

Earlier Response of Carbonyl Groups in Electric-Field-Induced Dynamics of a Ferroelectric Liquid Crystal with a Naphthalene Ring Studied by Submicrosecond Multichannel Asynchronous Time-Resolved FT-IR Spectroscopy

Yoshihisa Nagasaki,[†] Koji Masutani,[‡] Toshiaki Yoshihara,[§] and Yukihiro Ozaki^{*,†}

Department of Chemistry, School of Science, Kwansei-Gakuin University, Nishinomiya 662-8501, Japan, Micro Science Inc., 961-1, Fussa, Fussa-City, 197-0011, Japan, and Display Laboratory, Fujitsu Laboratories Limited, Ohkubo, Akashi 674-0054, Japan

Received: November 15, 1999; In Final Form: May 22, 2000

By use of submicrosecond multichannel asynchronous time-resolved FT-IR spectroscopy, we have investigated a time-dependent response of different molecular segments during dynamical switching in the electric-field-induced phase of a ferroelectric liquid crystal (FLC) with a naphthalene ring (FLC-1). From measurements of temporal response of absorption changes of infrared (IR) bands at different time delays, we demonstrate that two carbonyl groups of FLC-1 respond first on switching the electric field and then the alkyl chain and the mesogen follow.

Introduction

Ferroelectric liquid crystals (FLCs) constitute the basis for a new branch of material science and technology.^{1–6} Since theoretical prediction and experimental confirmation of ferroelectricity in DOBAMBC (*p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate) by Meyer et al.,^{7,8} a variety of FLCs have been synthesized and characterized. An FLC in smectic-*C** (Sm-*C**) phase placed inside a cell of a few micrometers thickness may interact with cell windows and form two stable states (surface-stabilized FLC). By changing the polarity of the applied electric field, FLC molecules can be switched back and forth from one state to the other state at a fast speed in the micro- or submicrosecond range. The surface-stabilized FLCs in the Sm-*C** phase are of particular importance because of their potential applications in high-resolution flat panel displays and fast electrooptic devices.^{1–6} The electric-field-induced dynamic behavior of FLCs strongly depends on the molecular conformation and orientation freedom of different segments about the average long molecular axis because the electric field interacts with the polarization and dielectric anisotropy of the FLC molecules. For the emergence of spontaneous polarization the alkyl chain orientation with respect to the rigid core and hindered rotation of molecular segments such as carbonyl groups having a large dipole moment located near the chiral carbon are expected to play an important role.

To explore dynamics of molecular reorientation and segmental mobility of LCs, time-resolved infrared (IR) spectroscopy has been extensively employed for the past decade.^{9–31} Time-dependent intensity changes in IR absorptions can provide very useful information about the reorientation rate, conformation, and hindered rotational motions of individual segments of LC molecules. For the time-resolved IR studies on LCs, three kinds of time-resolving IR techniques, step-scan time-resolved FT-

IR,^{9–11,13,14,16,32–34} asynchronous time-resolved FT-IR,^{17–20,35,36} and ac-coupled dispersive time-resolved IR technique^{12,15,21,37,38} have been used. We have been using mainly asynchronous time-resolved FT-IR technique.^{19,20,29–31} In this technique the signal-processing assembly for time-resolving measurements can be attached to any kind of commercial FT-IR spectrophotometer.^{17,18} In addition, in principle, there is no shortest limit in time for transient phenomena to be measured. Therefore, the asynchronous time-resolving system is a powerful tool for studying repetitive fast phenomena.

Recently a novel multichannel asynchronous time-resolving system with 32 time-resolving channels was developed.^{35,36} The system enables measurements at 32 time delays simultaneously. This reduces the measuring time substantially and decreases possible damage of a sample by the stimulus. Moreover, simultaneous time resolving by the multichannel system improves the reliability of the data.

