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Fluorescence Study on Intermolecular Interactions between Mesogenic Biphenyl Moieties of a Thermotropic Liquid-Crystalline Polyester (PB-10)

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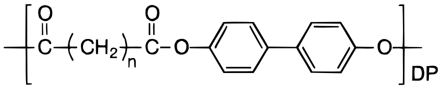
ABSTRACT: By applying fluorescence together with DSC and WAXD, structure analysis for a thermotropic liquid-crystalline (LC) polyester (PB-10), prepared from 4,4′-dihydroxybiphenyl and sebacic acid, containing 10 methylene units, was carried out. The PB-10 shows two enantiotropic transitions: One is the crystal−smectic H transition at 207 °C and the other the smectic H−isotropic phase transition at 257 °C. By measuring fluorescence spectra at 25−283 °C as well as those of diacetoxybiphenyl and biphenyl as model compounds, a high excitation wavelength dependence of various intermolecular ground-state complexes was found to depend on different degrees of overlap between mesogenic biphenyl moieties. Fluorescence spectra can be divided into three groups according to excitation wavelength: monomer fluorescence of biphenyl group excited at 260−300 nm (emission peak at 343 nm), fluorescence from intermolecular ground-state complexes excited at 320−360 nm, and fluorescence excited at 380−400 nm. The fluorescence peak wavelength excited at 320 nm shifts from 365 to 429 nm during heating. This is due to the change of molecular interactions between mesogenic moieties from the interaction between two fully overlapping biphenyl groups to that between a biphenyl and an ester moiety. Temperature dependence of the fluorescence peak wavelength excited at 320 nm and Arrhenius-type plots of fluorescence intensity excited at various wavelengths show a common break at 175 °C, a temperature a little lower than the crystal−smectic H transition temperature. This suggests that the phase transition starts initially from the local change in microstructure (intermolecular interaction between mesogenic moieties) and then extends to a change in macrostructure. Fluorescence is an effective tool for providing molecular level information on LC polymers.

Introduction

Liquid-crystalline polymers (LCPs) have been attracting much attention because of scientific interest and numerous technological applications. From a scientific point of view, macro- and microstructures of LCPs have been studied by numerous scientists.[1] From a technological point of view, LCPs are useful for various applications such as high-tensile materials, displays, and optical storage devices, etc. It is therefore important to analyze the macro- and microstructures to control physical properties of LCPs.

There are a variety of analytical methods to analyze the macro- and microstructures of LCPs. From a macroscopic point of view, differential scanning calorimetry (DSC) can provide information of thermal properties and polarizing microscope can distinguish the mesophase of LCPs. From a microscopic point of view, X-ray diffraction can provide information concerning the arrangement and mode of packing of molecules and the types of order present in a mesophase of LCPs. Specific interactions, e.g., charge transfer interaction, hydrogen bonding, and ionic bonding, are important factors affecting physical properties of polymers. For LCPs, the intra- and intermolecular interactions between mesogenic moieties may play important roles in determining the LCP properties. Hence, in order to elucidate the microstructure of LCPs, especially the intermolecular interaction between mesogenic moieties, we have used fluorescence to study the microstructure of LCPs.[2−5]

The synthesis and properties of thermotropic liquid-crystalline polyester series prepared from 4,4′-dihydroxybiphenyl and dibasic acids containing 5−12 methylene units have been already studied by Watanabe et al.[6−8] The repeating units of these LCPs can be represented as follows:



We designate these polymers by the letters PB followed by the number, *n*, of methylene units in the dibasic acid. Recently, the synthesis of these LCP series has been extended to the number of methylene units up to 22.[9] In the present paper, fluorescence together with wide-angle X-ray diffraction (WAXD) and DSC is applied to investigate the microstructure of PB-10 and intermolecular interaction between mesogenic moieties during the phase transition of PB-10.

