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Polarized infrared spectroscopic study on changes in molecular orientation and interaction during phase transitions of a ferroelectric liquid crystal with a naphthalene ring

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Temperature-dependent polarized infrared spectra were measured over the temperature range 105–30°C for a ferroelectric liquid crystal with a naphthalene ring (FLC-1) in the isotropic, smectic A (SmA), and chiral smectic C (SmC*) phases to investigate its molecular conformation, interactions, and alignment in each phase. It has been found, from the temperature-dependent spectral changes in the 1610–1600 cm^{-1} region, that the degree of twist between the naphthalene and benzene rings of FLC-1 changes with temperature. The peak intensity of the band at 1606 cm^{-1} containing contributions from both the benzene and naphthalene ring stretching modes begins to decrease, not suddenly but gradually, upon going from the SmA phase to the SmC* phase, suggesting that the molecular orientation of the two rings changes gradually between the two phases. The frequencies of two CH$_2$ stretching bands suggest that the disorder of the alkyl chain of FLC-1 is similar for the liquid crystal phase and the isotropic liquid phase. The splitting of the core C=O stretching band indicates that the resonance system consisting of the benzene ring and the C=O group in the core part of FLC-1 is involved in two kinds of intermolecular interaction between adjacent molecules in the liquid crystal phase.

1. Introduction

There are several kinds of liquid crystal (LC) phase, such as the nematic phase, the smectic A (SmA) phase, and the smectic C (SmC) phase. Relationships between the occurrence of each phase and molecular structures have not yet been clearly elucidated. To explore the relationships, inter- and intra-molecular interactions must be investigated at the molecular segmental level in each liquid crystal phase. The phase transitions of LCs have been investigated extensively by use of infrared and Raman spectroscopy [1–11]. In general, the molecules forming LCs have a variety of conformational and orientational states with equilibrium populations of several possible molecular conformations. Vibrational frequencies are very sensitive to the conformation and orientation of a molecule, so that one can explore the structure of LCs by means of infrared and Raman spectroscopy.

We have been investigating the mechanism of spontaneous polarization and the switching dynamics of ferroelectric liquid crystals (FLCs) by use of polarized infrared and time-resolved infrared spectroscopy [12–17]. The mechanism for the occurrence of the spontaneous polarization on phase transition is of note and needs to be elucidated in more detail. In the present study, changes in molecular orientation and interaction during the phase transitions of a FLC with a naphthalene ring (FLC-1, figure 1) in the structure are studied by polarized infrared spectroscopy. FLC-1 has two C=O groups (in the chiral part and the core part) that are highly polarizable. Thus, it is very likely that the two C=O groups are involved in the emergence of the spontaneous polarization and

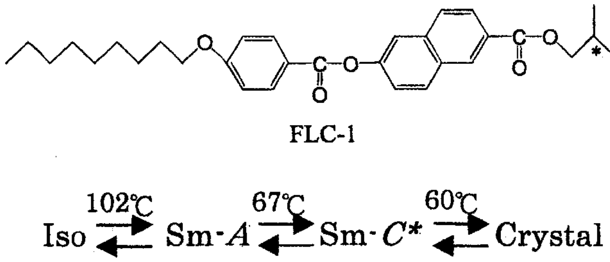

Figure 1. Structure and phase transition temperatures of FLC-1.

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in the intermolecular interactions. Furthermore, since FLC-1 has a bookshelf layer structure for films of the SmC* phase with a particular alignment, the orientation of each molecular segment of FLC-1 in the bookshelf layer structure is very interesting. For investigating the molecular structure, orientation, and intermolecular interactions of FLC-1 in the various phases, we measured the polarized infrared spectra over the temperature range 105–30°C. The novelty of the present study compared with previous infrared studies on the phase transitions of LCs lies in the detailed band assignments and band analysis. We investigated polarization angle-dependent infrared spectral variations of FLC-1 in the SmC* phase by use of two-dimensional (2D) correlation spectroscopy [16]. In that study, bands due to stretching modes of the two C=O groups were observed separately and those due to the benzene and naphthalene ring stretching modes were also observed separately. Therefore, the present study provides information on detailed temperature-dependent structural changes in each segment of FLC-1.

2. Experimental

2.1. *Sample*

The chiral ferroelectric liquid crystal, FLC-1, investigated was the same as that described in [16, 17]. Its molecular structure along with the phase transition temperatures are shown in figure 1. The sample cell was prepared by the same method as before [16].

