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Raman Spectroscopic Characterization of a Rod-Coil Liquid Crystalline Oligomer-LiCF₃SO₃ Complex

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The interactions between a rod-coil liquid crystalline oligomer, ethyl 4-[4'-oxy-4-biphenylcarbonyloxy]-4'-biphenylcarboxylate with poly(ethylene oxide) (DP=12) (12-4) and LiCF₃SO₃ have been characterized by using Raman spectroscopy. Band assignments were made comparing the spectrum of 12-4 with those of the poly(ethylene glycol) monomethyl ether(PEGME) (Mw=550) and the ethyl-4'-hydroxybiphenyl-4-carboxylate (EHBPC), which are the coil and mesogen analogues, respectively. Analyzing characteristic bands of the 12-4-salt complex, we have found that the bands belonging to the coil and mesogenic units are changed in both intensities and frequencies. The spectral changes were interpreted from the viewpoint of the complexation between 12-4 and the Li⁺ ion. However, the possibility that the spectral changes in the mesogenic unit are not due to the complexation with the Li⁺ ion, but due to the conformational changes by the intercalation of nondissociated LiCF₃SO₃, is not ruled out.

Introduction

Polymer electrolytes complexed with alkali-metal cations have been studied for a long time because of their numerous applications such as solid state batteries and electrochromic devices.¹ These polymers are normally comprised of poly(ethylene oxide) (PEO), and to a lesser extent, poly(propylene oxide) (PPO) as a spacer group because PEO shows better solvating power for salt than the others do. The in-depth study of this PEO has provided rich information regarding the conformational and/or structural changes due to varying temperatures and salt concentrations.²⁻⁶ For example, a change in a conformational distribution corresponding to either *gauche* or *trans* isomerism is known to occur as temperature increases or as alkali-metal cations interact with the ether oxygens in the coil unit.

The liquid crystalline (LC) polymers which have aromatic moieties as a rigid mesogenic unit and polyethers as a flexible coil unit are of recent interest because the mesogenic unit provides variable structures while the coil unit contributes to an ionic conduction.^{7,8} Thermotropic polyesters are one of the most well-studied families in the area of main-chain LC polymers.⁹⁻¹¹ However, very little research has been done on rod-coil diblock systems containing PEO coil unit.

X-ray,^{12,13} ²³Na NMR,^{14,15} DSC,^{16,17} and Raman spectroscopy^{18,19} are techniques used to elucidate the relationships

between structure and ionic conductivity within ionic conducting polymers. Amongst these, Raman spectroscopy has proved to be one of the most powerful technique to characterize the conformational and/or structural changes of the LC polymers complexed with alkali-metal cations at the molecular level. However, most Raman works have concentrated on the spectral region of CH₂ rocking modes in order to investigate the conformational changes in the polymer backbone upon binding with alkali-metal cations. This is because the polymer chain plays a major role in the ionic transport in the amorphous regions.^{20,21}

It is reported that an increase in the rigid segment fraction in thermoplastic polyurethane (TPU) lowers the overall conductivity, even though ionic conductivity is normally the result of local segmental motions of a polymer chain.²² This implies that the interaction of mesogenic units with alkali-metal cations would reduce the conductivity of polymers. Thus, whether both segments are able to interact with salt or not is a matter of concern. In order to address this matter, it is, therefore, necessary to investigate not only the coil but also mesogenic units to see if the latter is involved in complexation with alkali-metal cations.

In this paper we report Raman spectroscopic studies of a rod-coil diblock liquid crystalline oligomer (12-4), where rod is ethyl 4-[4'-oxy-4-biphenylcarbonyloxy]-4'-biphenylcarboxylate and coil is poly(ethylene oxide) with the degree of polymerization of 12, and the complexes with 0.15 and 0.30 mols of LiCF₃SO₃ per 1 mol ethylene oxide unit in 12-

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4. The main goal of this paper is to reveal the binding sites of the Li⁺ ion in 12-4-salt complex by monitoring spectral changes. The spectral regions corresponding to both the coil and mesogenic units were analyzed in detail.

Experimental

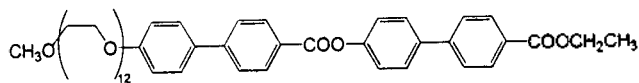
The chemical structure of 12-4 is outlined in Scheme 1. The details of the synthesis and characterization of 12-4, and the preparation of complexes of 12-4 were reported in a previous publication.²³

The Renishaw Raman micro system 2000 was used to get Raman spectra.²⁴ 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 objective lens. All the spectra were manipulated with the software provided by Renishaw, and background corrections were made when needed.

