Raman Spectroscopic Study on the Modification of the Mesogenic Unit in a Liquid Crystalline Oligomer under Two Different Conditions

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A liquid crystalline oligomer, ethyl 4-[4'-oxy-4-biphenyl-carbonyloxy]-4'-biphenylcarboxylate with poly(ethylene oxide) (DP=12) (12-4) has been characterized previously in our study focusing on the complexation with the Li^+ ion by monitoring the characteristic vibrational modes.[1] It was suggested that the spectral changes in the mesogenic unit might not be due to the complexation with the Li^+ ion, but due to the conformational changes caused by the intercalation of the nondissociated $LiCF_3SO_3$.

In this sense we are interested in the conformational changes of 12-4 caused by the intercalation of the non-dissociated $LiCF_3SO_3$. In order to see the effect of the Li^+ ion on the conformational changes, a similar work, which is the temperature dependent study of the conformational changes, is performed. This is because the elevated temperature usually accompanies the partial bond rotation about a certain linkage belonging to the mesogenic units giving rise to the conformational changes.[2]

Therefore, in this work we have compared the temperature dependent spectral changes with the salt dependent ones by focusing our attention on the modifications of the mesogenic units so as to reveal the mechanism of the spectral changes in the mesogenic units, which was in question in our previous paper.[1]

Experimental

The synthesis and characterization of 12-4, and the preparation of complexes of 12-4 were reported elsewhere.[3] The Renishaw Raman micro system 2000 was used to get the Raman spectra.[1] As an excitation source, the 632.8 nm with a maximum power of 25 mW from Spectra Physics Model 127-75RP HeNe laser was used. The laser power at the sample was *ca.* 5 mW and the spectra were recorded for between 20-50 scans depending on the samples. The resolution of all the spectra is within ± 2 cm^{-1}. All the samples were put on glass slides, and data were acquired by using an Olympus 20x ultra long working distance objective lense. For the temperature control, the Linkam heating and freezing stage (THMSE 600) and controller (TMS 92) were used. The samples were heated at 10 °C/min and left for 5 min. for equilibrium before collecting data. All the spectra were manipulated with the software provided by Renishaw, and the background corrections were made when needed.

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Results and Discussion

The modifications in Raman spectra were observed with increasing temperature as shown in Figure 1. As a whole, the Raman bands decrease in intensity with increasing temperature with an abrupt change in the region of phase transition; The polymer shows a transition from solid to smectic mesophase at 137 °C in DSC result.[3] All the bands in Figure 1 are normalized to the biggest band at 1599 cm^{-1} which is assigned to the aromatic C=C stretching mode. In order to see the thermal behavior of the polymer through the region of phase transitions, we have selected the 1184 cm^{-1} band as a representative of the Raman bands, and plotted its relative intensity to 1599 cm^{-1} band as a function of temperature in Figure 2. As shown in Figure 2 the relative intensity gradually decreases with increasing temperature and drops abruptly at the vicinity of phase transition from solid to liquid-crystalline being in accordance with the DSC result.

It should be noticed that the most important structural differences between the adjacent crystalline polymorphs occur in the mesogenic unit according to the literature.[4,5] Therefore, amongst mesogenic Raman bands, we are mostly interested in the bands at around 1270 cm^{-1} and 1730 cm^{-1}. The 1270 cm^{-1} band was assigned to the combination of the aryl C-C(=O)O stretching, and aromatic CH in-plane bending vibrations, and the 1730 cm^{-1} band was assigned
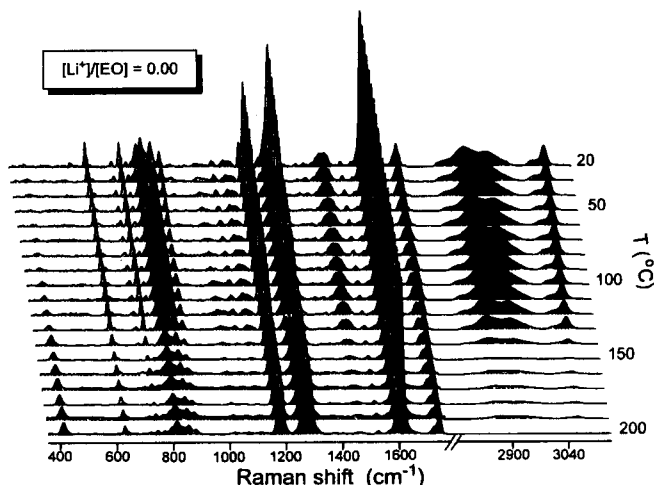