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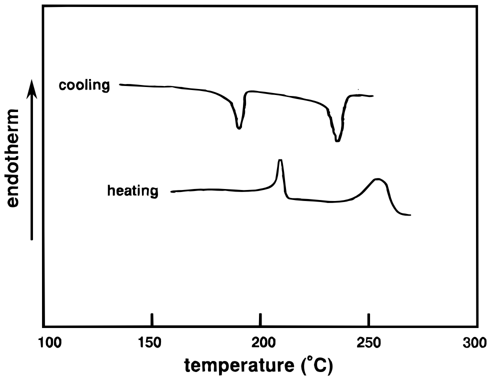

Figure 1. DSC first cooling and second heating curves for PB-10.

Experimental Section

Materials. PB-10 was prepared by melt transesterification using equimolar amounts of 4,4′-diacetoxybiphenyl and sebacic acid as reported previously.[6] In an effort to provide a common thermal prehistory, all the samples were placed on a quartz plate, annealed at isotropic temperature (270 °C) for 10 min, and then cooled to room temperature before fluorescence measurements. Two model compounds, diacetoxybiphenyl (DABP) and biphenyl, were purchased from Tokyo-Kasei Co. Ltd. and recrystallized from methanol before fluorescence measurements. Acetonitrile (spectroscopic grade) was purchased from Wako Pure Chemical Industries, Ltd, and used directly without purification.

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

WAXD measurements were carried out with a Rigaku-Denki RU-200 X-ray generator system equipped with a flat-plate camera using nickel-filtered Cu Kα radiation. The distance from the sample to the film was determined by using silicon powder. The sample temperature was controlled by a Mettler FP-80 hot stage with a FP-82 central processor.

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 10^{-4} M solution of model compounds were measured by using a 1-cm quartz cell in side-face detection. For the crystal of model compounds, the fluorescence spectra and its excitation spectra were measured at the surface of a 1-cm quartz cell. Those for the LCPs were measured in a front-face arrangement to minimize the self-absorption. The temperature of the LCPs was controlled by means of an Alpha Engineering thermostat coupled with a temperature-controlling unit.

Results and Discussion

Thermal Properties. In previous papers,[6,7] we have shown that the mesophase of PB-*n* series with an even number of methylene units in the dibasic acid is a smectic H type (S_H) and shows a low-temperature K crystalline phase. Typical examples of the first cooling and second heating DSC thermograms for PB-10 are illustrated in Figure 1. One can observe two endothermic peaks at 207 and 257 °C, which can be regarded as a K$-$S$_H$ transition and a S$_H$$-$isotropic transition, respectively.

Layer Spacing Change during Heating. The temperature dependence of some selected spacings for PB-10 is depicted in Figure 2. As shown in Figure 2, the layer spacing of the K phase for PB-10 (the top one) does not change before the LC transition temperature and decreases abruptly after the LC transition. Such an abrupt decrease of the layer spacing at K$-$S$_H$ transition has been commonly observed in other PB-*n* polyesters.[7]

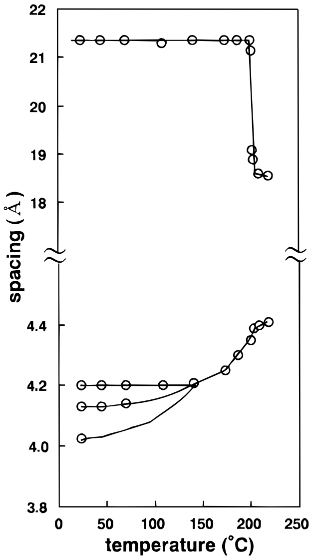

Figure 2. Temperature dependence of some selected spacings for PB-10.

On the basis of the WAXD results, we proposed the approximate molecular arrangements for K and S_H phases.[7] The main difference of the approximate molecular arrangement between K and S_H phases is that the mesogenic moieties overlap fully in the K phase but the mesogenic moieties overlap only partially in the S_H phase (see Figure 12 of ref 7). As in our previous studies[2−4] on studying the microstructure of LCPs by fluorescence, we now use fluorescence to investigate the change in intermolecular interaction between mesogenic moieties of PB-10 during the heating process from K to isotropic phase. First, it is necessary to investigate the fluorescence of the K phase, i.e., the fluorescence of two fully overlapping biphenyl groups.

