*) [7–11] and P-11TPE during phase transition, except for the slight increase around annealing temperature of PET40/OBA60, all of their temperature dependence of fluorescence intensity decreases gradually and shows breaks around the phase transition temperatures. This implies that the deactivation processes of fluorescence intensity for these LCPs are different in various phases. In addition, the characteristic change in fluorescence lifetime of P-11TPE during phase transition is observed and indicates the difference in radiationless deactivation process in various phases. According to the fluorescence studies of the above LCPs, the formation of an intermolecular complex between mesogenic moieties has been proved to show an essential relationship with molecular arrangement and exhibits various patterns of change in fluorescence peak wavelength and fluorescence lifetime during the phase transition processes.

4. Conclusions

The changes in intermolecular complex formation of an LC polyimide (P-11TPE) with mesogenic terphenyldiimide moieties during phase transitions have been studied principally with steady-state fluorescence and fluorescence lifetime measurements. The formation of an intermolecular ground-state complex between two terphenyldiimide moieties in P-11TPE was ascertained by comparing the fluorescence spectra and fluorescence lifetimes between P-11TPE and the model compound (11TPI). Temperature dependences of fluorescence peak wavelength, fluorescence intensity, and fluorescnece lifetime show obvious changes around phase transition temperatures. This indicates that the temperature dependences of the changes in the nature and number of intermolecular complexes and radiationless deactivation processes are different in various phases. Fluorescence method was proved to be an effective tool for elucidating the formation of intermolecular complexes between mesogenic moieties and showing the various patterns of the change in molecular interaction during phase transition processes for LCP.

Acknowledgements

H.W.H. is greatly indebted to the JSPS Research Fellowship for Young Scientists for supporting his research and Ph.D study in the University of Tokyo.

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