

Raman and Fluorescence Studies of Thermotropic Liquid-Crystalline Oligomers with Different Type of Coils

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Raman and fluorescence spectroscopies were employed to study the coil effects on the intermolecular structure of a rod-coil liquid crystalline (LC) oligomer, the esterification products of ethyl 4-[4'-oxy-4-biphenyl-carbonyloxy]-4'-biphenylcarboxylate with poly(propylene)oxides (PPO) (DP=12) and poly(ethylene oxide)s (PEO) (DP=12). Three different vibrational modes (carbonyl, aromatic C-H, and aromatic C=C) obtained from the Raman experiment at variable temperature indicate that PPO and PEO coils induce the hydrogen bonding in a different manner. Further information about the micro-environment around the mesogenic unit obtained by fluorescence excitation spectra of P12-4 (LC with PPO coil) and 12-4 (LC with PEO coil) suggests that the mesogenic unit of P12-4 is quite different from that of 12-4 in intermolecular structure. This study supports the results obtained only from Raman spectroscopy, providing more accurate information about the intermolecular structural changes of liquid crystalline polymers at a molecular level during the phase transitions.

Key Words : Raman, Fluorescence, Liquid crystalline, Intermolecular structure, Coil effect

Introduction

Liquid crystalline polymers (LCPs) have been intensively studied for their scientific and technological interests. Among LCPs, rod-coil types have recently drawn attention, particularly in relation to their likelihood to form various kinds of supramolecules depending on chain lengths.¹⁻⁴ The LCPs based on a biphenyl ester moiety can have different microscopic structures. Most poly(ethylene oxide)s (PEO)-based LCPs result in a layered smectic mesophase,⁵ whereas poly(propylene oxide)s (PPO)-based LCPs give rise to a layered smectic C, smectic A, bicontinuous cubic, and hexagonal columnar mesophases depending on the chain lengths.⁶ Considering the fact that the physical properties of LCPs are mainly characterized by the molecular interactions between the mesogenic moieties, the molecular-based information about the coil effects on the molecular interactions between the mesogenic moieties is very important in providing an insight into the mechanism for the formation of supramolecules.⁷

Fluorescence spectroscopy is among the most widely used optical methods to study intermolecular interactions between neighboring molecules with aromatic rings. Enormous efforts have been undertaken to investigate the intermolecular structure of LCPs using the fluorescence technique by Horie *et al.*⁸⁻¹² They utilized fluorescence spectroscopy to elucidate the intermolecular interaction of biphenyl-related LC polymers. Various kinds of intermolecular ground state complex were revealed with the help of highly sensitive fluorescence technique.

Although it is highly sensitive to the intermolecular structure as to detect only small differences in the chain lengths, this method is limited in yielding information regarding the

specific sites involved in the intermolecular interactions. Vibrational spectroscopy such as Raman is considered among the most efficient tools for this purpose, providing rich information on a molecular level.¹³⁻¹⁸ In this context, we utilized both Raman and Fluorescence techniques to characterize the conformational and structural changes as site-specific and sensitive methods.

In order to study the coil effects on the intermolecular structure, we have chosen a rod-coil liquid crystalline oligomer(P12-4) with twelve PPO units as a coil and compared its results with those of 12-4 with twelve PEO units, the esterification products of ethyl 4-[4'-oxy-4-biphenylcarbonyloxy]-4'-biphenylcarboxylate with PPO (DP=12) and with PEO (DP=12). To this end three different vibrational modes (carbonyl, aromatic C-H and aromatic C=C), and the excitation profiles were monitored by Raman and fluorescence spectroscopies, respectively. The combination of two techniques should provide complementary and accurate information about the intermolecular structure in the crystalline phase.

Experimental Parts

The details of the synthesis and characterization of P12-4 and 12-4 were reported in a previous publication,^{5,6} and their chemical structures are shown in Figure 1. The crystalline to LC (K-LC) phase transition temperatures (first heating at a rate of 10 °C min⁻¹) were observed at 36.9 °C and 135.2 °C, for P12-4 and 12-4, respectively, from a Perkin Elmer DSC-7 differential scanning calorimeter (DSC) equipped with a 1020 thermal analysis controller.