Fluorescence from Fully Overlapping Biphenyl Groups by Using Model Compounds. The crystal structure of biphenyl has been studied in detail by X-ray diffraction and is known to have a fully overlapping molecular arrangement of biphenyl molecules.[10−14] We use DABP (for biphenyl mesogenic moiety) and biphenyl (for comparison with DABP) as model compounds to investigate the fluorescence of two fully overlapping biphenyl groups. Figure 3 shows the fluorescence spectra and its excitation spectra for DABP and biphenyl in their crystal state (a and b) and in dilute solution (a* and b*).

According to Figure 3, we summarize the fluorescence peak wavelength and its excitation wavelength for DABP and biphenyl in Table 1. Table 1 indicates that DABP and biphenyl in dilute solutions (10^{-4} M) show a monomer fluorescence at 323 and 315 nm, respectively. DABP crystal shows a fluorescence peak at 362 nm, besides the monomer fluorescence at 322 nm. Similarly, the biphenyl crystal also shows a fluorescence at 360 nm, besides the monomer fluorescence at 321 nm. This indicates that the fluorescence at about 360 nm is due to two fully overlapping biphenyl groups. In addition, although the fluorescence excitation spectra for DABP (a_1' and a_2' in Figure 3a) and biphenyl crystal (b_1' and b_2' in Figure 3b) are all distorted by the monomer self-absorption and the multiscattering effect, shapes of their monomer fluorescence excitation spectra (a_1' and b_1') are not in accord with those monitored at 360 nm (a_2' and b_2'). This indicates that the fluorescence at about 360

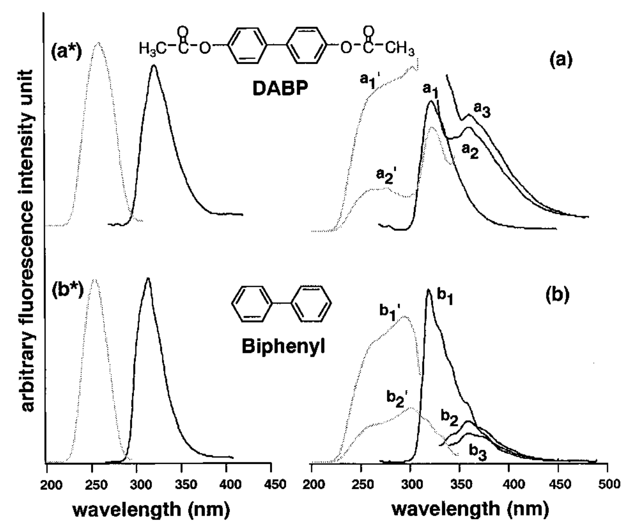

Figure 3. Fluorescence (black curves) and its excitation spectra (gray curves) for (a) DABP crystal, (a*) DABP in 10^{-4} M acetonitrile solution, (b) biphenyl crystal, and (b*) biphenyl in 10^{-4} M acetonitrile solution. (a) a_1, a_2, and a_3 are the fluorescence spectra excited at 260, 320, and 330 nm, respectively; a_1' and a_2' are the fluorescence excitation spectra monitored at 322 and 360 nm, respectively. (a*) The fluorescence spectrum is excited at 260 nm, and its excitation spectrum is monitored at 323 nm. (b) b_1, b_2, and b_3 are the fluorescence spectra excited at 260, 320, and 330 nm, respectively; b_1' and b_2' are the fluorescence excitation spectra monitored at 321 and 360 nm. (b*) The fluorescence spectrum is excited at 255 nm, and its excitation spectrum is monitored at 315 nm.

nm for both DABP and biphenyl crystal does not originate from an excimer but is due to the emission from an intermolecular ground-state complex. On the basis of the above fluorescence properties of DABP and biphenyl, we conclude that the fluorescence of two fully overlapping biphenyl groups at about 360 nm is due to an intermolecular ground-state complex.

