SHORT COMMUNICATIONS

Rigid-Rod Polyesters with Flexible Side Chains Based on 1,4-Dialkylesters of Pyromellitic Acid III. Charge Transfer Complex Formation in Layered Mesophase of B-C16 Analyzed with Fluorescence Spectroscopy

Masato SONE, Brian R. HARKNESS, Junji WATANABE,[†] Takashi YAMASHITA,*
Toshinori TORII,** and Kazuyuki HORIE**

*Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama,
Meguro-ku, Tokyo 152, Japan.*

** Research Center for Advanced Science and Technology, The University of Tokyo,
Komaba 4-6-1, Meguro-ku, Tokyo 152, Japan.*

*** Department of Reaction Chemistry, Faculty of Engineering, The University of Tokyo,
Hongo 7-3-1, Bunkyo-ku, Tokyo 113, Japan.*

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There are several reports in the literature showing that rigid-rod polymers with long flexible side-chains are capable of forming thermotropic liquid crystalline phases.¹⁻¹⁴ A classic example of this type of material is poly-(γ -octadecyl-L-glutamate), which can form cholesteric, smectic and columnar phases.¹⁻³ It has also been reported that rigid-rod aromatic polyesters with long alkyl side-chains form novel layered structures that exhibit mesomorphic properties.⁴⁻¹⁴ These layered structures are characterized by a lateral packing of the aromatic main chains into layers with the flexible alkyl side-chains occupying the space between the layers. The driving force for the adoption of such a structure has been considered to be a type of microsegregation of the aliphatic and aromatic domains. In these layered structures, the liquid crystallinity can be created by the fluid-like disordered alkyl side-chains between the layers.

In a previous study¹³⁻¹⁵ we have also pre-

pared several new rigid-rod polyesters with long alkyl side-chains. These were synthesized by the condensation of 1,4-dialkylesters of pyromellitic acid with hydroquinone or 4,4'-biphenol to generate a series of polymers denoted as H-C_n or B-C_n, respectively, where *n* refers to the number of carbon atoms in the alkyl side-chain. The H-C_n polyesters in which the alkyl side-chain length was greater than 10 carbon atoms formed highly ordered thermotropic mesophases that have a layered structure like those observed for similar types of rigid-rod polyesters with long flexible side-chains.¹⁴ On the other hand, the B-C_n polyesters with *n* = 14, 16, and 18 were found to form two novel thermotropic mesophases with the nature of the layered structure depending on temperature. These two structures were different from the layered structure observed for the H-C_n polyesters with respect to the degree of order and the packing arrangement of the chains within the layers.^{13,15}

[†] To whom correspondence should be addressed.

Figure 1. An illustration of the proposed structure for the layered mesophase of B-C16 observed in the lower temperature region. In this layered structure, the aromatic main chains in the extended form are packed into a layer with the molten alkyl side chains occupying the space between the layers. The spacings given in the figure are based on X-ray observations.^{13,15}

Among them, the layered structure which is formed in the lower temperature range and illustrated in Figure 1 is interesting. In this layered structure, it has been clarified from the X-ray diffraction pattern that the aromatic main chains are in an extended form (repeat length of 16.6 Å) and are packed into a layered structure with positional order along their long axes. We further found that the averaged lateral packing distance of main chain within a layer is around 4 Å, indicating that the aromatic main chains are closely associated with each other.^{13,15} These implies the specific interaction or association of the pyromellitic ester group and biphenyl group which are included in the repeat unit of main chain. Unfor-

tunately, X-ray diffraction analysis does not reveal the arrangement between these two groups within a layer in the liquid crystalline phase.

Recently, several studies 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.¹⁶⁻²⁰ The value of this technique lies in the fact that fluorescence measurements are sensitive to interactions between neighboring chromophores which in turn can be translated to give some information concerning the spatial geometry of these groups. This communication describes our attempt to deduce the spatial

arrangement of the biphenyl and pyromellitic ester groups in the layered liquid crystalline phase by examining the fluorescence behavior of the B-C16 polyester;

Initially, the excitation and emission spectra of the fluorescence were measured for the chloroform solutions of B-C16 polyester as a function of concentration by using a Hitachi 850 type of fluorescence spectrometer. The data are shown in Figure 2. The fluorescence spectrum for the dilute solution of the B-C16 polyester at the concentration of 10^{-4} M (mole repeat unit l^{-1}) shows a structured band with a maximum at 355 nm (excitation wavelength

Figure 2. The fluorescence and its excitation spectra of B-C16 in chloroform solutions at the concentrations of (a) 10^{-4} M, (b) 10^{-3} M, (c) 10^{-2} M, and (d) 10^{-1} M. A pair of the fluorescence and excitation spectra are given by the solid curves or dashed curves.