Results and Discussion

Band Assignments. To study the conformational and/or structural changes in the LC oligomer after the introduction of salt, we have obtained the Raman spectra for 12-4 and 12-4-salt complex. The spectra are shown in Figures 1, 2, and 3 of which (a) corresponds to salt-free 12-4 itself, and (b), 12-4-salt complex with the compositions of [Li⁺]/[EO]=0.30, where [EO] represents the concentration of ethylene oxide units of 12-4.

There are four spectral regions of interest in Figures 1(a)



Scheme 1. The chemical structure of the rod-coil oligomer (12-4).

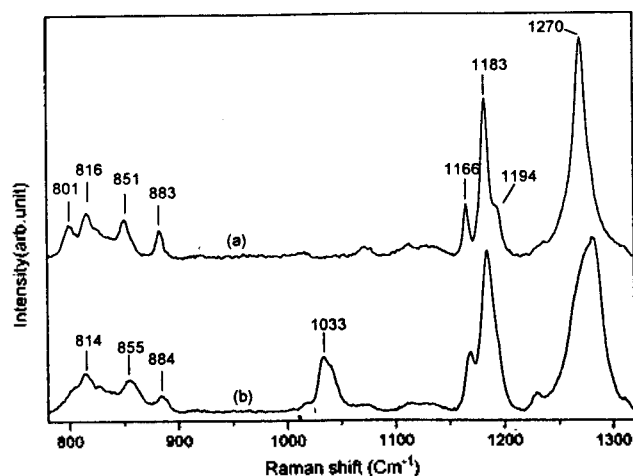


Figure 1. Raman spectra (780-1320 cm⁻¹) of 12-4 and 12-4-salt complex. (a) Salt-free 12-4, (b) [Li⁺]/[EO]=0.30.

and 1(b). Two spectra are different from each other in both intensity and frequency. The bands in the first region of 780-900 cm⁻¹ which belong to the coil unit are mainly attributed to the CH₂ rocking modes of the *gauche* and *trans* conformations of the polymer backbone.^{25,26} The band at around 1033 cm⁻¹ in the second region is responsible for the SO₃ stretching mode²⁷ of LiCF₃SO₃, therefore it appears only in Figure 1(b). The triple bands at 1166, 1183, and 1194 cm⁻¹ in the third region which have merged into the double bands, are attributed to the aromatic nuclei,¹⁰ and confirmed from the spectrum of EHBPC which is the mesogen analogue as shown in Figure 4. The band at around 1270 cm⁻¹ in the fourth region is assigned to the combination mode arising from ring-carbonyl stretching, O-C (ethylene oxide) stretching, and aromatic CH in-plane bending vibrations in the literature.^{10,25} However, an elaborate work is needed to assign this band unambiguously because its change in either fre-

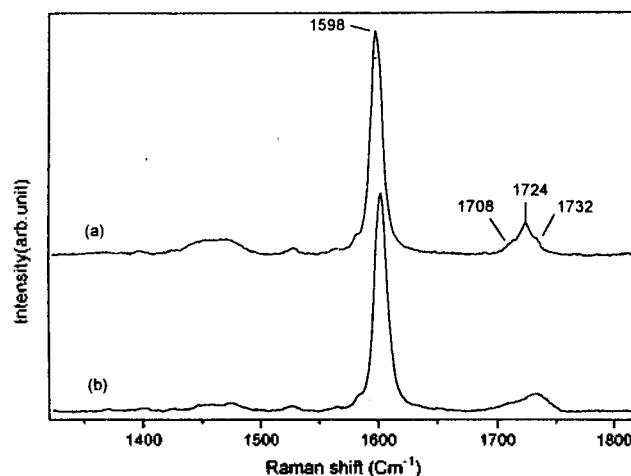


Figure 2. Raman spectra (1320-1820 cm⁻¹) of 12-4 and its salt complex. (a) Salt-free 12-4, (b) [Li⁺]/[EO]=0.30.

