# Rigid-Rod Polyesters with Flexible Side Chains Based on 1,4-Dialkyl Esters of Pyromellitic Acid and 4,4′-Biphenol. 7. Fluorescence Studies on Crystalline and Liquid Crystalline Layered Phases over a Wide Range of Temperatures

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ABSTRACT: Rigid-rod polyesters with flexible side chains denoted as B-C*n* form two types of layered crystals and two types of layered mesophases. These layered phases are characterized by a layered structure, in which the aromatic main chains are paced into a layer with the side chains occupying the space between the layers. The detailed aggregated structures for these two crystalline phases were studied by fluorescence spectroscopy, from which it was found that the ground-state charge-transfer complexes are formed between the biphenyl and pyromellitic moieties in the adjacent main chains and that these two moieties have an alternating lateral alignment inside a layer. Two layered crystals, K1 and K2, show charge-transfer fluorescence (475 and 505 nm) and its excitation spectra (400 and 425 nm) in different wavelengths, respectively. This difference in wavelengths is related to the difference in lateral packing distances (4.6 Å for K1 and 3.45 Å for K2 crystals) and suggested to be due to the distance between the electron-donating and -accepting units in the adjacent chains. In the isotropic phase, the charge-transfer bands were also observed. This result means that the isotropic state in this polymeric system can be defined by the state that a layered segregation is maintained, but the molecular ordering and the interlayer correlation are lost. It is well-known that the driving force of the adoption for layered structures is a segregation of aliphatic and aromatic domains. We have demonstrated here, moreover, that a charge-transfer interaction between the electron-donating and -accepting units in the neighboring main chains contributes to the organization of phase structures and spatial arrangements.

## Introduction

There has been a great deal of interest in rigid-rod polyesters with flexible side chains in the past decade or since the discovery of their capability to form thermotropic liquid crystalline phases.[1−29] Their liquid crystalline states have been characterized by a layered segregated structure in which the rigid-rod main chains are laterally packed into monolayer with the flexible side chains occupying the space between the layers. It has been postulated that the driving force for the adoption of such a structure is a segregation of the aliphatic and aromatic domains. In these layered structures, the liquid crystallinity is the result of a partial or total lack of positional order with respect to the main chain packing within the layers and also by the fluidlike disordered alkyl side chains between the layers. Moreover, these layered liquid crystalline phases are classified on the basis of the positional order with respect to the main chain packing within the layers.[22]

In the previous papers we have also prepared several new rigid-rod polyesters with long alkyl side chains based on 1,4-dialkyl esters of pyromellitic acid with 4,4′-biphenol (B-C*n*) and *p*-hydroquinone (H-C*n*), where *n* refers to the number of carbon atoms in the alkyl side chain.[10,11,22] The H-C*n* polyesters with alkyl side chains longer than 10 carbon atoms form highly ordered thermotropic mesophases with a layered structure common to those observed for rigid-rod polyesters with long flexible side chains.[11] On the other hand, the B-C*n* polyesters with $n = 14$, 16, and 18 showed two novel thermotropic mesophases with the nature of a layered structure depending on temperature.[22] These two structures of the mesophases are different from the layered structure observed for the B-C*n* polyesters in crystals with respect to the degree of ordering and the packing arrangement of the chains within the layers. In a layered structure of the mesophases, it has been clarified from the X-ray diffraction pattern that the aromatic main chains are in an extended form (repeating length of 16.6 Å) and are packed into a layered structure with positional order parallel to their long axes. We further found that the average lateral packing distance of main chains within a layer is 3.45 Å, indicating that the aromatic main chains are closely associated with each other.[22] This implies that specific interaction or association may exist between the pyromellitic ester groups and biphenyl groups which are included in the repeating units of the main chains.

Several recent studies[30−37] have shown that fluorescence measurements can be a valuable tool in elucidating the state of intra- and intermolecular aggregation of aromatic polymers in solid and liquid crystalline phases. The value of this technique lies in the fact that fluorescence measurements are sensitive to interactions between neighboring chromophores, which in turn can

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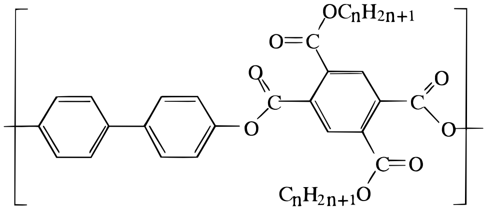
be translated to give some information concerning the spatial geometry of these groups. Our preliminary study on a B-C16 polyester[13] has shown the existence of charge-transfer fluorescence between pyromellitic moieties and biphenyl moieties. In the present study, we aim to clarify the intermolecular aggregation in the layered crystals and mesophases of B-C*n* ($n = 6$, 12, 14, 16, and 18) by examining charge-transfer fluorescence spectra of these polyesters and comparing them with the results of wide-angle X-ray diffraction (WAXD) measurements. Moreover, we demonstrate the change in the intermolecular aggregation between different layered structures during the phase transitions by using fluorescence spectroscopy at 25−240 °C.