The Raman spectra were obtained using a Renishaw Raman micro system 2000 with the 632.8-nm line of a HeNe laser as excitation source.^{15,16,19} The laser power at the sample

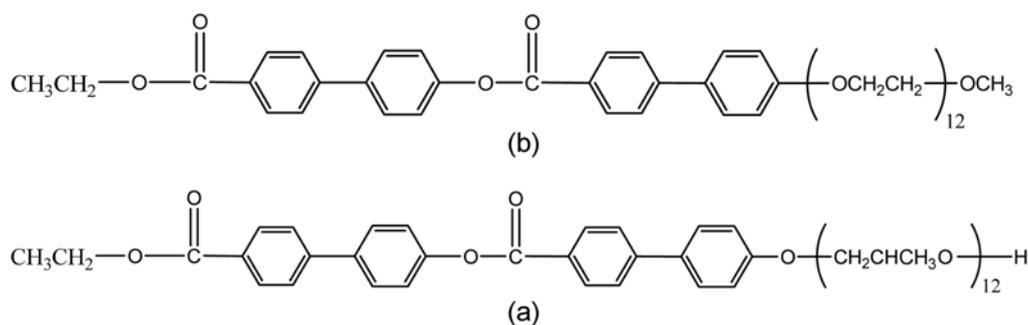


Figure 1. The chemical structures of (a) P12-4 and (b) 12-4.

was *ca.* 5 mW and the resolution of the spectra was within $\pm 2 \text{ cm}^{-1}$. Putting the samples on glass slides, the data were acquired by using a Linkam heating and freezing stage (THMSE 600) with a controller (TMS 92), and then calibrated to the silicon band at 521 cm^{-1} .

The fluorescence spectra were obtained using a Time-master (PTI)²⁰ coupled with an optical fiber suitable for measurement from the horizontal stage, THMSE 600. The reflection mode from the horizontal stage rendered us to take spectra at variable temperature while minimizing self-absorption. The fluorescence excitation was scanned while monitoring emission at 380 nm. The integration time was 1 sec. with 2 nm as a step scan.

Results and Discussion

Raman and fluorescence studies of P12-4 and 12-4 were performed to determine the intermolecular interaction at the molecular level. With the fingerprinting capability of Raman spectroscopy, the change in the specific functional groups was elaborately monitored. The complementary disclosure about the intermolecular interactions between the mesogenic units was also made by using fluorescence spectroscopy.

We first considered carbonyl modes in Raman spectra. Normally there are only two carbonyl bands in the spectra of both P12-4 and 12-4 unless intermolecular interactions exist. The two carbonyl groups in each molecule are surrounded by different environments, retaining a different force constant around the C=O bond. Of the two bands, the low wavenumber band corresponds to the C=O group between the biphenyl moieties, while the high wavenumber band corresponds to the C=O group near the ethyl terminal.¹⁶ For both P12-4 and 12-4, however, three bands, 1709, 1715, 1731 cm^{-1} for P12-4, and 1717, 1725, 1734 cm^{-1} for 12-4 were observed at low temperatures as can be seen in Figure 2, indicating the existence of intermolecular interactions in the crystalline phases.

The locations of the two free carbonyl bands for P12-4 should be nearly the same as those of 12-4 since the two molecules have the same mesogenic units. Therefore, the bands at 1715 cm^{-1} and 1717 cm^{-1} for P12-4 and for 12-4, respectively, are assignable to the C=O groups between the biphenyl moieties, whereas the bands at 1731 cm^{-1} and 1734 cm^{-1} for P12-4 and for 12-4, respectively, to the C=O groups