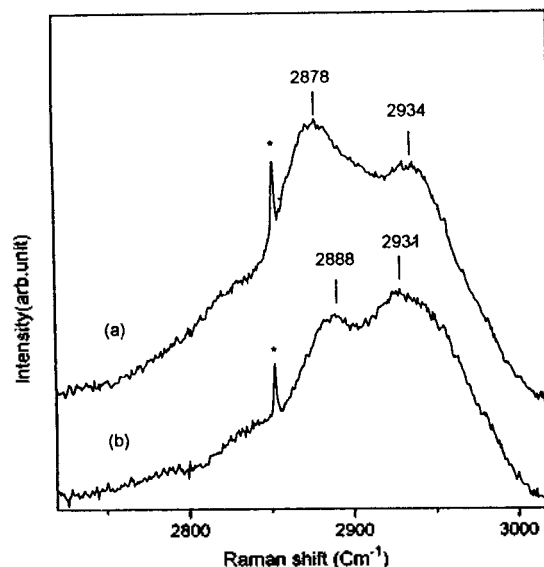


Figure 3. Raman spectra (2720-3020 cm⁻¹) of 12-4 and 12-4-salt complex. (a) Salt-free 12-4, (b) [Li⁺]/[EO]=0.30. *Laser plasma line.

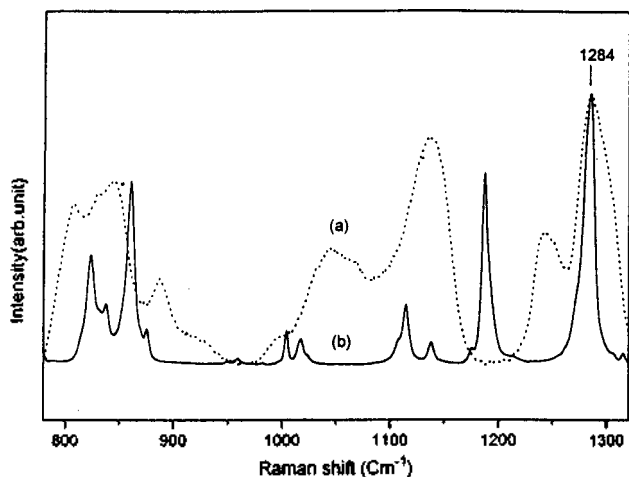


Figure 4. Raman spectra (780-1320 cm^{-1}) of the coil and mesogen analogues. (a) PEGME (b) EHBPC.

quency or intensity provides a clue to answer the questions about which unit is mainly involved in complexation with salt.

To reveal whether this band is originated from only the mesogenic unit itself or other sources, we recorded the spectra of the analogous molecules, PEGME and EHBPC, which resemble the coil and mesogenic units of 12-4, respectively. Figure 4 shows corresponding spectra, and no band appears at 1270 cm^{-1} . Instead, the bands appear at 1284 cm^{-1} in both spectra. The 1284 cm^{-1} band appears to have shifted to the lower frequency of 1270 cm^{-1} , because the reduced mass is increased as the segments of the coil and mesogenic units are incorporated into one segment of 12-4. Suppose that the assumption mentioned above is correct. The question remains as to whether both of these bands contribute to the 1270 cm^{-1} band of 12-4. In fact, it is difficult to know with accuracy by only comparing the intensity of each spectrum which molecule contributes more to the 1270 cm^{-1} band because there are no internal modes to calibrate both spectra. Therefore, we have utilized LiCF_3SO_3 as an internal standard to study the extent of the contribution from each component.

For the purpose of calibration, LiCF_3SO_3 is introduced into PEGME such that the $[\text{Li}^+]/[\text{EO}]$ is the same as that of 12-4-salt complex in Figure 1(b). Since the number of repeat units of ethylene oxide is the same in both, the same amount of LiCF_3SO_3 is introduced into both, and therefore the concomitant Raman bands at 1033 cm^{-1} should have the same intensities. If the 1033 cm^{-1} bands are normalized to be equal in intensity in Figure 5, one can easily find that the 1270 cm^{-1} band is mainly attributed to 12-4 rather than PEGME which is identical with the coil unit except for the hydroxyl group. It means, in turn, that only the mesogenic unit is responsible for this band in contrast to the previous reports.^{10,25}

The 1598 cm^{-1} band in Figure 2 is assigned to the aromatic C=C stretching mode.²⁸ The triplet bands at 1708, 1724, and 1732 cm^{-1} in the same figure belong to the carbonyl stretching modes. The 2878 cm^{-1} band in 12-4 and the 2888 cm^{-1} band in 12-4-salt complex in figure 3 are assigned to the symmetric stretching mode of $-\text{OCH}_2(\text{CH}_2$ of ethylene