B-Cn (n = 6, 12, 14, 16, and 18)

## Experimental Section

The preparation of B-C*n* polyesters (*n* is the number of carbon atoms in the alkyl side chain) has been described in previous papers.[10,11] Here the B-C14 polyester is mainly employed.

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

## Results and Discussion

**Thermotropic Phase Behavior and Phase Structure of the B-C*n* Polyesters.** In previous studies,[10,22] we reported that the B-C*n* polyesters form two layered crystals (K1 and K2) and two liquid crystalline phases (LC-1 and LC-2). The phase behavior depends on the side chain length as depicted in Figure 1.

In the layered K1 and K2 crystalline phases, the aromatic main chains are in a fully extended conformation with a repeating length of 16.6 Å, and these are regularly packed within a layer. In addition, the side chains are also in a crystalline state between the layers. The X-ray pattern is indicative of a crystal structure with three-dimensional order, which demands that the positional correlation between adjacent layers is maintained through the side chain crystals. Thus, the crystal structure is likely built up by a close coupling of the main chain crystals and the side chain crystals. It is interesting to note that the main chains in the K1 and K2 crystals are packed in a different manner. For the K1 crystal, which is formed from the B-C*n* polyesters with side chains equal to and shorter than $n = 12$, the lateral packing distance of the main chains within a layer is 4.6 Å, but this reduces to 3.45 Å for the K2 crystal in the B-C*n* polyesters with side chains equal to and longer than $n = 14$. The packing distance of 4.6 Å in the K1 crystal is reasonable for the main chains in a stable twisted conformation. In contrast, the short spacing of 3.45 Å in the K2 crystal indicates an unusually dense packing of the main chains that requires a conformation in which all the phenyl rings adopt a coplanar arrangement. Actually, we clarified the conformation of B-C*n* polyesters by the solid-state $^{13}$C NMR method.[23]

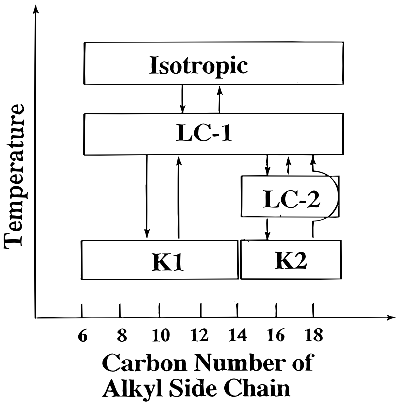


**Figure 1.** Schematic illustration of thermotropic phase behavior in B-C*n* polyesters.

The LC-2 phase, the lower temperature mesophase, also has a layered segregated structure similar to that of the crystalline phase although its fundamental structure is remarkably altered in several aspects from the crystal structure. The main chains are still in an elongated conformation (a repeating length of 16.6 Å) as in the crystalline phase, but they are packed into a layer having positional order only along the chain axis but not in the lateral direction. The side chains placed between the layers are in a molten state, which gives rise to the liquid crystalline fluidity of the phase. This type of liquid crystalline phase appears for the cooling process of B-C*n* polyesters in which the alkyl side chains are equal to and longer than $n = 14$ (see Figure 2).

The LC-1 phase, a higher temperature mesophase observed for all specimens, displays a nematic-like optical texture, but a classic nematic phase cannot be postulated because it still exhibits a lateral packing spacing as large as that in the LC-2 phase. A biaxial nematic phase has been tentatively proposed such that the layers are retained, but there are frequent irregularities in their packing.