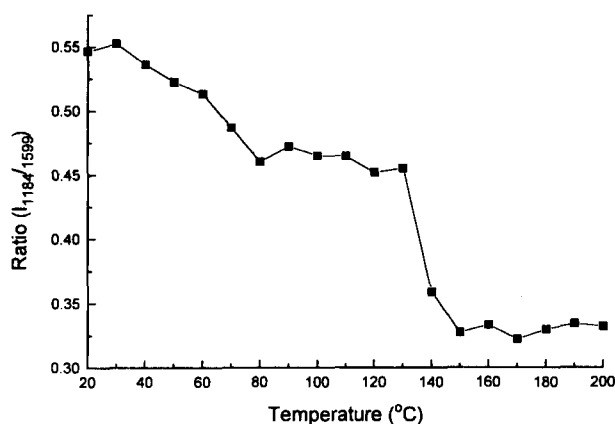**Figure 1.** Raman spectra (360-3150 cm^{-1}) of 12-4 as a function of temperature.

Figure 2. Relative intensity of the 1184 cm^{-1} mode to the 1599 cm^{-1} mode of 12-4 as a function of temperature.

to the carbonyl stretching mode.[1] Thus, the monitoring of two bands will allow us to observe the conformational changes around the carbonyl groups.

As shown in Figure 3(a) the 1270 cm^{-1} band continuously broadens upto 130 °C and splits finally into two features between 130 and 140 °C (Sa=137 °C) at which temperature the crystalline phase changes to the liquid-crystalline phase. A similar behavior was also observed in our previous study[1] when the salt concentration was increased upto [Li$^+$]/[EO]=0.3, where [EO] represents the concentration of ethylene oxide units of 12-4, and this observation
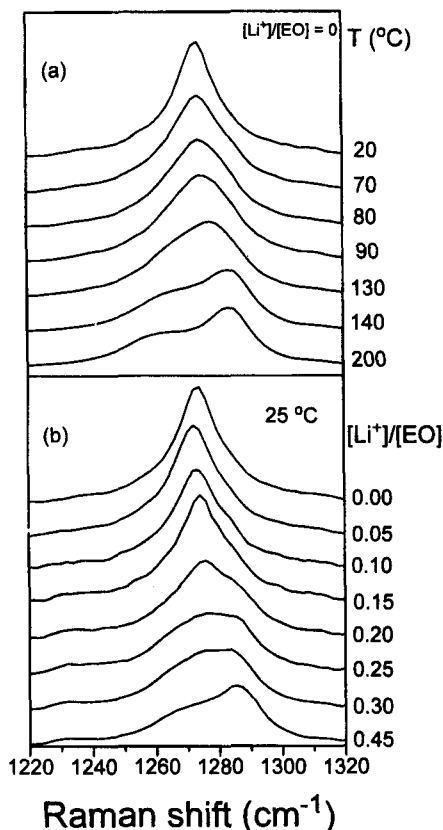

Figure 3. The evolution of the 1270 cm^{-1} mode as a function of (a) temperature; (b) salt concentration.

was regarded as being attributed to the collapse of the degeneracy as a result of the complexation with the salt. However, in the same study it was found that the Li$^+$ ion binds to 12-4 completely when the [Li$^+$]/[EO] reaches 0.15. This means that there are some nondissociated LiCF$_3$SO$_3$ at [Li$^+$]/[EO]=0.3 as redundants, and some of the redundant salts may exist as intercalations between the mesogenic units, while the others may exist between the coil units. The modification of the band shape is continuous by the stepwise increment of salt concentration upto [Li$^+$]/[EO]=0.45 as shown in Figure 3(b), resulting in a pattern strikingly similar to that in the temperature variation. This fact implies that not only dissociated LiCF$_3$SO$_3$ but also nondissociated LiCF$_3$SO$_3$ affect the band shape giving us an indication of the changes in the intermolecular interactions regardless of whether or not the complexation occurs. Considering the origin of the 1270 cm^{-1} band and the fact that the elevated temperature usually brings about conformational changes, the modification of this band seems to be related to the conformational change in the mesogenic unit. Thus, the possible mechanism for the behavior of the 1270 cm^{-1} band can be explained as follows: the intermolecular interactions were gradually weakened at the beginning stage by either stepwise addition of salts or increment of temperature leading to the release of the steric strain about the aryl C-C(=O) O, and they were finally broken down giving rise to the conformational change which results from the bond rotation.