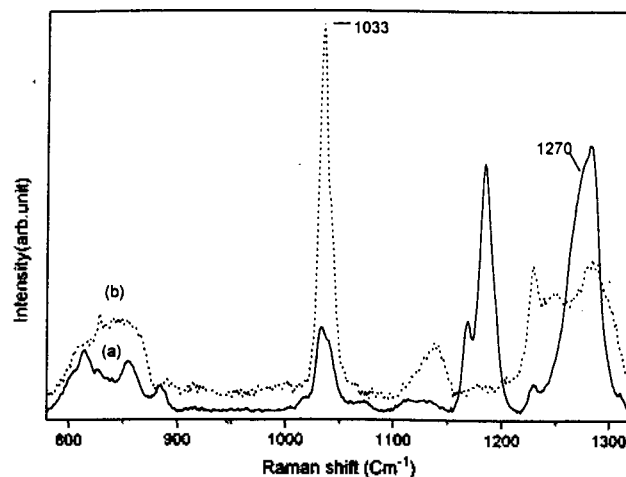


Figure 5. Raman spectra (780-1320 cm^{-1}) of 12-4-salt and PEGME-salt complexes. ($[\text{Li}^+]/[\text{EO}]=0.30$). (a) 12-4-salt, (b) PEGME-salt.

oxides). However, the 2934 cm^{-1} band in 12-4 and the 2931 cm^{-1} band in 12-4-salt complex are assigned to the asymmetric stretching mode of $-\text{OCH}_2$.²⁸ The assignments for all the bands are listed in Table 1.

Changes of Salt Band. In order to test whether salt binds to 12-4 or not, we have tried to observe the change of the Raman bands for LiCF_3SO_3 since SO_3 stretching mode can be used as a characteristic vibrational mode for this purpose. Salt exists as three types upon binding to the 12-4; free ion of CF_3SO_3^- , ion pair of $\text{Li}^+\text{CF}_3\text{SO}_3^-$, and aggregate. Petersen *et al.*²⁷ found these three components in LiCF_3SO_3 -diglyme complex at different temperatures. In the corresponding Raman bands, the 1033 cm^{-1} band is assigned to free ion, the 1044 cm^{-1} , ion pair, and the 1053 cm^{-1} , aggregate. On the basis of this information, interpretation was made for the spectra in figure 6. The spectra of figures 6(a), (b), and (c) represent $[\text{Li}^+]/[\text{EO}]=0, 0.15,$ and $0.30,$ respectively. From the band centered at 1033 cm^{-1} , we can see that there exist only free ions when $[\text{Li}^+]/[\text{EO}]$ is 0.15, which is the same as the value available in the literature.²⁷ As the concentration is increased to $[\text{Li}^+]/[\text{EO}]=0.30,$ the new band assigned to the ion pair appears at about 1044 cm^{-1} . Therefore, we propose that most salt binds to the rod-coil oligomer at a lower salt concentration ($[\text{Li}^+]/[\text{EO}]=0.15$), however, some salt remain unbound at a higher salt concentration ($[\text{Li}^+]/[\text{EO}]=0.30$).

Changes in Coil Unit. The coil unit of 12-4 comprises the repeat units of ethylene oxide, and it is generally accepted that ether oxygens interact with the Li^+ ion with four oxygens coordinated to one Li^+ ion.²⁹ To confirm the binding sites of salt in 12-4, we have observed the changes in the spectral region of 780-900 cm^{-1} corresponding to the coil unit. The spectra of figures 7(a), (b), and (c) represent $[\text{Li}^+]/[\text{EO}]=0, 0.15,$ and $0.30,$ respectively. As can be seen in figure 7, the bands are not changed until $[\text{Li}^+]/[\text{EO}]$ reaches 0.30. As $[\text{Li}^+]/[\text{EO}]$ reaches 0.30, the bands are changed, apparently, in both intensity and frequency. The four bands at 801, 816, 851, and 883 cm^{-1} in figures 7(a) and (b) have merged into three bands at 814, 855, and 884 cm^{-1} in figure 7(c). In the Li^+ ion-complexed methoxy-terminated PEO with

