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Raman Spectroscopic Observation of the Intramolecular Interactions within the Poly(Ethylene Oxide) Unit in a Liquid Crystalline Molecule

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One of the most fascinating properties of rod-coil molecules consisting of a rigid rod and a flexible coil is their ability to microphase separate into a rich variety of ordered microstructures. Theoretical works have shown that the various supramolecular structures such as nematic, layed smectic, and cylindrical phases can be induced by temperature change depending on the relative volume fraction of blocks in rod-coil diblock systems.[1] With increasing the coil length, the microphase separation between each block occurs due to the large chemical differences between the stiff rod and flexible coil segments to form layered smectic assembly. As the coil length is further increased, molecular layers may collapse into discrete cylindrical micellar structures due to the modifications of the inter- or intramolecular interactions between the coil units.[2,3] The characteristic features of the inter- or intramolecular structure include structural regularity, bond flexibility, close packing ability, and interchain attraction.[4]

The overall chain shape related to the conformational distribution of the coil unit affects the inter- or intramolecular interactions depending on the nature of the coil unit. For example, the ordering of chain structure in cooperation with the secondary forces, such as hydrogen bonding, dipole interactions, or van der Waals interactions allows the chains to pack into a regular crystal lattice, and thus raises the crystalline melting point.[5] Therefore, the examination of the interactions in the coil units is necessary to have an insight into the physical properties of the rod-coil type liquid crystalline molecules.

This report will demonstrate for the first time that chain folding occurring within the long flexible coil unit of the liquid crystalline rod-coil molecule can induce phase transition via the change of intramolecular interaction. The investigation of the inter- or intramolecular interactions in the coil unit of a rod-coil liquid crystalline molecule was performed by using the Raman spectroscopic method, which is superior to other methods for the study of the motion of carbon backbones. Among the liquid crystalline molecules, a series of molecules with the following structure is selected;[6]

$CH_3O\text{-}(CH_2CH_2O)_n\text{-}C_6H_4C_6H_4COO\text{-}C_6H_4C_6H_4COO\text{-}(CH_2)_{21}\text{-}CH_3$

, where n=7, 12, 17, 22

Hereafter, the molecules of n=7, 12, 17, and 22 will be designated by 350-22, 550-22, 750-22, and 1000-22, respectively. These molecules are derivatives for the esterification product of ethyl 4-[4'-oxy-4-biphenylcarbonyloxy]-4'-biphenylcarboxylate with poly(ethylene oxide) (DP=12) (12-4), which is characterized previously by our group.[7,8] These molecules are of particular interest since they can form complexes with alkali metal cations through poly(ethylene oxide) chains to induce the various liquid crystalline supramolecular structures.

The corresponding Raman spectra are shown in Figure 1. The Raman bands in the range 800-900 cm^{-1} mostly assigned to the ethylene oxide modes except the 863 cm^{-1} band which is found to be originated from the methylene group.[7] For the PEO unit, although the sequence of the trans and gauch conformers is well characterized by the vibrational spectroscopy,[9] it is not easy to assign each band to a specific vibrational mode because of the variation of the Raman modes in different environments.

It is noteworthy that the 846 cm^{-1} band increases in intensity with increasing the coil length, while the other bands are not affected by the variation of coil length. The behavior of the 846 cm^{-1} band indicates that a large extent of conformational changes are related to the coil unit. Two possibile mechanisms can be accounted for the coil length-dependent variation of this band. One is due to the change in the intermolecular interactions between the neighboring