at 287 nm). This band can be attributed to an overlap of the fluorescence bands of both the biphenyl and pyromellitic ester moieties; individually, the fluorescence band for the biphenyl moiety may appear around 327 nm (excitation at 260 nm) as has been deduced from the fluorescence spectrum for 4,4'-diacetoxy biphenyl and that for the pyromellitic ester moiety may appear at 354 nm (excitation at 267 nm) as measured for the 1,4-dihexadecyl ester of pyromellitic acid (see later curves a and b in Figure 3). Increasing the concentration of the polymer results in a profound change in both the excitation and emission spectra. The new excitation and emission bands (given by dashed curves) appear at longer wavelengths with the increase of the concentration from 10^{-4} M to 10^{-1} M. Finally they become predominant at the concentrations above 10^{-1} M; an excitation at 410 nm gives rise to a fluorescence band at 490 nm. Further, we found that these bands are structureless. These results simply indicate that an increase in the concentration of B-C16 causes a change in the electronic state of the biphenyl and pyromellitic ester chromophores. This would be due to an aggregation process which results in a ground state dimerization to give a charge transfer complex.¹⁸ With respect to the B-Cn 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 groups when they are in a suitable geometry and at a suitable distance.

To test this hypothesis, the fluorescence spectrum for a mixture of two model compounds, 4,4'-diacetoxy biphenyl and the 1,4-dihexadecylester of pyromellitic acid, was examined at a concentration of 10^{-1} M. Figure 3 shows the fluorescence spectra for the individual compounds (curves a and b) and their equimolar mixture (curve c). Visually, the mixing of the two compounds gave a slightly yellow color as a result of molecular complex

Figure 3. The fluorescence and its excitation spectra for (a) 4,4'-diacetoxy biphenyl, (b) 1,4-hexadecyl pyromellitic acid, and (c) their equimolar mixture in chloroform solution of 10^{-1} M.

formation.¹⁹ In addition, the fluorescence spectrum for the mixture appeared similar to that observed in concentrated solution of B-C16, exhibiting a structureless fluorescent band with a maximum at 480 nm that is completely absent in the spectra of the individual compounds. This observation supports the proposal that the ground state molecular complex between biphenyl and pyromellitic ester groups exists in the concentrated solutions of B-C16. For forming such a complex, it is necessary that the pyromellitic ester and biphenyl groups achieve a spatial orientation in which these groups are adjacent to one another in an alternating fashion although at this time we can give no detailed aggregation structure in the concentrated solutions.

With these results in mind the fluorescence spectra were measured for the layered liquid crystalline phase of B-C16. Here, a small amount of the sample was heated to the mesophase temperature at 100°C using a

Figure 4. The fluorescence and its excitation spectra for the frozen-in layered mesophase of B-C16, which was prepared between quartz slides by quenching the mesophase at 100 °C to room temperature. The sample thickness is about 20 μ m.

Figure 5. The illustration for ideal packing structure of aromatic main chains within a layer, as proposed according to the fluorescence studies, in which the biphenyl moieties (open ellipses) lie adjacent to the pyromellitic ester groups (closed ellipses).

standard hot plate, spread between quartz slides, and then quickly cooled to room temperature. The sample thickness is about 20 μ m. For this specimen, the frozen-in liquid crystalline layered structure as illustrated in Figure 1 was ascertained by X-ray measurement.^{13,15} The fluorescence spectrum is shown in Figure 4. It is obvious that the fluorescence behavior is very similar to that observed in the concentrated solution of 10^{-1} M (refer to curve d of Figure 2), again indicating that a charge transfer complex is formed between two components, the biphenyl and pyromellitic ester moieties. Although we cannot estimate the amount of charge transfer complex only from the fluorescence spectra, this observation

dictates that the main chains within a layer are laterally packed in such a way that the biphenyl moieties of one polymer chain are adjacent to the pyromellitic ester moieties of the neighboring chain. The ideal packing structure is illustrated in Figure 5. Such a packing can produce the positional order along their chain axes which has been proposed in the X-ray measurement since the pyromellitic ester group is approximately the same length as the biphenyl group. In addition, the formation of a ground state complex may help explain the unusually short distances between the main-chains in the individual layers ($d \sim 4 \text{ \AA}$).

Finally, we comment on 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 difference in polarity and/or geometric shape between the aromatic main chain and aliphatic side chains. However, this study suggests that the formation of interchain complex in the aromatic main chains also plays a significant role in the stability of layered segregation structure.

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