We have also employed the ac-coupled dispersive time-resolved IR technique,²¹ which allows time resolution as high as 50 ns with the minimum detectable change $\Delta A/A \sim 10^{-6}$ in the region 4000–600 cm^{-1} .^{37,38} We applied this technique to a study of submicrosecond preliminary process of electric-field-induced reorientation of a FLC, 5-(2-fluoroalkoxy)-2-(4-*n*-alkylphenyl)pyrimidine.²¹ The observed absorbance decay for a band at 1440 cm^{-1} due to a ring stretching mode of the phenylpyrimidine group indicates that the FLC molecule reorients from a stationary state with a slight delay (less than 1 μs) just after the upswing of the electric field, while counter-reorientation occurs with a delay time of a microsecond after the reverse of the electric field.²¹ It was demonstrated that the ac-coupled dispersive time-resolved technique is powerful in investigating the preliminary and counter-reorientation process of the FLC molecule by a pulse electric field.

Although time-resolved IR spectroscopy has made remarkable progress in recent years, there is a still often dispute whether all the molecular segments reorient nearly simultaneously^{20–22,26} or one particular segment reorients faster than other segments.^{29,30} The exact simultaneous reorientation is very unlikely because each molecular segment should show significantly

* To whom all correspondence should be sent. Fax: +81-798-51-0914. E-mail: ozaki@kwansei.ac.jp.

[†] Kwansei-Gakuin University.

[‡] Micro Science Inc..

[§] Fujitsu Laboratories Limited.

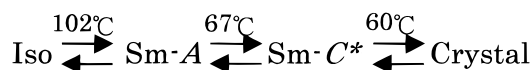
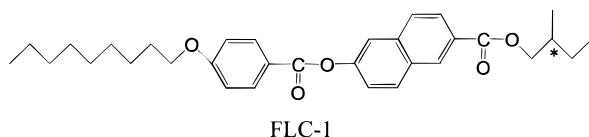


Figure 1. Structure of FLC-1 and phase transition temperature.

different response to the electric field. Probably, the rate of the reorientation of each segment is so close to each other that the technique used cannot detect the significant difference in the rate of the reorientation. The purpose of the present study is to yield clear answer to such a dispute. We have explored the dynamics of molecular reorientation and segmental mobility of a FLC in the Sm-C* phase having a naphthalene (FLC-1; Figure 1) by use of the multichannel asynchronous time-resolving FT-IR system. FLC-1 has been known to have a bookshelf layer structure for a particular alignment film in the Sm-C* phase.³⁹ The use of the novel asynchronous time-resolving system has allowed us to monitor the motion of each segment of FLC-1 at a submicrosecond range with a high signal-to-noise ratio. Our study has provided unambiguous evidence that the two carbonyl groups response earlier than other segments.

Experimental Section

Sample. The chemical structure along with the phase transition temperatures of the investigated chiral ferroelectric liquid crystal, FLC-1, are shown in Figure 1. The synthesis of FLC-1 was reported in ref 39. The sample cell consisted of two BaF₂ plates coated with conducting layer of indium tin oxide (ITO) and polyimide rubbed in one direction. The thickness between the two plates, as determined from the interference fringe pattern, was adjusted to be 1.7 μm with silicone spacers. The cell was filled from the melted sample by capillary action, heated to the isotropic phase, and then slowly cooled to a temperature in the Sm-C* phase. Temperature was controlled to an accuracy of ± 0.05 $^{\circ}\text{C}$ with the aid of METTLER FP80HT. The approximate size of the monodomain was in a several hundred μm range.

Infrared Spectroscopy. Time-resolved IR measurements were made by use of the multichannel asynchronous time-resolving FT-IR system. The details of this novel system were described in ref 35. The measurement geometries were illustrated in our previous papers.^{19,29,31} A rectangular electric field of ± 40 V and 5 kHz repetition rate was applied between the electrodes of the cell from a function generator (SONY AFG310). The gate of the multichannel system was opened for 0.5 μs after 0.5*n* (*n* = 1, 2, ..., 16) μs and after 1 + 5*m* (*m* = 0, 1, ..., 15) μs . Thus, the time-resolved spectra were measured from 0.5 to 8.0 μs at intervals of 0.5 μs and from 1.0 to 76.0 μs at intervals of 5.0 μs at a resolution of 4 cm^{-1} . As the largest intensity changes were observed when the polarizer direction was at 45 $^{\circ}$ to the rubbing direction, the time-resolved spectra were measured with this fixed position of the polarizer at 45 $^{\circ}$. In the following discussion we simply use untreated experimental data.