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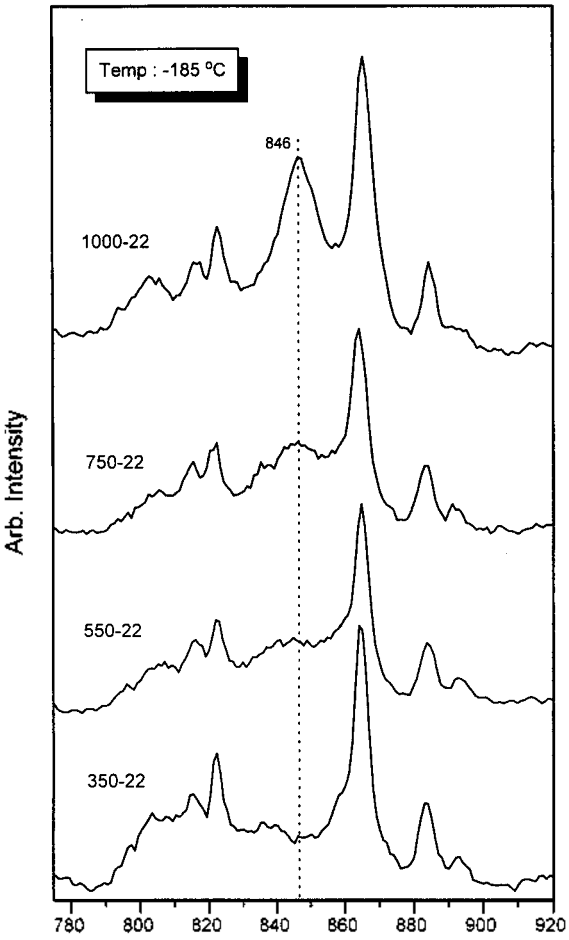

Figure 1. Raman spectra (780-900 cm^{-1}) of 350-22, 550-22, 750-22, and 1000-22. The spectra were recorded at − 185 °C under liquid nitrogen matrix. The dotted line marks the 846 cm^{-1} band, which is indicative of the chain folding in the PEO unit.

coil units, the other is due to the change in the intramolecular interactions within a coil unit. The former possibility, however, is unlikely because of the following reasons: If the conformational change is caused by the intermolecular interactions, the new band should exist even in 350-22 because even the shortest number (*n*=7) of the coil unit used in this study is long enough to provide interactions between the neighboring units. This can be easily conjectured by the fact that the small increase in the coil length of normal alkane hydrocarbon molecules greatly affects the melting temperature even though these molecules can provide only the nonpolar interactions.[4] It was reported previously by us that the complex formation of the salt-added 12-4 leads to only a small amount of frequency shift as a result of the conformational change.[7] It should be pointed out that the complexation between the PEO unit and the cation of the salt is stronger than the intermolecular interactions between the bare PEO units.[4,5,10] Therefore, the change in the intermolecular interactions between the coil units is not considered to be the main reason for the appearance of the 846 cm^{-1} band.

The band shape of the vibrational mode belonging to the

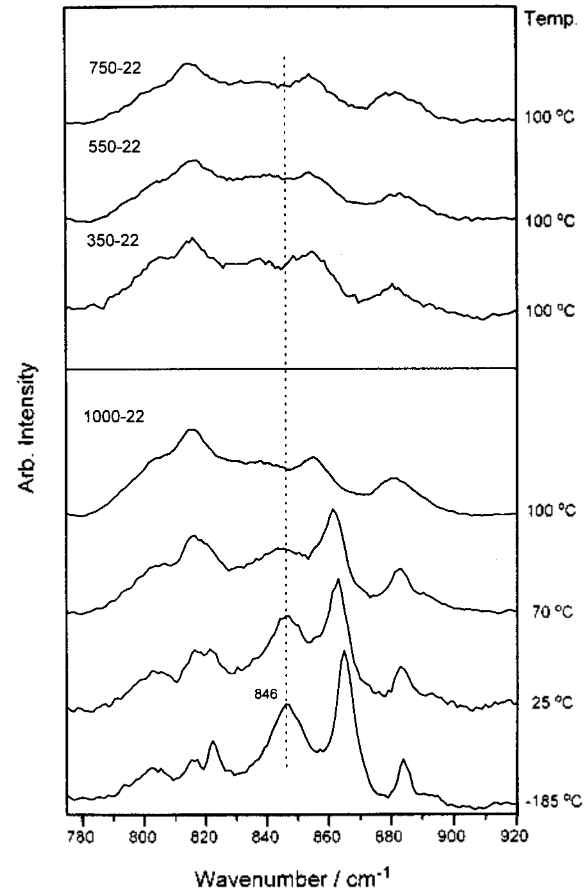

Figure 2. Temperature dependent Raman spectra (780-900 cm^{-1}) of 1000-22 (bottom) and high temperature spectra of 350-22, 550-22, and 750-22 (top). For 1000-22, the 846 cm^{-1} band at − 185 °C gradually diminishes at higher temperatures until its spectrum becomes similar to those of the other derivatives at 100 °C (top).