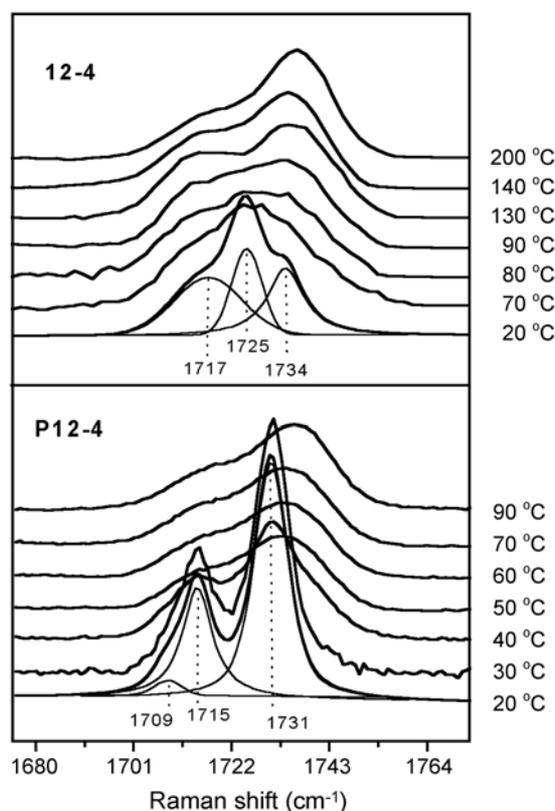


Figure 2. Temperature dependence of the carbonyl modes for P12-4 (bottom) and 12-4 (top). The three solid lines are obtained through curve-fitting of the corresponding spectrum at 20 °C.

near the ethyl terminal. Accordingly, the bands at 1709 cm^{-1} and 1725 cm^{-1} for P12-4 and 12-4, respectively, can be assigned to the hydrogen bonded carbonyl modes. Considering the fact that the C=O band shifts to lower wavenumbers upon hydrogen bonding,¹⁷ the band at 1709 cm^{-1} originates from the C=O group between the biphenyl moieties, whereas the band at 1725 cm^{-1} originates from the C=O group near the ethyl terminal.

It is noteworthy that the C=O band at higher frequency shifts abruptly around the phase transition temperature for P12-4 (compare the spectrum at 40 °C with that at 50 °C),²¹ whereas that of 12-4 shifts gradually over the entire temperature range. This seems to be mainly due to the different disruption mechanism for intermolecular interactions during

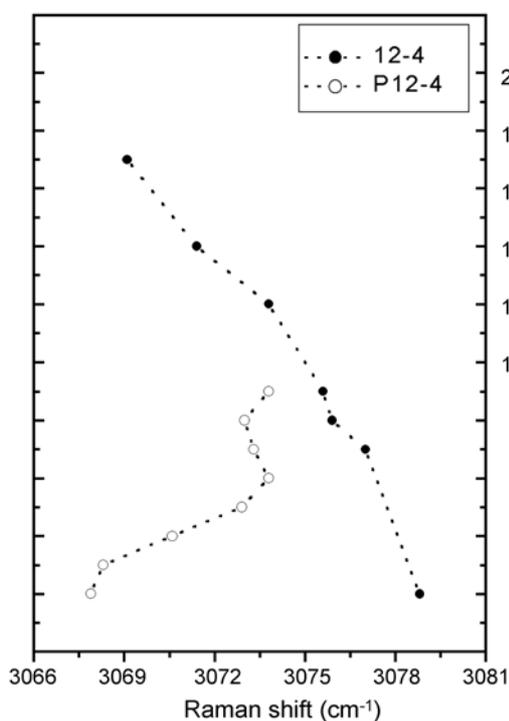


Figure 3. Temperature dependence of the C-H stretching modes for P12-4 (○) and 12-4 (●).

phase transitions. According to our previous results, the carbonyl group near the ethyl terminal was easier to rotate than the one between the biphenyl groups during the phase transition.¹⁶ Therefore, the bond rotation about the aromatic C-(C=O) is gradually followed by bond breaking, resulting in the continuous frequency shift owing to the conformational change for 12-4. On the other hand, as the hydrogen bonding is broken down, only the distance between the neighboring mesogens changed, without giving rise to bond rotation about the aromatic C-(C=O) (between the biphenyl moiety) participating in the hydrogen bonding for P12-4. Accordingly, the frequency shift is not developed above 50 °C, the phase transition temperature, which is slightly different from DSC measurement, but is reasonably acceptable.