2.2. *Polarized infrared measurements*

The measurement geometries for the polarized infrared spectroscopy have been illustrated schematically in figure 2 of [14]. Polarized infrared measurements were carried out at a 4 cm^{-1} resolution with a JEOL JIR-6500 FTIR spectrometer equipped with a JEOL IR-MAU100 microattachment and a MCT detector. The spectra were measured at $\omega = 0°$ and $\omega = 90°$ under an applied d.c. voltage of 40 V of positive polarity over the temperature range 105–30°C. Temperature control was achieved by using a Mettler FP80HT temperature controller that gives a temperature stability of better than ± 0.05°C.

3. Results and discussion

Figure 2 shows polarized infrared spectra of FLC-1 at 60°C in the parallel ($\omega = 0°$) and perpendicular ($\omega = 90°$) polarization geometries. It is found from figure 2 that the degree of orientational order in the SmC* phase is high.

Figures 3 (*a*) and 3 (*b*) show polarized infrared spectra and their second derivatives in the 1620–1590 cm^{-1} region of FLC-1 measured at $\omega = 0°$ over the temperature range 105–40°C, at intervals of 5°C. The spectrum of FLC-1 in the crystalline state at 30°C is shown in the same figure. A band at 1606 cm^{-1} is attributed to ring stretching modes of the benzene and naphthalene rings whose transition moments coincide with the molecular long axis. 2D correlation analysis revealed that the band at 1606 cm^{-1} consists of two bands at 1608 and 1604 cm^{-1} due to the ring stretching modes of the benzene and naphthalene rings [16]. The second derivatives shown in figure 3 (*b*) cannot distinguish between these two component bands. It is apparent from figure 3 (*a*) that the intensity of the band at 1606 cm^{-1} changes and its peak shifts with decrease in temperature. The intensity jump from the isotropic phase to the SmA phase is particularly

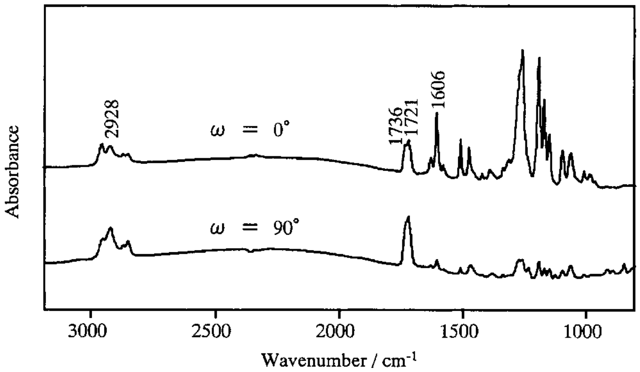

Figure 2. Polarized infrared spectra of FLC-1 at 60°C in the parallel ($\omega = 0°$) and perpendicular ($\omega = 90°$) polarization geometries.

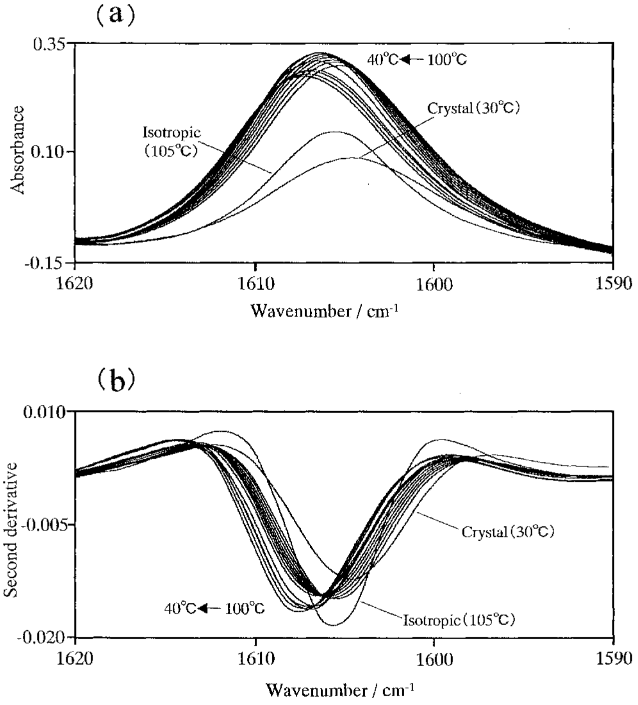

Figure 3. Polarized infrared spectra (*a*) and second derivative spectra (*b*) of FLC-1 measured over the temperature range 105–40°C and the corresponding spectra of the crystal state (1620–1590 cm^{-1} region).

notable. The peak shift is more clearly recognized in the second derivative spectra. However, the peak shift is not real, but apparent; probably, the relative intensity change of the two component bands at 1608 and 1604 cm^{-1} produces the apparent shift.