**Fluorescence Study of B-C*n* Polyesters. Origin of Fluorescence.** Initially, the excitation and emission spectra of fluorescence were measured for THF solutions of the B-C14 polyester as a function of concentration. The results are shown in Figure 3. The fluorescence spectrum for the dilute solution of the B-C14 polyester at the concentration of $1 \times 10^{-4}$ M (mol repeating unit/L) shows a structured band with a maximum at 341 nm (excitation wavelength at 295 nm). This band can be attributed to an overlap of monomer fluorescence bands of both biphenyl and pyromellitic ester moieties, since the fluorescence for the biphenyl moiety may appear about 330 nm (excitated at 264 nm) as has been deduced from the fluorescence spectrum for diacetoxybiphenyl, and the fluorescence for the pyromellitic ester moiety may appear at 351 nm (excitated at 268 nm) as measured for the 1,4-ditetradecyl ester of pyromellitic acid (see curves a and b in Figure 4).

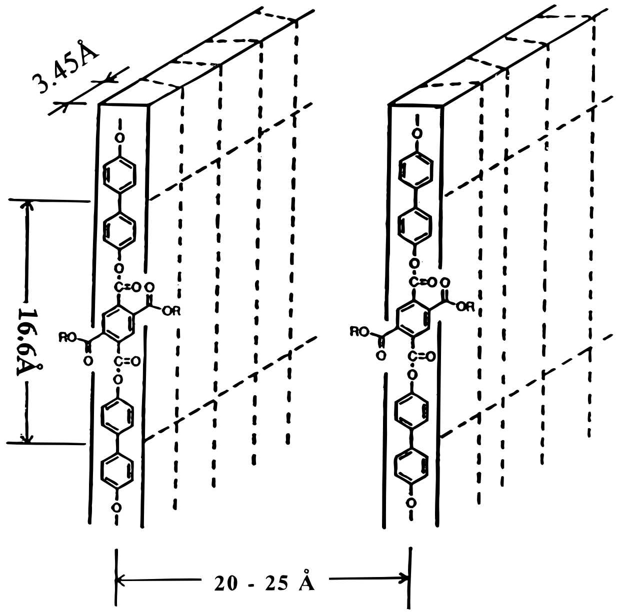


**Figure 2.** A proposed layered structure for the liquid crystalline phase of B-C*n* polyesters with $n = 14$, 16, and 18. In this layered structure, the aromatic main chains in the extended form pack into layers with positional order only in the lateral direction, and the aliphatic side chains in the disordered form occupy the space between the layers.

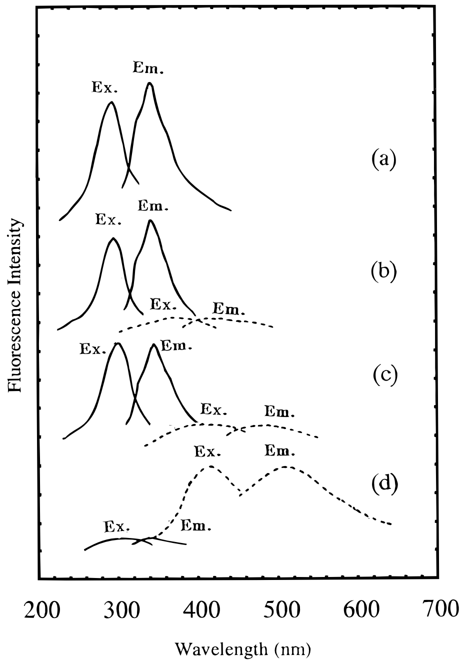


**Figure 3.** Fluorescence and its excitation spectra of B-C14 in chloroform solutions at concentrations of $1 \times 10^{-4}$, $1 \times 10^{-3}$, $1 \times 10^{-2}$, and $1 \times 10^{-1}$ M. A pair of fluorescence and excitation spectra are given by solid lines or dashed lines.

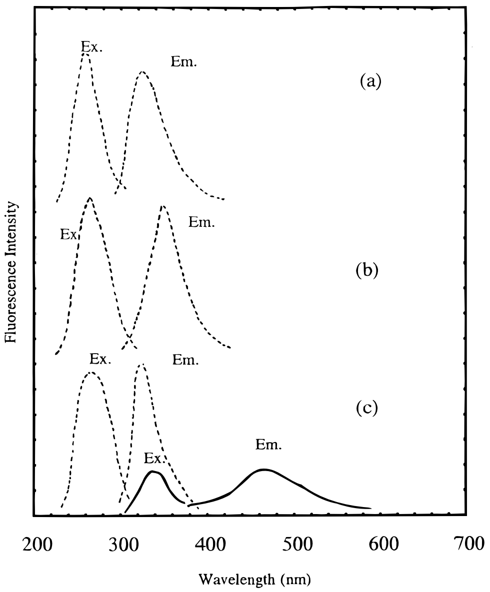


**Figure 4.** Fluorescence and its excitation spectra for (a) diacetoxybiphenyl, (b) 1,4-ditetradecylpyromellitic acid, and (c) their equimolar mixture in $1 \times 10^{-1}$ M chloroform solution.