The above argument can be clarified by the counterpart of the C=O group involved in the hydrogen bonding. This is supported by the observation of the temperature dependent behavior of the aromatic C-H stretching modes. Assuming that one of the aromatic hydrogen atoms is responsible for the hydrogen bonding, the aromatic C-H stretching mode is, then, anticipated to shift to a higher frequency upon breaking down the hydrogen bonding since the weakened C-H bond will be reinforced. The result for P12-4 showed that the frequency shift to higher wavenumbers from 3068 cm⁻¹ in the crystalline phase to 3074 cm⁻¹ in the molten is consistent with our assumption (Figure 3). The result for 12-4, however, shows the reverse direction to lower wavenumber, ruling out the hydrogen bonding with the aromatic hydrogen atoms. The downward frequency shift of this aromatic C-H stretching band from 3078 to 3069 cm⁻¹ is found to be due to expansion of the packing structure.²² The possibility of the

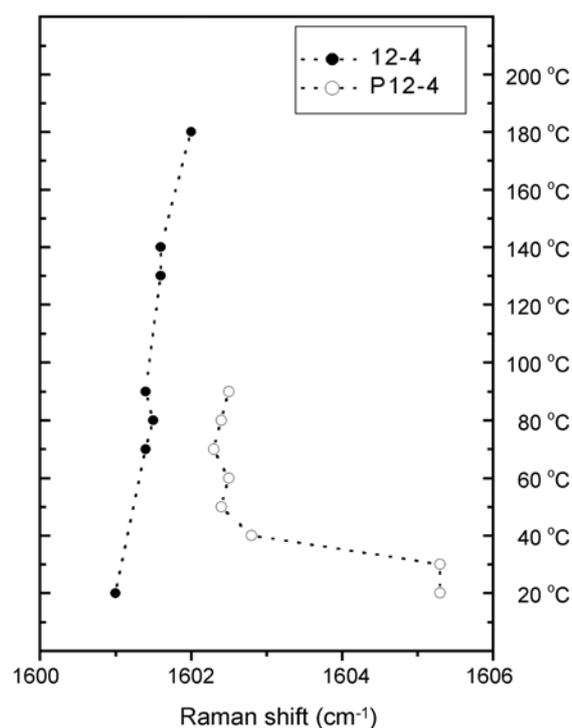


Figure 4. Temperature dependence of the C=C stretching modes for P12-4 (○) and 12-4 (●).

hydrogen bonding of the C=O group with one of the hydrogen atoms of the PEO group for 12-4 was suggested in our previous report,¹⁶ and is confirmed through the observations described above.

This can be further confirmed by observing the C=C stretching mode. The aromatic C=C band displays a downward shift in frequency for P12-4, whereas it displays an upward shift for 12-4 (Figure 4). Considering the fact that a downward shift in frequency of the C=C band is generally due to the decrease in the inter-chain force constant,^{17,18} the downward shift for P12-4 seems to be due to the decrease in the force constant about the C=C bond, probably resulting from the formation of the conjugation between the neighboring mesogens. In the crystalline phase, hydrogen bonding is formed through the carbonyl bond between the biphenyl moieties with the adjacent aromatic hydrogen atom, maintaining a certain distance between neighboring mesogens. As the hydrogen bonding is broken down at the phase transition temperature, this distance becomes closer, resulting in a π - π stacking between neighboring mesogens by either partial or full overlapping. Thus the π - π stacking causes the frequency shift to lower wavenumber since the π electrons of the benzene ring participating in the π - π stacking reduce the force constant of the C=C bond. The upward shift in 12-4 can be explained by a quite opposite interpretation. It seems that the π - π stacking formed between the biphenyl groups below the phase transition temperature becomes loosened upon reaching the phase transition temperature giving rise to the upward shift. As is the case for the aromatic C-H stretching mode, the frequency shift occurs only during the phase transition for P12-4, while it