Figure 4 plots the peak intensity of the 1606 cm^{-1} band as a function of temperature over the temperature range 105 → 40°C. The plot clearly reveals that the transition from the isotropic to the SmA phase around 102°C is a first order transition, while that from the SmA to the SmC* phase is a second order transition. It is noted that the absorbance of the ring stretching band increases suddenly at 102°C. The steep change of the absorbance shows that the FLC molecules align along the rubbing direction upon transition from the isotropic phase to the SmA phase at 102°C. The absorbance increases gradually in the temperature range 101 → 65°C, suggesting that the order of the molecular alignment becomes higher with decrease in the thermal mobility. However, the absorbance decreases below 65°C, probably because the molecules begin to tilt with respect to the rubbing direction upon transition from the SmA phase to the SmC* phase. The phase transition temperatures estimated from the plot in figure 4 are in a good agreement with those measured by a polarizing optical microscopy, but they are different from those measured by differential scanning calorimetry because of supercooling.

As described above, the intensity ratio between the two bands (the apparent shift) due to the benzene and naphthalene rings changes with decrease in temperature. This result suggests that the degree of twist structure between the two aromatic rings in FLC-1 varies with temperature.

Figures 5 (*a*) and 5 (*b*) show polarized infrared spectra and their second derivates in the 3000–2820 cm^{-1} region of FLC-1 measured at $\omega = 90°$ over the temperature range 105–40°C at intervals of 5°C. The corresponding spectrum of the crystalline state at 30°C is given in the same figure. Bands at 2960, 2928, 2874, and 2856 cm^{-1} are assigned to CH_3 asymmetric stretching, CH_2 antisymmetric stretching, CH_3 symmetric stretching, and CH_2 symmetric stretching modes, respectively. It is well known that the frequencies of CH_2 antisymmetric and symmetric stretching bands are sensitive to the conformation of an alkyl chain [18, 19]. When the chain is highly ordered (*trans*-zigzag conformation), the bands appear near 2918 and 2848 cm^{-1}, respectively, and if conformational disorder is included in the chain, the bands appear at higher frequencies, i.e. 2928 and 2856 cm^{-1} depending upon the content of *gauche* conformation [18, 19]. It is important to note that the frequency (2928 cm^{-1}) of the CH_2 antisymmetric stretching band in the liquid crystal phase is almost identical with that in the isotropic liquid phase, but is significantly higher than that in the crystal phase. These observations show that the alkyl chain of FLC-1 has some *gauche*-conformers in the liquid crystal phase as in the case of the isotropic liquid phase. The polarized spectrum in the 3000–2800 cm^{-1} region changes little between the SmA and SmC* phases, suggesting that the alkyl chain does not undergo a significant conformational change in these phases.

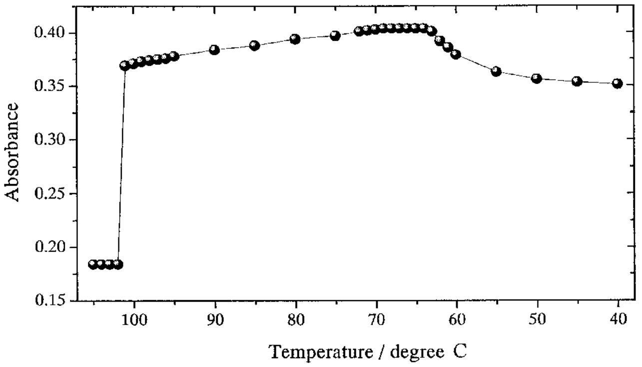

Figure 4. Peak intensity of the ring stretching band of FLC-1 near 1606 cm^{-1} as a function of temperature.