mesogenic unit (1100-1300 cm^{-1} region not shown here) can be used as another probe. Our previous study[8] demonstrated that when the mesogens are loosely packed due to the intercalation of undissociated salts, the broadening of the Raman band is induced by the change in the intermolecular interactions between the mesogens. This phenomenon can also be applied to the present system. If the intermolecular interactions in the PEO unit were strong enough such that the new band appears, the mesogens might be strongly packed together, giving rise to the narrowing of the bands. However, we could not found any prominent narrowing with increasing the coil length. Therefore, the change in the intermolecular interactions between the neighboring coil units is ruled out as the origin of the 846 cm^{-1} band.

As for the intramolecular interactions, we can consider the two experimental aspects. The first one is that the new Raman band at 864 cm^{-1} gradually increases with increasing the PEO chain length, while the other bands remain unchanged in both frequency and relative intensity. This implies that the various *trans* and *gauche* conformers retain their original sequence regardless of the coil length while the transition to a new conformation takes place. This result can be explained only by the generation of the intramolecular interactions due to the chain folding at a certain seg-

Table 1.

Molecules	Phase transition (°C)[a]	Enthalpy change (kJ/mol)
350-22	46 °C	13.3
550-22	64 °C	16.7
750-22	68 °C	76.8
1000-22	68 °C	112.9

[a] Temperatures are determined by DSC heating scan and attributed to the conformational change in the PEO unit as compared to the temperature dependent Raman spectroscopy.

ment in a coil unit. If the coil is bent, the bond angle along either the carbon-carbon or the carbon-oxygen axis near the junction is subject to change, leading to a new conformer, with the rest segments remained unchanged.

A temperature dependent Raman experiment was performed to further check whether or not the intramolecular interactions are the origin of the 846 cm^{-1} band. As the temperature increases the 846 cm^{-1} band in 1000-22 gradually diminishes and finally all the bands in 1000-22 become similar to those of the other derivatives at 100 °C, reflecting the unfolding of the coil unit at high temperature (Figure 2). This observation is supported by the DSC study. The coil length dependent variation of the enthalpy change (ΔH) during the phase transition is considered to be associated with the motion of the PEO unit; the value of ΔH for 1000-22 is by far the greatest among the derivatives as shown in Table 1. It is noteworthy that the ΔH increases slightly from 350-22 to 550-22, but suddenly rises at 750-22 indicating that a significant physical change starts with the coil length of n=17. This behavior can be also interpreted in terms of the intramolecular interaction resulted from the folding within a long coil unit. For 1000-22, the folding of the coil unit, which is accompanied by the bending of the segment, is more easily formed than for 750-22, thereby generates the modified conformer of which overall molecular shape is significantly different from those of the other derivatives. As a result, the recovery from the folding to the unfolding configuration, which occurs *via* the breaking of the dipole interaction within the folded chains, will need more energy than that only from the intermolecular interactions, as clearly supported by the DSC result.

In summary, the intramolecular interactions within the coil unit in the liquid crystalline rod-coil molecule was observed for the first time by Raman spectroscopy. As the PEO coil length increases the 846 cm^{-1} band becomes distinct at low temperature and gradually disappears with increasing temperature. Judging from the experimental results of both Raman spectroscopy and DSC, we conclude that the chain folding of the PEO coil unit is induced as its length is increased.

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Thermogravimetric Study on Reactivity of Carbon Dioxide and Methane over Supported Nickel Reforming Catalysts

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Formation of coke over catalysts during reforming process of methane has been considered seriously as a main reason for catalyst deactivation.[1] In particular, in the CO_2 reforming of methane (so-called "*dry reforming*") coke formation was known to be more serious than any other reforming reactions. This has prevented the easy commercialization of the dry reforming process. However, this process provides one of the useful methods as the chemical utilization of CO_2 and CH_4 since these gases are considered as notorious greenhouse gases.[2] In addition, from the industrial viewpoint the reaction is also potentially beneficial since it produces CO-rich synthesis gas (H_2/CO) with high