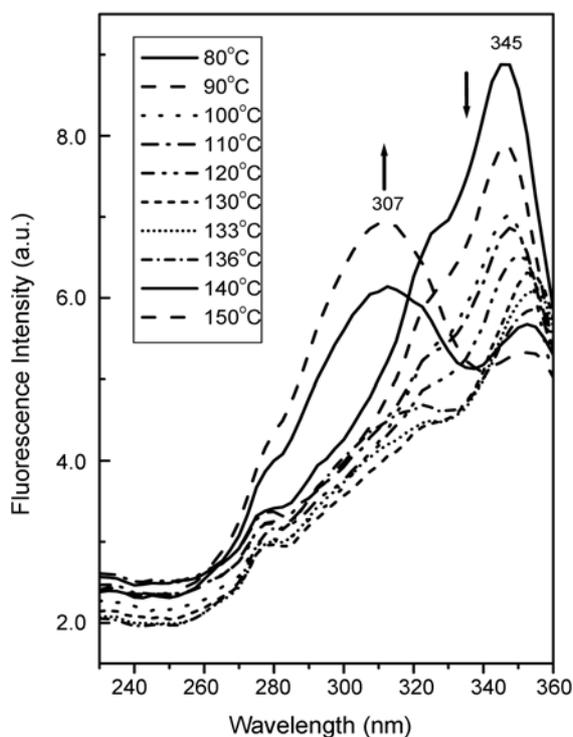


Figure 5. Temperature dependence of fluorescence excitation spectra for 12-4.

occurs monotonously with increasing temperature for 12-4.

Fluorescence excitation spectroscopy was employed to support the above arguments. The main advantage of excitation method exists in the fact that it reflects the electronic ground state configurations of the molecule and thus represents the distribution of absorbing species in the absence of structural perturbations that arise from electronic excitation.²³ Therefore, its results are comparable to Raman results, which were mostly attributed to the electronic ground state intermolecular complex. It is noteworthy to understand the features of fluorescence spectroscopy in amorphous polymer. For the thermotropic liquid crystalline polymers or oligomers, the overlapping between the mesogenic moieties in the adjacent molecules is continuously changing with increasing temperature. Consequently, the distance between the mesogenic moieties becomes closer or farther depending on the pattern of intermolecular interactions as they are broken down at the phase transition temperature. This, in turn, results in a change in a π - π stacking, thus a shift of the fluorescence excitation to either a longer or shorter wavelength.

Horie *et al.*¹² found the changes in the fluorescence profile with varying temperature in a rod-coil polyester with flexible side chains, and ascribed them to the different distance between the electron donor and acceptor groups. This is true for our molecules. The fluorescence excitation spectra for 12-4 (Figure 5) were obtained by monitoring the fluorescence emission at 380 nm. Considering the spectral pattern with respect to the temperature, the band between 340 nm and 350 nm could be attributed to the intermolecular ground-state complex (dimer) between the biphenyl and the

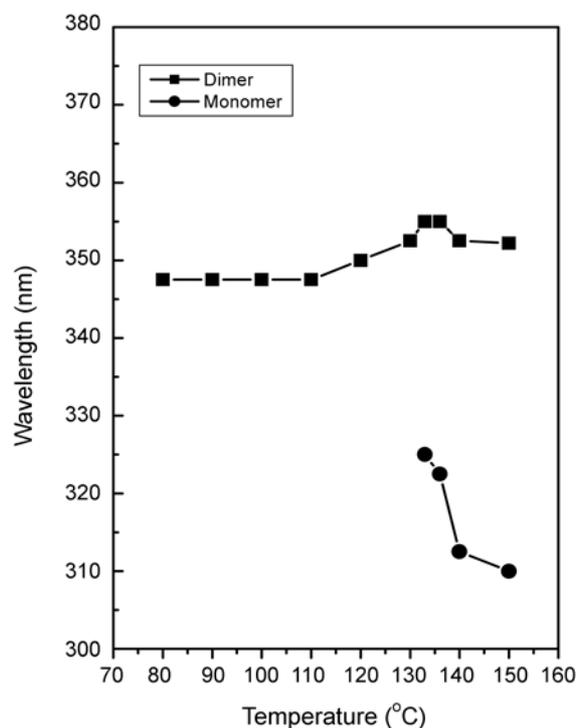


Figure 6. Temperature dependence of excitation peaks for 12-4.