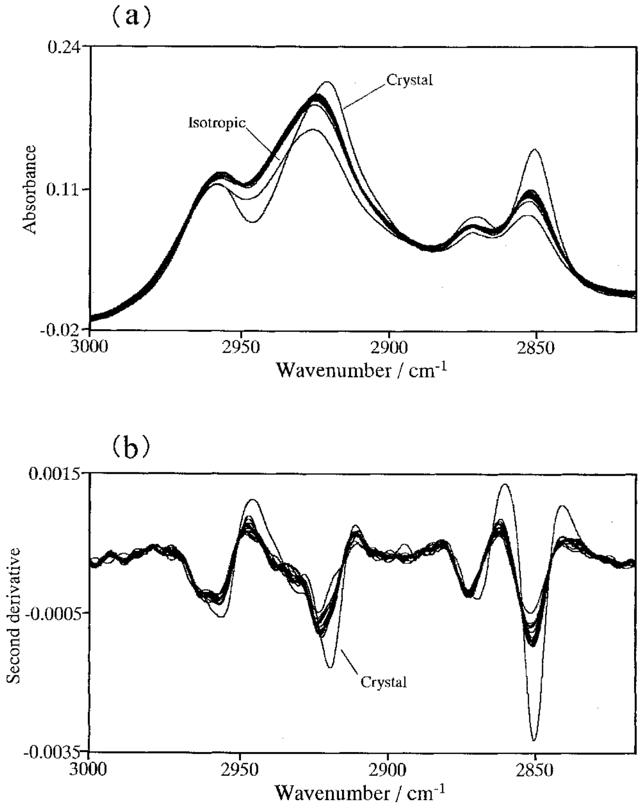

Figure 5. Polarized infrared spectra (*a*) and second derivative spectra (*b*) of FLC-1 measured over the temperature range 105–40°C and the corresponding spectra of the crystal state (3000–2820 cm^{-1} region).

In figures 6(*a*) and 6(*b*) are shown polarized infrared spectra and their second derivative spectra in the 1780–1680 cm^{-1} region of FLC-1 measured under the same conditions as those for figures 5(*a*) and 5(*b*). Again, the corresponding spectrum of the crystal state at 30°C is shown in the same figure. In a previous paper [16], we assigned bands at 1736 and 1721 cm^{-1} to C=O stretching modes of the core and chiral parts, respectively. Figure 6 gives three notable observations. First, is the appearance of three C=O stretching bands at 1733, 1726 and 1714 cm^{-1} in the crystal state, and their low frequency shifts compared with the frequencies of the C=O stretching bands of the liquid crystal states. It seems that the bands at 1733 and 1726 cm^{-1} arise from the core C=O group and that at 1714 cm^{-1} is attributable to the C=O group of the chiral segment. Second, is a small but significant shift of the C=O stretching band of the core part between the isotropic and liquid crystal states. Third, is a splitting of the C=O stretching band due to the core part in the spectra of the liquid crystal and crystal states. The low frequency shifts of the C=O stretching bands in the crystal state mean that the C=O groups are more strongly involved in resonance interactions with the benzene and naphthalene rings. Hence, the twist between the C=O group (core) and the benzene ring and that between the C=O group (chiral segment) and the naphthalene ring are smaller in the crystal state. The splitting of the core C=O stretching band in the liquid crystal and crystal states indicates that the resonance structure involving the core C=O group and the benzene ring is involved in two kinds of intermolecular interaction. At the moment the nature of the intermolecular interaction is not clear, but it is likely that there are π–π interactions between the core parts of neighbouring LC molecules. The slight difference in the π–π interactions may yield the splitting. The intermolecular interaction involving the core C=O group and the benzene ring is quite different between the liquid crystal states and the isotropic state.

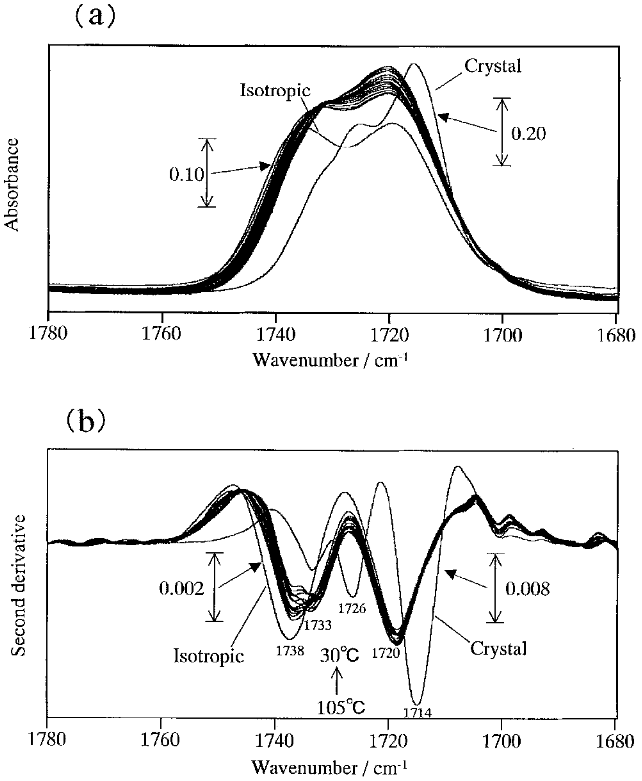

Figure 6. Polarized infrared spectra (*a*) and second derivative spectra (*b*) of FLC-1 measured over the temperature range 105–40°C and the corresponding spectra of the crystal state (1780–1680 cm^{-1} region).