Based on the fact that the salt is found to bind to the carbonyl group of the aryl C-C(=O)O[1], the linkage about which the partial bond rotation occurs could be the ketone linkage of aryl C-C(=O)O. This is supported by the behavior of the 1730 cm^{-1} band because as the partial bond rotation occurs, the different type of carbonyl groups in terms of the force constant may be generated.[6,7] The evolution of the 1730 cm^{-1} region with increasing temperature is shown in Figure 4(a). This region is comprised of two prominent components at 20 °C. With increasing temperature the 1724 cm^{-1} band gradually decreases in intensity, whereas the 1737 cm^{-1} band increases. A similar behavior is also observed when the salt concentration is gradually increased, as can be seen in Figure 4(b), although the extent of the frequency shift is slightly different. These observations directly represent the change in the force constant around the C=O double bond, and is ascribed to the change in either the strong interactions between the C=O dipoles[8] or hydrogen bonding between C=O of the ester group and hydrogen of the benzene in adjacent polymer chains[9] causing the change in the force constant around the C=O double bond.

For illustration purpose, suppose that the hydrogen bonding is involved. If the hydrogen bonding has been formed, the 1724 cm^{-1} band dominates because the electrons are attracted to the hydrogen atom of the benzene ring leading to a weak force constant around the C=O double bond. However, if the hydrogen bonding is broken down by either the temperature or the salt, the 1737 cm^{-1} band will dominate because the population of the free carbonyl groups increases. Although the interactions between the C=O dipoles are considered, the explanations will be similar.

In conclusion, both salt and temperature dependent studies on the conformational changes were carried out by comparing spectral changes belonging to the mesogenic unit.
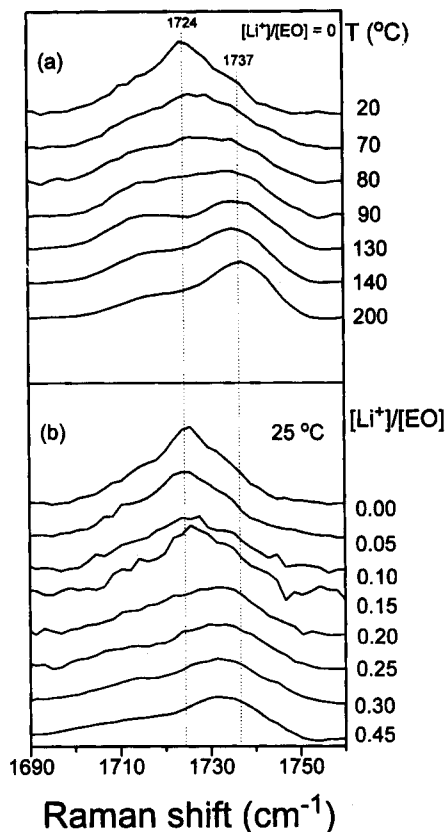
Figure 4. The evolution of the carbonyl stretching mode as a function of (a) temperature; (b) salt concentration.

As the temperature increases, the partial bond rotation seems to occur around the ketone linkage of the aryl C-C(=O)O giving rise to the breakage of the intermolecular interactions between the mesogens. Also, a similar phen-

omenon occurs in the case of the increase of the salt concentration. As the excess Li^+ ions are introduced for complete binding, the redundant Li^+ ions seem to play a role in breaking down the intermolecular interactions. Concomitantly, the free carbonyl groups are rearranged to release the steric strain about the aryl C-C(=O)O. Our experimental results, therefore, strongly indicate that the conformational changes in the mesogenic units occur not only due to the complexation of the dissociated salts, but also due to the intercalation of the nondissociated ones.

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Preparation of Ag-Deficient Delafossite-Type Compounds Ag$_x$CoO$_{2-\delta}$ (x=0.95, 0.75)

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Delafossite type compounds[1] have a general formula $A^I B^{III} O_2$ (A=Cu, Ag, Pt, Pd; B=Al, Fe, Co, Ni, Rh, Ln...), and are characterized by their two-dimensional structure as represented in Figure 1. B^{3+} cations are octahedrally coordinated by oxides to form BO_6 units, which are developed in **ab** plane by edge share, giving rise to $[BO_2]$ plates in the plane. These plates are stacked along **c** axis and generate 2-fold linear sites between them where the monovalent

cations, generally being of d^{10} configurations, are situated. According to the stacking way of these $[BO_2]$ plates in c direction, several structural polytypes are geometrically possible, among which 3R (S.G. R3m) and 2H (P6₃/mmc) structures are shown in Figure 1(b). The factors determining polytype structure have not been well understood, but the majority of delafossite phases have been reported to crystallize in 3R-type whereas only a few ones in 2H-type.[2,3]