Fluorescence of PB-10 in the Crystalline Phase and Its Excitation Wavelength Dependence. Figure 4 shows the fluorescence (right part) and its excitation spectra (left part) of PB-10 at 26 °C excited or monitored at various wavelengths as 3D plots (intensity vs excitation and emission wavelengths). At first, we refer to the fluorescence spectra excited at various excitation wavelengths (right part of Figure 4). The fluorescence at 343 nm (excited at 260 and 300 nm; A and a) is independent of excitation wavelength, but the fluorescence at 365−469 nm (excited at 320−400 nm; b−i) depends strongly on excitation wavelength. The fluorescence at 343 nm of PB-10 (A and a) shows a longer wavelength than the monomer fluorescence of DABP crystal (322 nm). This would be due to the electronic distribution of biphenyl group which is affected more easily by the neighboring molecules in the polymer than in low molecular weight crystal owing to the main-chain stiffness of the polymer. This provides a more stable excited state to emit at a longer wavelength. Furthermore, the fluorescence at 343 nm does not show excitation wavelength dependence as other fluorescence at 365−469 nm. Consequently, we conclude that the fluorescence at 343 nm is the monomer fluorescence of PB-10.

On the other hand, the shapes of fluorescence excitation spectra (left part of Figure 4) for the fluorescence at 365−469 nm (b′ and c′) disagree with those for the monomer (a′). This indicates that the fluorescence at 365−469 nm is not due to excimer or exciplex but to various intermolecular ground-state complexes. Since we concluded that the fluorescence of two fully overlapping biphenyl groups is at about 360 nm, we suggest that the intermolecular ground-state complexes at 365−469 nm are due to the approximate molecular arrangements of mesogenic moieties illustrated at the bottom of Figure 4. In other words, the intermolecular ground-state complexes emitting at a wavelength longer than 365 nm are formed by the molecular arrangements with less overlapping, which induce a stronger intermolecular interaction (electronic distribution change) between the ester and biphenyl moieties than those between two fully overlapping biphenyl segments.

To the best of our knowledge, this kind of strong excitation wavelength dependence on fluorescence in the crystalline phase of PB-10 is an uncommon phenomenon in polymer fluorescence. This may suggest that the WAXD method only provides the average molecular arrangements of PB-10. In fact, by using fluorescence, the existence of various local molecular arrangements is observed. Only a few papers[15,16] have discussed the excitation wavelength dependence of fluorescence for chromophores in amorphous polymer solids. This suggests that fluorescence can distinguish various aggregation structures corresponding to different degrees of overlap between mesogenic moieties, which cannot be detected by other methods.

Change in Fluorescence Peak Wavelength during Heating. The fluorescence spectra of PB-10 excited at various wavelengths during heating are depicted in Figure 5. The wavelength of fluorescence peak excited at 320 nm (b) shifts gradually from 365 (1) to 389 (4) nm below isotropic transition temperature. This is because the fully overlapping molecular arrangement at room temperature changes gradually to partially overlapping molecular arrangement with increasing temperature, namely, the main intermolecular interaction between mesogenic moieties is changed from the one between two fully overlapping biphenyl groups to the one between a biphenyl moiety and an ester moiety, altering the electronic distribution between mesogenic moieties to strengthen molecular interaction leading to a red-shifted fluorescence. Correspondingly, it is not surprising that other fluorescence peak wavelengths related to the various degrees of overlap between two biphenyl groups (c−f) do not shift as much as for two fully overlapping biphenyl groups (b), owing to the molecular arrangement with a smaller overlap. The monomer fluorescence peak at 343 nm (a) and emission at 453−469 nm (g−i) are observed invariably during heating. It is reasonable that the monomer fluorescence peak does not shift during heating, considering the consistency of the electronic distribution in an independent mesogenic moiety. Unfortunately, it is difficult to confirm the origin of fluorescence at 453−469 nm, which may be due to the larger aggregate domain or the much stronger molecular interaction between the biphenyl and ester moieties.