To separate two bands due to two carbonyl groups the time-resolved IR spectra in the 1760–1680 cm^{-1} region were subjected to curve-fitting. It was carried out by using GRAMS software. A Gaussian function was assumed for the band shapes. The baseline was approximated by a straight line between the two points at 1760 and 1680 cm^{-1} . Peak positions were assumed at 1736 and 1721 cm^{-1} based upon the second derivatives of

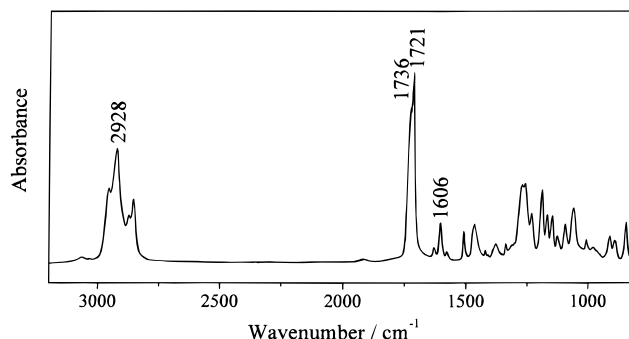


Figure 2. An infrared spectrum of FLC-1 in a solid state.

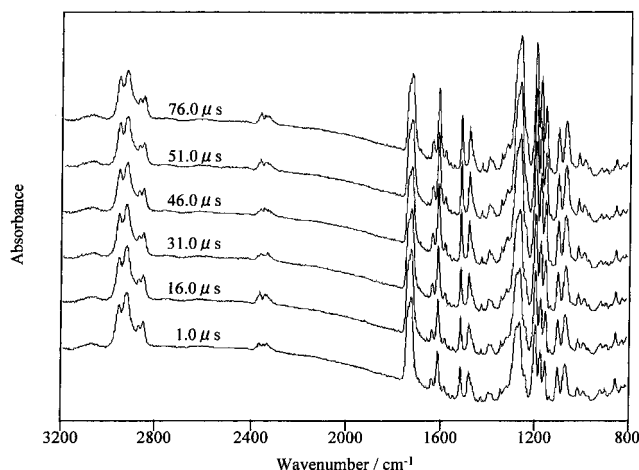


Figure 3. Time-resolved IR spectra in the 3200–800 cm^{-1} region of FLC-1 in the Sm-C* phase at 60 $^{\circ}\text{C}$ under an electric field of 40 V and 5 kHz repetition rate as a function of delay time from 1.0 to 76.0 μs .

the spectra. The bandwidths were fixed at 13 and 22 cm^{-1} for the bands at 1736 and 1721 cm^{-1} , respectively.

Results and Discussion

Figure 2 shows an infrared spectrum of FLC-1 in a solid state. Band assignments have been proposed for major bands in our previous study.³¹ The assignments for the key bands to probe switching dynamics are following: 2928 cm^{-1} ; CH₂ antisymmetric stretching, 1736 cm^{-1} ; C=O stretching (core), 1721 cm^{-1} ; C=O stretching (chiral), 1606 cm^{-1} ; ring stretching.

Figure 3 displays time-resolved IR spectra in the 3200–800 cm^{-1} region of FLC-1 in the Sm-C* phase at 60 $^{\circ}\text{C}$ under an electric field of ± 40 V and 5 kHz repetition rate as a function of delay time from 1.0 to 76.0 μs . It can be seen from Figure 3 that almost all the bands change their intensity when polarity of the field is reversed, confirming that all segments of the molecule participate in the reorientation process.³¹

In parts A and B of Figure 4 are compared time-resolved IR spectra of FLC-1 in the Sm-C* phase for the delay time at 0.5 and 8.0 μs at 40 $^{\circ}\text{C}$ under the same conditions as those in Figure 3. The difference spectrum in the 1780–1550 cm^{-1} region between the spectrum measured at the delay time of 0.5 μs and that at 8.0 μs is also shown in Figure 4C. Note that the intensities of the bands at 1736 and 1721 cm^{-1} due to the C=O stretching modes of the core and chiral parts, respectively, decrease significantly with time while those of bands in the region of 3000–2800 cm^{-1} arising from the C–H stretching modes and that at 1606 cm^{-1} due to the ring stretching modes of benzene and naphthalene rings do not show an appreciable change. This