The increase in the concentration of B-C14 results in a profound change in both the excitation and emission spectra. The new broad excitation and emission bands (given by dashed curves) appear at longer wavelengths with the increase in the concentration from $1 \times 10^{-4}$ to $1 \times 10^{-1}$ M. Finally, they become predominant at concentrations above $1 \times 10^{-1}$ M; an excitation at 410 nm gives rise to a fluorescence band at 500 nm. Further, we found that these are structureless. This result simply indicates that the increase in concentration of B-C14 causes a change in the electronic state of the biphenyl and pyromellitic ester chromophores. This would be due to an aggregation process that results in a ground-state complex of charge-transfer nature between the donor and acceptor groups. With respect to the B-C*n* polyesters, there exists a donor group (biphenyl moiety) and an acceptor group (pyromellitic ester moiety) within an aromatic main chain; thus, it can be predicted that a charge-transfer complex is formed between these two units when they are in a suitable geometry and at a suitable distance.

To confirm this suggestion, the fluorescence spectrum for a mixture of two model compounds, 4,4′-diacetoxybiphenyl and 1,4-ditetradecyl ester of pyromellitic acid, was examined at a concentration of $1 \times 10^{-1}$ M. Figure 4 shows the fluorescence spectra for the individual compounds (curve a and b) and their equimolar mixture (curve c). In addition, the mixture showed a structureless fluorescence band with a maximum at 470 nm which is similar to that observed in the concentrated solution of B-C14 and is completely absent in the spectra of the individual compounds. This observation supports the proposal that a ground-state molecular complex between biphenyl and pyromellitic ester groups exists in the concentrated solutions of B-C14, although at this time we can give no detailed structure of the interacting state in the concentrated solutions.

**Aggregated Structure Proposed by Fluorescence Study.** The fluorescence spectra were measured for the layered liquid crystalline phase of B-C14 as shown in Figure 5. It is obvious that the fluorescence behavior with a peak at 505 nm and an excitation peak 425 nm is almost similar to that observed in the concentrated solution of $1 \times 10^{-1}$ M (curve d of Figure 3), again indicating that a charge-transfer complex is formed between two components: biphenyl and pyromellitic ester moieties. The absorption spectrum of the B-C14 cast film is shown in Figure 6 (solid line). By comparing it to the absorption spectrum for B-C14 in dilute solution (dashed line), a marked tailing of absorption for the longer wavelength region is observed for the B-C14 film. This difference at the longer wavelength is considered to be due to the ground-state aggregation.[38] These observations suggest that the main chains within a

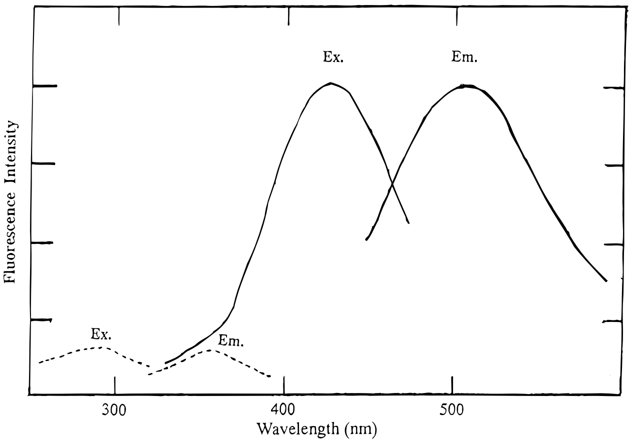


**Figure 5.** Fluorescence and its excitation spectra for the layered liquid crystalline phase of B-C14 polyester observed at 124 °C between quartz slides. The sample thickness is about 0.5 mm.