ester groups in the adjacent molecular axes. The frequency shift from 345 nm to 354 nm occurred continuously before the K-LC phase transition temperature at 135.2 °C (Figure 6). This may indicate that the biphenyl moieties between adjacent molecules are getting closer to each other until the bond breaking occurs presumably through the rearrangement between the adjacent molecules. Accordingly, the conjugation between two biphenyl moieties are formed resulting in a lower excitation energy. As the temperature increased further, a new band appeared at around 307 nm while the longer one disappeared. This means that the distance between the adjacent molecules is getting farther, resulting in a monomer eventually. Horie *et al.*¹² observed the fluorescence spectrum for the monomer molecule of biphenyl or pyromellitic ester moieties at shorter wavelength than the polymer with these units. They ascribed the fluorescence spectrum at longer wavelength to the intermolecular ground state complex between the biphenyl group and the ester group. This phenomenon is quite in good agreement with our fluorescence as well as Raman studies. To further confirm that the spectrum at 307 nm is attributed to the monomer, we acquired the spectrum of 12-4 in a methyl chloride (MC) solution. As can be seen in Figure 7, the band appeared at 300 nm in a diluted solution, which is very close to 307 nm.

The fluorescence excitation profile for P12-4 is quite opposite to that of 12-4. The fluorescence excitation spectra at 2 °C interval were obtained by monitoring the fluorescence emission at 370 nm for P12-4, and displayed in the range between 240 and 350 nm as can be seen in Figure 8. As temperature increases the intensity gradually decreases,

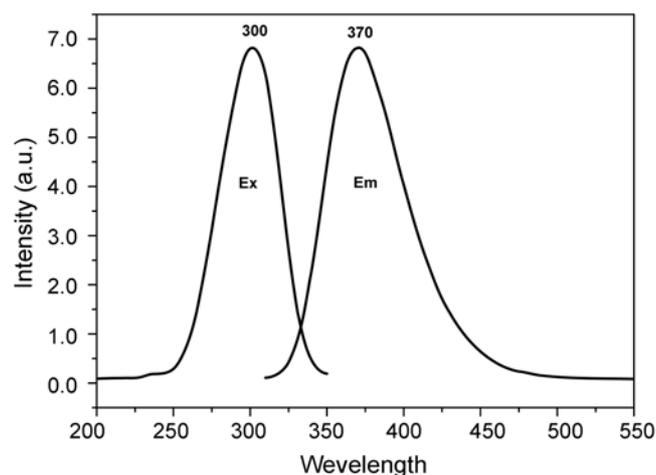


Figure 7. The spectrum of 12-4 in a methyl chloride (MC) solution.

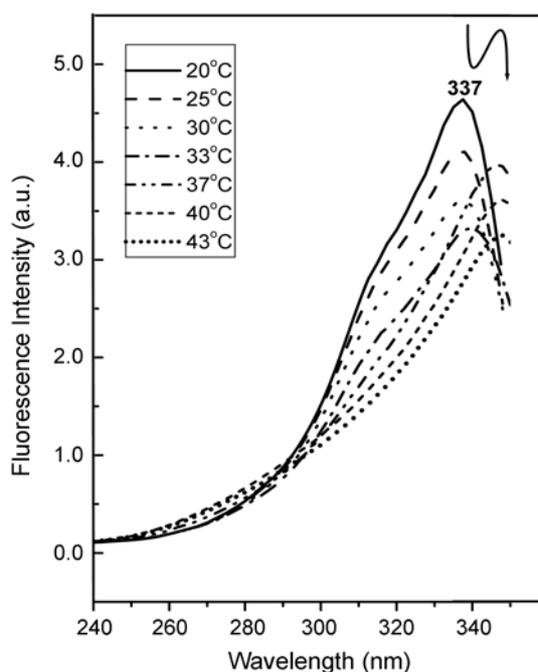


Figure 8. Temperature dependence of fluorescence excitation spectra for P12-4.