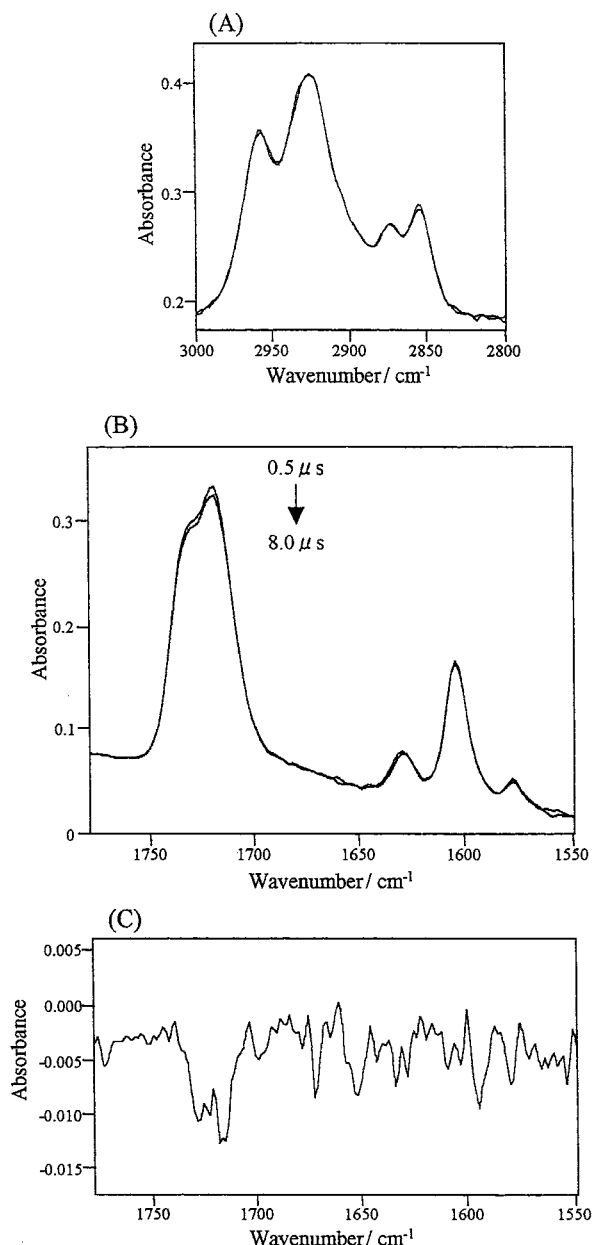


Figure 4. (A, B) Time-resolved IR spectra in the (A) 3000–2800 and (B) 1780–1550 cm⁻¹ regions of FLC-1 at 60 °C and 40 V for delay times at 0.5 and 8.0 μs. (C) Difference spectrum in the 1780–1550 cm⁻¹ region between the spectrum measured at the delay time of 0.5 μs and that at 8.0 μs.

is unambiguous evidence that the two carbonyl groups undergo earlier response on switching the electric field than other segments.

For a quantitative comparison of the reorientation rates of molecular segments, we calculated the normalized absorbance changes dAn as follows:

$$dAn = [A(t) - A(1)]/[A(3) - A(1)] \text{ (from 0.5 to 8.0 } \mu\text{s)}$$

$$dAn = [A(t) - A(2)]/[A(3) - A(2)] \text{ (from 1.0 to 76.0 } \mu\text{s)}$$

where $A(t)$ is the peak absorbance at time t , and $A(1)$, $A(2)$, and $A(3)$ are the peak absorbance values at time 0.5, 1.0, and 76.0 μs, respectively. The two bands due to the two carbonyl groups were separated by the curve-fitting method described in the Experimental section. These plots also give information about fractional reorientation of the segments of the molecule at a particular time.