Table 1. Band assignments of 12-4 and 12-4-salt complex

Raman (cm ⁻¹)	Shift	Assignment ^a
12-4	12-4-salt ([Li ⁺]/[EO]=0.3)	
801 w ^b	814 w	CH ₂ rocking
816 w		
851 w		
883 w		
	855 w	SO ₃ stretching
	884 w	
1033 m	1271 ^c s	CH in-plane bending
1166 m		
1183 s		
1194 m, sh		
1270 vs		
1598 vs	1602 vs	aromatic C=C stretching
1708 vw, sh	1708 vw, sh	aromatic C=O stretching
1724 w		
1732 w, sh		
2878 s		
	2888 s	-OCH ₂ symmetric stretching
	2931 s	
2934 s		-OCH ₂ asymmetric stretching

^aSee text. ^bAbbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. ^cCurve-fitted results.

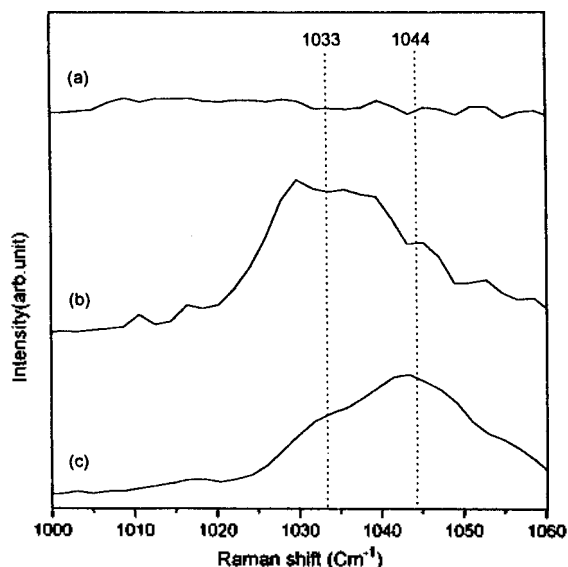


Figure 6. Raman spectra (1000-1060 cm⁻¹) of 12-4 and 12-4-salt complexes. (a) Salt-free 12-4, (b) [Li⁺]/[EO]=0.15, (c) [Li⁺]/[EO]=0.30.

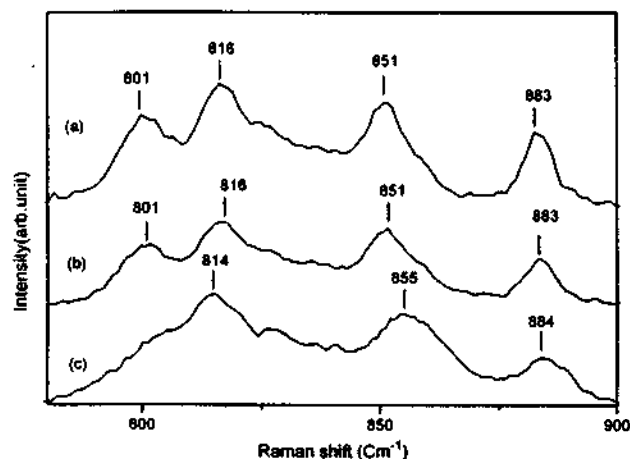


Figure 7. Raman spectra (780-900 cm⁻¹) of 12-4 and 12-4-salt complexes. (a) Salt-free 12-4, (b) [Li⁺]/[EO]=0.15, (c) [Li⁺]/[EO]=0.30.

various salt concentration, a similar behavior was observed by Hsu *et al.*³ By comparison with the calculated data, they regarded it as being due to the change in the conformation of the O-C-C-O bond to either of TGT (*trans-gauche-trans*) or TTT (*trans-trans-trans*). These spectral changes, therefore, account for a change in the conformational distributions in the coil unit implying the binding of the Li⁺ ion to the ether oxygens.

As another evidence for the change in the conformational distribution in the coil unit, we have illustrated the change of the -OCH₂ stretching bands of which symmetric and asymmetric stretching modes exist at lower and higher frequencies, respectively, in figures 8(a), (b), and (c). As salt concentration is increased the symmetric mode is decreased in intensity, but is increased in frequency, whereas, the asymmetric mode is *vice versa*. This phenomenon occurs because the salt interacts with the ether oxygens, thus it reduces the symmetry, on the other hand, increases the asymmetry of -OCH₂ vibration. These results allow us to have strong confidence that the Li⁺ ion binds to the ether oxygens in the coil unit.