and then it abruptly goes up at 37 °C, the phase transition temperature (Figure 9). The abrupt increase in intensity at phase transition temperature is probably due to the new structure with a different quantum yield from that of crystalline phase. The discrete change in intensity may imply that a quite different structure is formed at K-LC transition as suggested in Raman results, where the C=O and aromatic C-H frequencies changed abruptly.

It is quite interesting to note that the fluorescence excitation shifts all the way to the longer wavelength with increasing temperature. This behavior is opposite to that of 12-4, which reverts from the red shift to blue shift above LC temperature. It could imply that the monomer is not obtained for P12-4 even in a relatively high temperature above the phase transition temperature, indicating the intermolecular

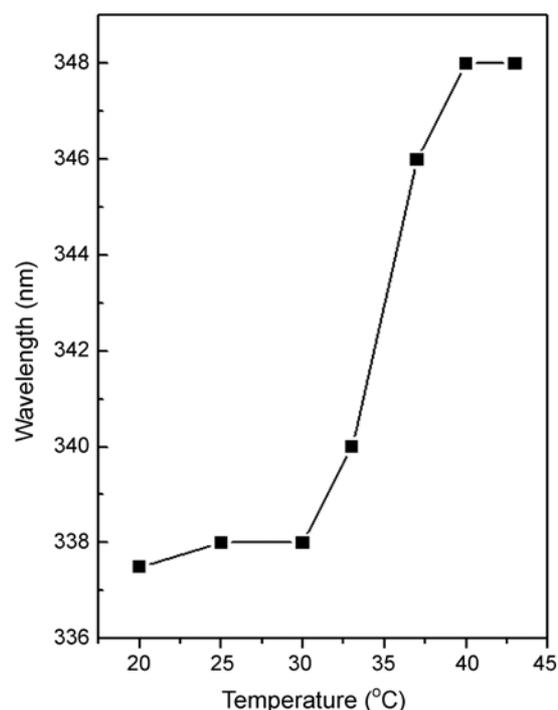


Figure 9. Temperature dependence of excitation peaks for P12-4.

ground state complex is quite different from each other. It is hard to explain the reason for not being detected the monomer form of P12-4 to the best of our knowledge.

From the Raman and Fluorescence studies we suggest the schematic diagram for the changes in the intermolecular interactions around the phase transition temperatures as shown in Figure 10.

Conclusions

The coil effects on the intermolecular structure in the crystalline phase were studied by observing the three Raman modes, C=O, aromatic C-H, and aromatic C=C. PPO and PEO coils are found to influence the intermolecular structures in a different way. The complementary results from the vibrational modes indicate that in P12-4 with PPO coils, the hydrogen bonding is induced through the carbonyl group between the biphenyl groups with the aromatic hydrogen atom of the adjacent molecule. In contrast, in 12-4 with PEO coils, the hydrogen bonding is induced through the carbonyl group near the ethyl terminal with the hydrogen of PEO coil of the adjacent molecule. Regardless of whether or not the intermolecular interaction can be assigned to a hydrogen bonding, our conclusion that PPO and PEO coils affect the molecular arrangement in a different way is still valid. The fluorescence studies also support the above arguments. The details in fluorescence excitation spectra for P12-4 and 12-4 are in good agreement with Raman data suggesting the mechanism for the structural changes during the phase transitions. These different arrangements in the crystalline phases may play an important role in making different LC structures.