Figure 6 shows the fluorescence excitation spectra during heating. In spite of the distortion due to monomer self-absorption and multiscattering effects, the fluorescence excitation spectra monitored at 450 nm (c′; solid curves) show a broad shoulder around 390 nm during heating. This indicates that the fluorescent species at longer wavelength become the main fluorescent species at high temperatures and that the change in fluorescence peak wavelength is not only due to the

Table 1. Fluorescence Peak Wavelengths and Their Excitation Wavelength for Model Compounds

compd	*C* (M)	excitation wavelength (nm)	fluorescence peak (nm)	fluorescent species
DABP	10^{-4}	260	323	monomer
	crystal	260	322	monomer
	crystal	320, 330	362	intermolecular ground-state complex
biphenyl	10^{-4}	255	315	monomer
	crystal	260	321	monomer
	crystal	320, 330	360	intermolecular ground-state complex

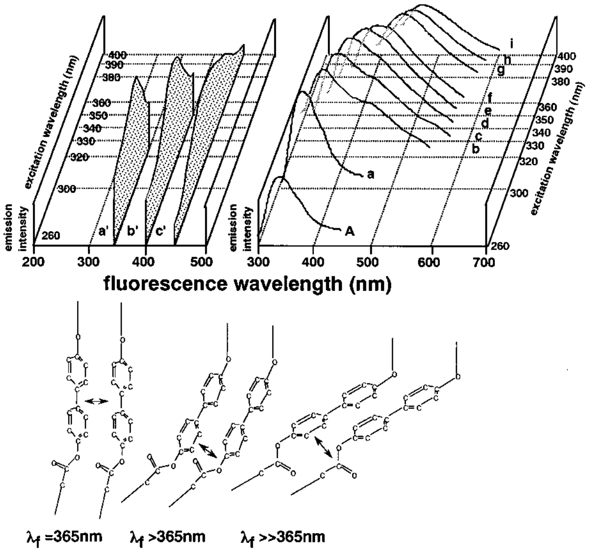

Figure 4. Fluorescence (right) and its excitation spectra (left) for PB-10 cooled from 270 °C and measured at 26 °C. A and a–i are the fluorescence spectra excited at 260, 300, 320, 330, 340, 350, 360, 380, 390, and 400 nm, respectively. a′–c′ are the fluorescence excitation spectra monitored at 343, 400, and 450 nm, respectively.

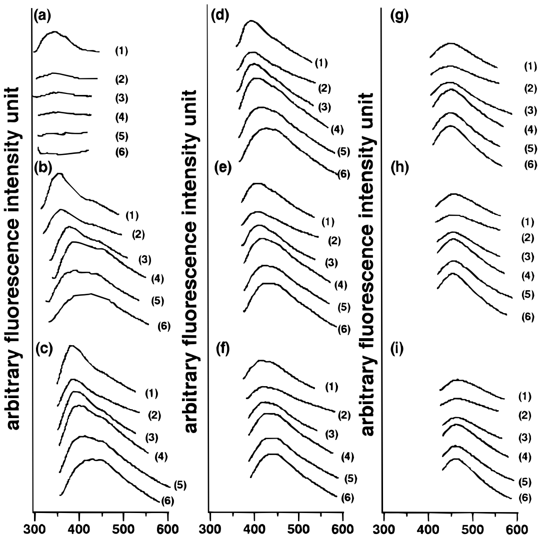

Figure 5. Typical fluorescence spectra excited at 300 (a), 320 (b), 330 (c), 340 (d), 350 (e), 360 (f), 380 (g), 390 (h), and 400 (i) nm at various phases. K phase: 97 (1) and 175 (2) °C. S_H phase: 215 (3) and 243 (4) °C. Isotropic phase: 266 (5) and 283 (6) °C.

change in the excited state but also to the change in the ground state.