Changes in Mesogenic Unit. In order to investigate whether the Li⁺ ion binds to the mesogenic unit or not, we have observed the bands belonging to the mesogenic unit. The single band at 1270 cm⁻¹ in figure 1(a) is broadened in figure 1(b) of which [Li⁺]/[EO] is 0.30. Since the band is not a single Lorentzian feature, we have curve fitted it with each component fixed in the Lorentzian curve. The curve-fitted spectrum resulted in two components at 1271 and 1283 cm⁻¹, as shown in figure 2. This seems to imply that the Li⁺ ion binds to the mesogenic unit because the 1270 cm⁻¹ band is mainly attributed to the combination of ring-carbonyl stretching, and aromatic CH in-plane bending vibrations. The reason why the single band split into two bands is possibly because the two ester functional groups, which were degenerated in energy without salt, face a different environment resulting in different energy distribution as one of them becomes the binding site to the Li⁺ ion.

To further investigate the complexation between the Li⁺ ion and the mesogenic unit, we have studied the carbonyl

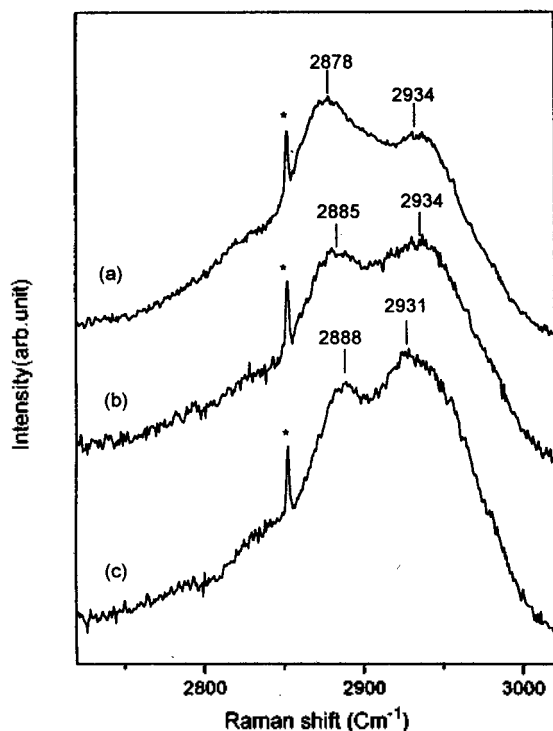


Figure 8. Raman spectra ($2720\text{--}3020\text{ cm}^{-1}$) of 12-4 and 12-4-salt complexes. (a) Salt-free 12-4, (b) $[\text{Li}^+]/[\text{EO}]=0.15$, (c) $[\text{Li}^+]/[\text{EO}]=0.30$. *Laser plasma line.

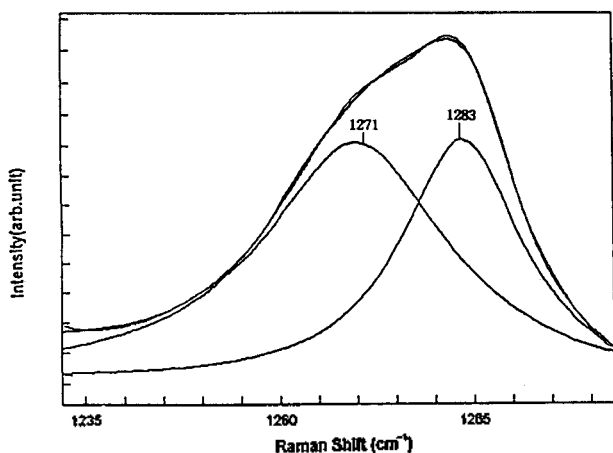


Figure 9. The curve-fitted Raman spectrum ($1232\text{--}1303\text{ cm}^{-1}$) of 12-4-salt complex ($[\text{Li}^+]/[\text{EO}]=0.30$).

stretching modes in detail as a function of $[\text{Li}^+]$ as shown in figure 10. There are two kinds of carbonyl groups within the ester groups of the mesogenic unit, but the frequencies of the carbonyl modes will be different from each other because both terminals of the ester groups have different moieties. Therefore, the Raman bands for each carbonyl stretching mode should be different to some extent. The bands at around 1724 and 1732 cm^{-1} in figure 10 are thought to be due to two different carbonyl stretching modes. In fact, it is not easy to answer the question about which frequency is assigned to which band because both the electron donating and withdrawing groups are attached alternately to each