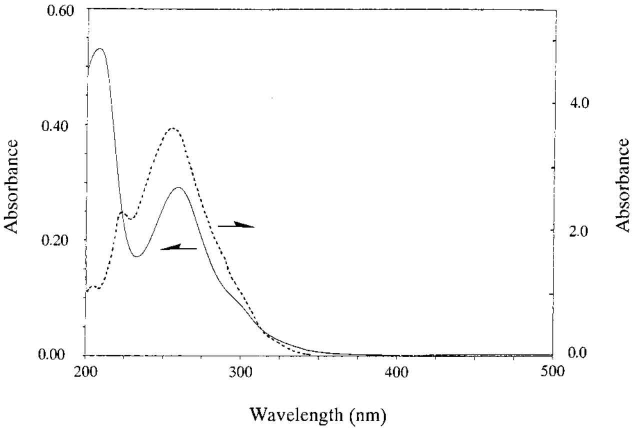


**Figure 6.** Absorption spectra of B-C14 cast film (solid line) and B-C14 in 5 × $10^{-5}$ M chloroform solution (dashed line).

layer are laterally packed in such an alternating way that the biphenyl moieties of one polymer chain are adjacent to the pyromellitic ester moieties of the neighboring chain as illustrated in Figure 7. This can produce positional order of main chain packing along their chain axes which has been proposed in the X-ray measurement,[22] since the pyromellitic ester group is approximately the same length as the biphenyl group. In addition, the formation of a charge-transfer complex may help to explain the unusually short distances between the main chains in the individual layers ($d$ = 3.45 Å).[38]

Moreover, it is interesting that the fluorescence wavelengths of K1 and K2 crystals are different from each other as shown in Figure 8. Observed data are summarized in Table 1. The fluorescence peaks for K1 crystals of B-C6 and -12 polyesters are observed at 480 nm (excited at 400 nm) and 473 nm (excited at 400 nm), respectively. The fluorescence peaks for K2 crystals of B-C14, -16, and -18 are observed at about 505 nm (excited at 425 nm) for B-C14 and -16 and at 500 nm (excited at 420 nm) for B-C18.

Mulliken clarified the relationship between the frequency ($\nu$) of the absorption band and the intermolecular length ($r$) between the electron donor and the acceptor as[38]

$$h\nu = I_p - E_a - e^2/r \qquad (1)$$

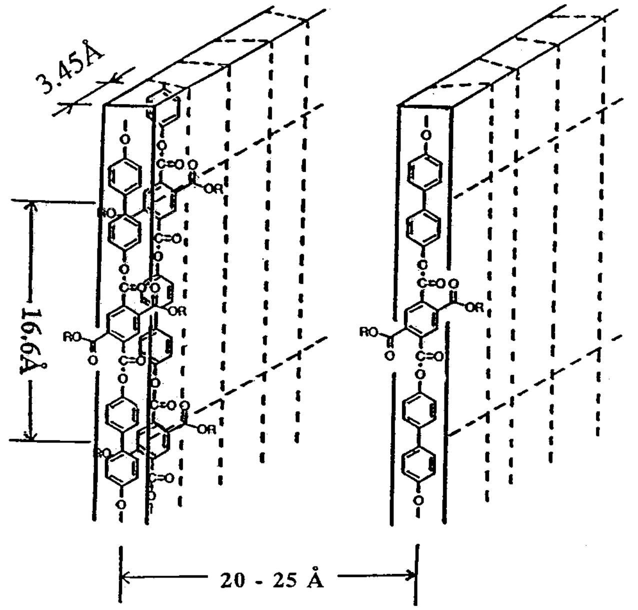


**Figure 7.** Illustration for ideal packing structure of aromatic main chains with an alternating lateral alignment of biphenyl and pyromellitic moieties within a layer, as proposed according to the fluorescence studies.

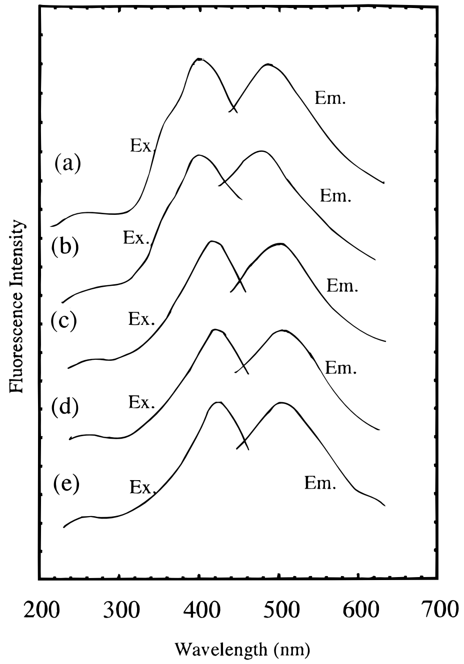


**Figure 8.** Fluorescence and its excitation spectra for the layered K1 crystal of (a) B-C6 and (b) B-C12 polyesters and the K2 crystal of (c) B-C14, (d) B-C16, and (e) B-C18 polyesters, which were prepared between quartz slides. The sample thicknesses are about 0.5 mm.