The changes in fluorescence peak wavelengths excited at various excitation wavelengths during heating are plotted in Figure 7. The peak wavelength change for fluorescence excited at 320 nm (◆) is the largest one. This is reasonable since two fully overlapping biphenyl groups at room temperature change interaction structure most clearly during heating. The plot shows two breaks at 175 and 253 °C; the temperature dependence of the molecular interaction changes first at 175 °C, a temperature significantly lower than the K–S_H transition temperature measured by DSC and WAXD (207 °C). This shows that the temperature effect initially makes the phase transition start in a local microstructure change (molecular interaction between mesogenic moieties), and then it extends to the macrostructure change (the entire phase transition). This kind of microscopic pretransition was also observed in the fluorescence intensity change of PET40/OBA60 (Figure 7 of ref 2). The rate of the change in molecular interaction changes again at 253 °C, which is near the S_H–isotropic transition temperature (257 °C). Conse-

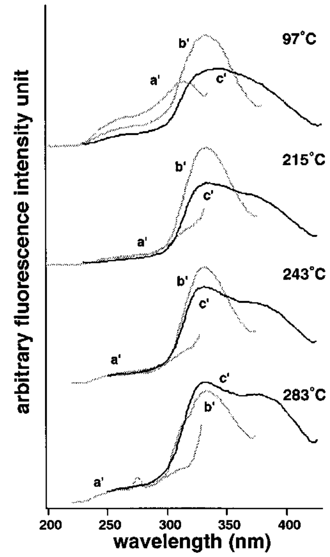

Figure 6. Typical fluorescence excitation spectra at various temperatures. a′–c′ are the fluorescence excitation spectra monitored at 343, 400, and 450 nm, respectively.

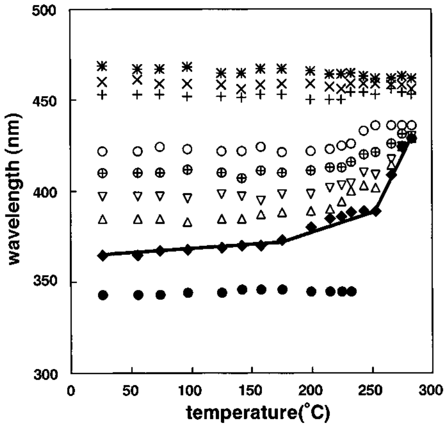

Figure 7. Temperature dependence of the fluorescence peak wavelengths excited at various excitation wavelengths during heating: (●) 300, (◆) 320, (△) 330, (▽) 340, (⊕) 350, (○) 360, (+) 380, (×) 390, and (*) 400 nm.