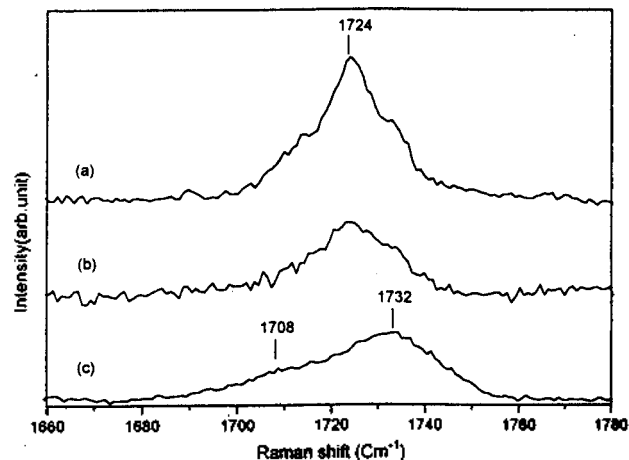


Figure 10. Raman spectra ($1660\text{--}1780\text{ cm}^{-1}$) of 12-4 and 12-4-salt complexes. (a) Salt-free 12-4, (b) $[\text{Li}^+]/[\text{EO}]=0.15$, (c) $[\text{Li}^+]/[\text{EO}]=0.30$.

other terminal of ester functional groups while influencing electron density on the carbonyl groups inversely. When the Li^+ ion binds to the mesogenic unit, the low frequency component at 1724 cm^{-1} is decreased in intensity, whereas the high frequency one remains unchanged. This fact implies that the Li^+ ion binds to one of the carbonyl groups with lower frequency. As the Li^+ ion binds to the carbonyl group, the Li^+ ion-bound carbonyl stretching band should appear to shift to a lower frequency than the 1724 cm^{-1} because the electrons around the double bond will be withdrawn to the Li^+ ion leading to a weak force constant. According to the FT-Raman results the frequency shift of about 30 cm^{-1} occurs upon binding of the Li^+ ion to the carbonyl group in TPU.⁸ We could not, however, find the corresponding band in our spectrum. It may be thought that the corresponding band exists around 1708 cm^{-1} , but its intensity is not high enough to be detectable.

In spite of the above evidence, we do not completely rule out the existence of the conformational changes in the mesogenic unit without complexation with the Li^+ ion. This is because the bands belonging to the mesogenic unit are reported to be very sensitive to the environmental changes, such as phase changes.^{10,30} Therefore, the spectral changes in the mesogenic unit in our results might have occurred not because of the complexation with the Li^+ ion, but because of the conformational changes by the intercalation of the nondissociated LiCF_3SO_3 . To confirm this idea, the comparison of the salt dependence of the spectral changes with the temperature dependence of the spectral changes in the mesogenic unit is required.

Conclusions

We employed the Raman spectroscopic technique to find the binding sites of the metal cations in the liquid crystalline oligomer. The clear assignments of the various modes of the rod-coil oligomer were made by analogy with both the coil and mesogen analogues, that is, PEGME and EHBPC, respectively. The spectral analysis of two distinct regions for each unit strongly indicates that the Li^+ ion interacts

with the coil unit through the ether oxygens, and possibly, with the mesogenic unit through the carbonyl groups. A further investigation to reveal the mechanism for the spectral changes in the mesogenic unit is currently underway by performing both the salt and temperature dependent studies.

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New Radical Allylation Reactions Using 2-Bromo-3-(phenylthio)propene and Their Application to the Synthesis of Carbocyclic Compounds¹

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A study on the application of vinyl radical cyclization *via* free radical allylation reaction in the synthesis of various carbocyclic compounds is described. In connection with this study, a new allyl transfer reagent, 2-bromo-3-(phenylthio)propene **1** is developed and it was shown that vinyl radical cyclization through free radical allylation reaction using reagent **1** provides a valuable approach to carbocyclic systems with a reactive *exo*-alkylidene moiety, which is advantageous for further transformations.

Introduction

Over the last 10 years, many free radical methods have

demonstrated their efficiency in synthetic organic chemistry and particularly free radical cyclization has emerged as one of the most important methods in the construction of a va-