where $I_p$ is the ionization potential of the electron-donating molecule, $E_a$ is the electron affinity of an electron-accepting molecule, $r$ is the distance between electron-donating and -accepting molecules, and $h$ is the Planck constant. This equation shows that the change in frequency of the absorption band corresponds to the change in distance between the electron-donating and -accepting units. It should be noted that the packing distance in the K1 crystal is 4.6 Å while that in the K2 crystal is 3.45 Å.[10,22] The longer wavelengths (lower frequency) of the excitation spectra are realized for the

**Table 1. Wavelengths of the Observed Fluorescence and Excitation Spectra for the Layered Crystals of B-C*n* Polyesters and the $CHCl_3$ Solution of Model Compounds**

| sample | wavelength (nm) | |
|---|---|---|
| | excitation peak | emission peak |
| $CHCl_3$ solution | | |
| B-C14 ($1 \times 10^{-4}$ M) | 295 | 341 |
| B-C14($1 \times 10^{-1}$ M) | 298, 410 | 336, 500 |
| DAB$^a$($1 \times 10^{-1}$ M) | 264 | 330 |
| 16P$^b$ ($1 \times 10^{-1}$ M) | 268 | 351 |
| mixture of DAB and 16P ($1 \times 10^{-1}$ M) | 270, 338 | 326, 470 |
| biphenyl crystal | 330 | 360 |
| biphenyl solution$^c$ | 255 | 321 |
| charge-transfer band | | |
| K1 crystal | | |
| B-C6 | 400 | 480 |
| B-C12 | 400 | 473 |
| K2 crystal | | |
| B-C14 | 425 | 505 |
| B-C16 | 425 | 505 |
| B-C18 | 420 | 500 |

[a] Diacetoxybiphenyl. [b] Dihexadecyl ester of pyromellitic acid. [c] Acetonitrile solution.

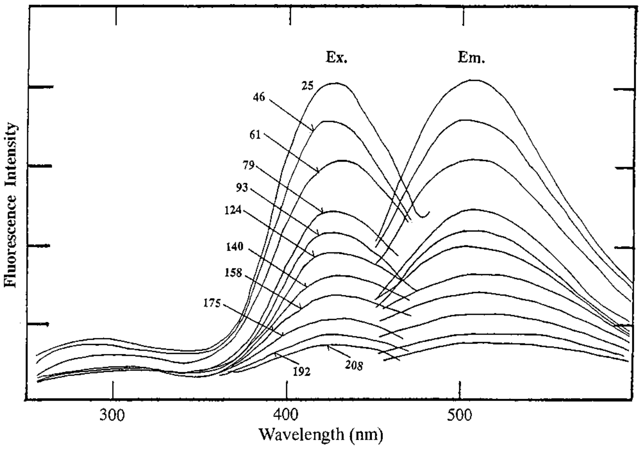


**Figure 9.** Fluorescence and excitation spectra of B-C14 polyester in the heating process. The temperature (°C) of the sample is indicated beside the curves.

K2 crystals than those for the K1 crystals due to the smaller interchain distance in the aromatic layers. This tendency is consistent with eq 1. The difference in the distance in the ground state would also influence the distance in the excited states. Thus, it has been found that fluorescence is sensitive to the intermolecular distance between the donor and acceptor groups.

**Change in Fluorescence Wavelength of the Ground-State Complex of B-C14 during Phase Transition as a Function of Temperature.** Figure 9 shows the fluorescence and excitation spectra of B-C14 polyester from 25 to 208 °C. Phase transitions occur at 124 °C from K2 to LC-1 and at 165 °C from LC-1 to the isotropic phase. The fluorescence of the interchain charge-transfer complex between the biphenyl and pyromellitic ester moieties was observed in the K2 crystal, the layered liquid crystalline phase, and the isotropic phase. This means that the segregated structure between the aromatic and aliphatic domains is maintained in all the phases. It is interesting that the charge-transfer fluorescence is observed also in the isotropic phase. The wavelengths of the excitation and emission spectra do not change so much in all phases. This result suggests that the layered segregated structure is maintained in the isotropic phase, while the anisotropy of the molecular order is lost.