4. Conclusion

In the present study, four important conclusions can be reached from the temperature-dependent polarized infrared spectral variations of bands of FLC-1 over the temperature range 150–30°C. First, the peak shift of the band near 1606 cm^{-1} suggests that the degree of twist between the naphthalene ring and the benzene ring of FLC-1 changes with temperature. Second, the alkyl chain of FLC-1 has some *gauche* structure in the liquid crystal phase, as in the case for the isotropic liquid phase. Third, the lower frequencies of the C=O stretching bands of the crystal state indicate that the resonance system including the C=O groups, the benzene ring, and the naphthalene ring in the crystal state is stronger than that in the liquid crystal state. Fourth, the splitting of the C=O stretching band due to the core part indicates that the resonance system consisting of the benzene ring and the C=O group is involved in two kinds of molecular interaction between adjacent molecules in the liquid crystal phase.

References

[1] Dvorjetski, D., Voterra, V., and Wienner-Avnear, E., 1975, *Phys. Rev. A*, **12,** 681.
[2] Fontana, F. P., and Bine, S., 1976, *Phys. Rev. A*, **14,** 1555.
[3] Venugopalan, S., and Prasad, N., 1980, *J. chem. Phys.*, **72,** 1153.
[4] Arendt, P., Koswig, H. D., Reich, P., and Pilz, W., 1981, *Mol. Cryst. liq. Cryst.*, **72,** 295.
[5] Venugopalan, S., and Rossabi, J., 1986, *J. chem. Phys.*, **85,** 5273.
[6] Pogorelov, V., and Estrela-Liopis, I., 1995, *Mol. Cryst. liq. Cryst.*, **265,** 237.
[7] Dash, S. K., Singh, R. K., Alapati, P. R., and Verma, A. L., 1997, *J. Phys. Condens. Matter*, **9,** 7809.
[8] Pogorelov, V., Pinkevich, I., Estrela-Liopis, I., and Bukalo, V., 1998, *Mol. Cryst. liq. Cryst.*, **320,** 29.

[9] Estrela-Liopis, I., Pogorelov, V., Bukalo, V., and Astashkin, Y., 1998, *Mol. Cryst. liq. Cryst.*, **320,** 45.

[10] Shao, Y., and Zerda, T. W., 1998, *J. phys. Chem.*, **102,** 3387.

[11] Dash, S. K., Singh, R. K., Alapati, P. R., and Verma, A. L., 1999, *J. Raman Spectrosc.*, **30,** 81.

[12] Czarnecki, M. A., Katayama, N., Satoh, M., Watanabe, T., and Ozaki, Y., 1995, *J. phys. Chem.*, **99,** 14 101.

[13] Katayama, N., Sato, T., Ozaki, Y., Murashiro, K., Kikuchi, M., Saito, S., Demus, D., Yuzawa, T., and Hamaguchi, H., 1995, *Appl. Spectrosc.*, **49,** 977.

[14] Verma, A. L., Zhao, B., Jiung, S. M., Shen, J. C., and Ozaki, Y., 1997, *Phys. Rev. E*, **56,** 3053.

[15] Verma, A. L., Zhao, B., Terauchi, H., and Ozaki, Y., 1999, *Phys. Rev. E*, **7,** 1868.

[16] Nagasaki, Y., Yoshihara, T., and Ozaki, Y., 2000, *J. phys. Chem. B*, **104,** 2846.

[17] Nagasaki, Y., Masutani, K., Yoshihara, T., and Ozaki, Y., *J. Phys. Chem. B* (in the press).

[18] Kamata, T., Umemura, J., Takenaka, T., and Koizumi, N., 1991, *J. phys. Chem.*, **95,** 4096.

[19] Sapper, H., Cameron, D. G., and Mantsch, H. H., 1981, *Can. J. Chem.*, **59,** 2543.