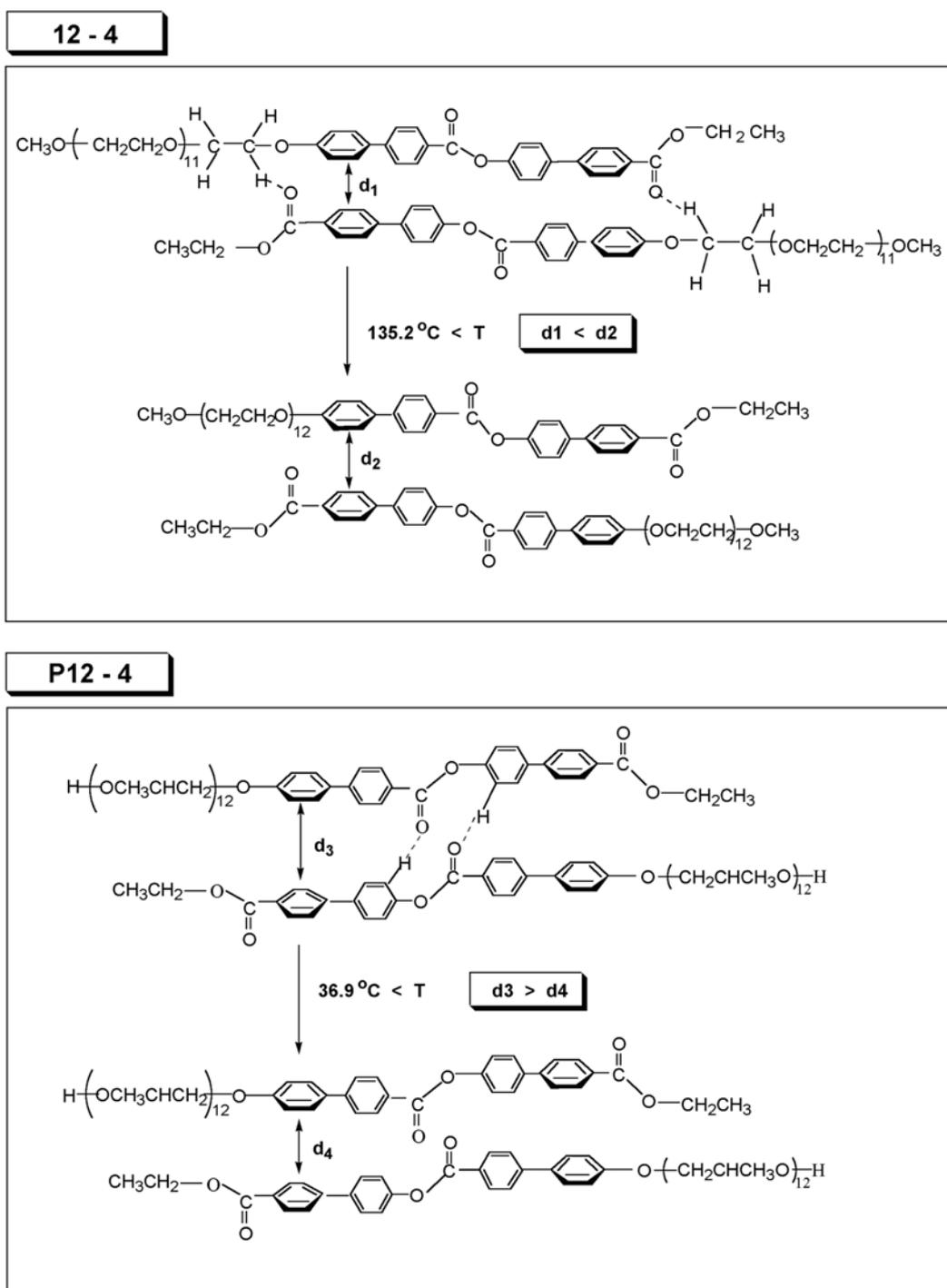


Figure 10. Schematic diagram for the intermolecular arrangements of P12-4 and 12-4 before and after the phase transition temperatures. The distance between neighboring mesogens is designated by d_i ($i = 1, 2, 3, 4$).

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