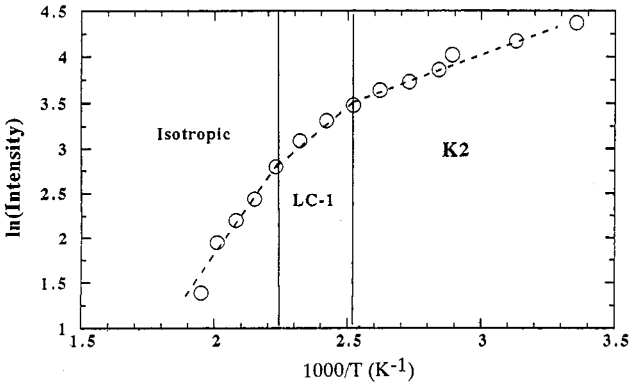


**Figure 10.** Arrhenius-type plots for the change in fluorescence intensity of the intermolecular ground-state complex of B-C14 polyester during heating process.

**Molecular Motion in Various Phases Proposed by the Fluorescence Intensity as a Function of Temperature.** To investigate the deactivation process of various intermolecular ground-state complexes during the heating process, we illustrated their Arrhenius plots for the change in fluorescence intensity in the heating process as shown in Figure 10 with the boundaries of the three regions determined by DSC measurement.[22] From this figure we notice that the fluorescence intensity decreases gradually from 25 to 240 °C. This change is considered to be due to the increase in radiationless transition. This is also due to the differences in the states and in the molecular arrangements of main intermolecular interaction for various temperature ranges. In addition, since the degree of the molecular motion increases with the increase in temperature, the frequency of quenching the excited state increases.

The temperature dependence of fluorescence intensity is generally affected by both the activation energy for radiationless transition and the change in the number of species emitting fluorescence. In this case, since the layered structure is maintained in various phases, there would be no change in the number of ground-state complexes, at least within each phase. Hence, the main reason for the decrease in fluorescence intensity of the ground-state charge-transfer complexe is considered to be the radiationless transition. The quenching of the excited states between the biphenyl and the pyromellitic moieties becomes more frequent with the increase in molecular motion. The observed temperature dependences of the fluorescence intensity (18 kJ/mol for K2 crystal, 23 kJ/mol for LC-1 phase, and 35 kJ/mol for isotropic phase) are considered to reflect activation energies for the nonradiative deactivation processes of the charge-transfer complex in each phase. These values are compared to the activation energies for dynamic quenching of benzophenone phosphorescence in polymer solids (23−40 kJ/mol)[39] below their glass transition temperatures and support again the formation of the layered segregated structure in the liquid crystalline mesophase and even in the isotropic phase.

## Concluding Remarks

Fluorescence measurements at various temperatures have provided detailed information about the aggregation states and structure of B-C*n* polyesters in the crystalline, liquid crystalline, and isotropic phases. In the K2 crystal, the ground-state charge-transfer fluorescence was observed at 500−505 nm (excited at 420−425 nm), and that in K1 was about 475 nm (excited at 400 nm). The sample quenched from the layered mesophase shows the charge-transfer fluorescence at 495 nm and its excitation spectra at 425 nm. This charge-transfer complex is found between the biphenyl and pyromellitic ester moieties in the neighboring chains within a layer. Moreover, the wavelengths for the fluorescence and its excitation spectra are found to be sensitive to the intermolecular length between the electron-donating and -accepting units. These results show that the fluorescence measurement is a powerful tool to elucidate the intermolecular interaction in liquid crystalline phases.

The wavelengths of the excitation and emission spectra do not change so much through the phases. This means that the polarization of the electronic state in the ground and excited states does not change in all phases. In the isotropic phase we also observed the charge-transfer fluorescence at 500 nm, which means that even in the isotropic phase the segregated structure is maintained between the aliphatic and aromatic domains while the molecular ordering becomes isotropic. This conclusion is supported by the results that in this phase we could not observe the increase in the intensity of fluorescence from isolated chains.

Hence, we can discuss driving forces responsible for the organization of these molecules into layered liquid crystalline structures. As has been widely accepted, the most reliable force is the segregation between the aromatic and aliphatic domains. However, this study suggests that the formation of an interchain complex in the aromatic main chains also plays a significant role in the formation of the characteristic layered structure.

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