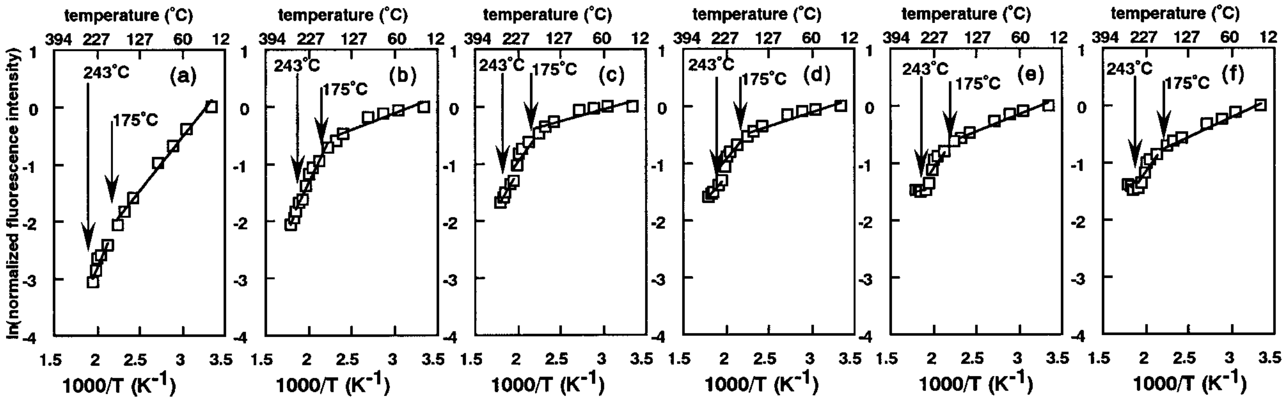

Figure 8. Arrhenius-type plots for the change in fluorescence intensity of monomer and various intermolecular ground-state complexes during heating: (a) 343 nm (excited at 300 nm), (b) 365 nm (excited at 320 nm), (c) 385 nm (excited at 330 nm), (d) 397 nm (excited at 340 nm), (e) 410 nm (excited at 350 nm), and (f) 422 nm (excited at 360 nm).

quently, this indicates that that the rate of change in molecular interaction for various phases are different. Above the isotropic transition temperature, except for the monomer fluorescence (●) and fluorescence at 453–469 nm (+, ×, and *), the fluorescence peak wavelengths related to the various degrees of overlap between two biphenyl groups (◆, △, ▽, ⊕, and ○) show only a broad structureless emission peak centered at 429 nm. Thus, only one kind of steady-state molecular interaction between mesogenic moieties exists in the isotropic phase. This is reasonable because of the mobile surroundings around chromophores in the isotropic phase at high temperatures.

Change in Fluorescence Intensity during Heating. In order to investigate the deactivation process of monomer and various intermolecular ground-state complexes during heating, we present in Figure 8 Arrhenius-type plots for the change in fluorescence intensity during heating. The fluorescence intensity decreases with the increasing temperature owing to the increase in radiationless transition, showing two breaks at 175 and 243 °C in accord with the change in peak wavelength of fluorescence excited at 320 nm shown in Figure 7. This suggests that the deactivation processes of fluorescent species are different in various phases. However, the temperature dependence of fluorescence intensity is affected by both the activation energy for radiationless transition and the change in the number of various intermolecular ground-state complexes. For example, the large temperature dependence of monomer fluorescence intensity (a) may be affected also by the decrease in the number of species emitting monomer fluorescence with increasing temperature.

Ikeda et al.[17–19] studied the relationship between the excimer formation and phase structure of main-chain and side-chain LCPs. We first reported the relationship between the intermolecular ground-state complex formation and microstructure change in a thermotropic liquid–crystalline polyester and showed that the change in fluorescence peak wavelength during heating is caused only by the change in intermolecular interaction between mesogenic moieties during excited state and has no relation to that in the ground state.[3] However, a strong dependence of fluorescence spectra of intermolecular ground-state complexes on excitation wavelength, which is due to the difference in the overlapping structure, has been observed for the first time in the present paper. Moreover, we have found that the rate of the change in molecular interaction between mesogenic biphenyl moieties and deactivation processes of the fluorescent species is different in various phases. Intermolecular interaction between mesogenic moieties has proved to play a pivotal role in the macro- and microstructures of LCPs.

Conclusions

By introducing fluorescence together with DSC and WAXD, structure analysis, particularly on the change in intermolecular interaction between mesogenic moieties, for a thermotropic liquid-crystalline polyester (PB-10) was carried out from a microscopic viewpoint. As in our previous papers,[6–8] DSC and WAXD were used to examine the thermal properties and layer-spacing change, respectively. The formation of various intermolecular ground-state complexes owing to their different degree of overlap between mesogenic biphenyl moieties was ascertained by fluorescence. The increase in temperature makes the interaction of these intermolecular ground-state complexes change and indicates that the phase transition starts initially from the local change in microstructure (intermolecular interaction between mesogenic moieties) and then extends to a change in macrostructure. Different deactivation processes of intermolecular ground-state complexes during heating are distinguished by the temperature dependence of fluorescence intensity.

Work is presently underway to compare the fluorescent properties of PB-*n* ($n = 8-22$) with the results of DSC and WAXD. It is expected that fluorescence will also shed light on the difference in microstructure of PB-*n* with various spacer lengths.

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