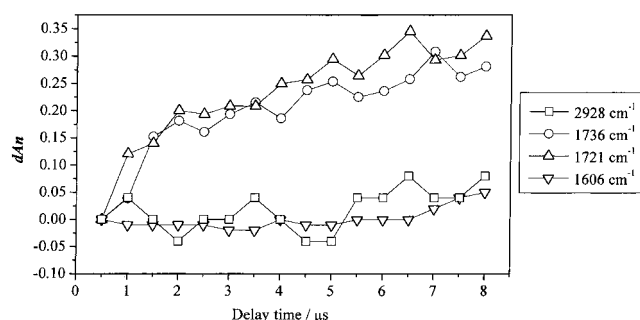


Figure 5. Time dependence of intensity changes (dAn) vs delay time from 0.5 to 8.0 μs for the IR bands at 2928 cm⁻¹ due to the CH₂ antisymmetric stretching mode of alkyl chain, at 1736 and 1721 cm⁻¹ due to two carbonyl groups, and at 1606 cm⁻¹ due to the ring stretching modes of the benzene and naphthalene rings of FLC-1 in the Sm-C* phase at 60 °C under an electric field of 5 kHz repetition at 40 V.

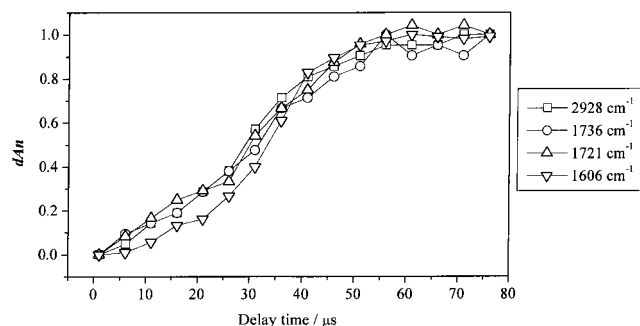


Figure 6. Time dependence of intensity changes (dAn) vs delay time from 1.0 to 76.0 μs for the IR bands at 2928 cm⁻¹ due to the CH₂ antisymmetric stretching mode of alkyl chain, at 1736 and 1721 cm⁻¹ due to two carbonyl groups, and at 1606 cm⁻¹ due to the ring stretching modes of the benzene and naphthalene rings of FLC-1 in the Sm-C* phase at 60 °C under an electric field of 5 kHz repetition at 40 V.

Figure 5 plots dAn vs delay time during the course of switching for selected bands characterizing the alkyl chain, mesogen, and two carbonyl groups at 60 °C at ± 40 V amplitudes of the voltage pulse. This figure makes it clear that the two C=O groups starts immediately on change of polarity of the applied field and after a certain time, other segments start the reorientation. This observation demonstrates the potential of new multichannel asynchronous time-resolving FT-IR system in probing molecular dynamics in a submicrosecond range.

The time-resolution and gate width of the multichannel system are both 0.5 μs³⁵ while those of the single-channel asynchronous time-resolving FT-IR system are 3.0 μs, respectively.¹⁷ Thus, the new system is much more powerful than the old one in monitoring the initial process of the electric-field induced reorientation of FLCs.

Figure 6 gives time dependence of normalized intensity change dAn of representative infrared bands vs delay time for a wider time range of 1.0–76.0 μs. The experimental conditions for Figure 6 were the same as those for Figure 5. There is no significant difference in the reorientation rate among the C=O groups (both core and chiral parts), mesogen, and alkyl chain of FLC-1. However, in the initial process, the C=O groups response slightly earlier and then the alkyl chain and mesogen follow. From these results, we infer the mechanism of the electric-field-induced reorientation process of FLC-1 as follows. Since the electric field interacts with the polarization and dielectric anisotropy of the FLC molecules, on switching the polarity of the applied electric field, the state of the hindered rotation or the orientation freedom of different segments about the average long molecular axis is changed. The effects of such

changes in the hindered rotation appear first in the two C=O groups with large polarization. In other words, the two C=O groups respond to the change of the polarity of the electric field earlier than the other segments. However, the FLC molecules do not begin the reorientation on the whole at that moment. The next, the effects extend to other segments and they start reorientation.

Thus far, the mechanism of the electric-field-induced reorientation has been explored by use of time-resolved FT-IR spectroscopy for numerous FLC and AFLC samples. Many reports claimed that all molecular segments reorient simultaneously in the course of the switching.^{20–22,26} On the other hand, other studies proved that the mesogens respond earlier as compared to the alkyl chain.^{29,30} Since each segment should have different electronic structure and properties, each should show different response rate to the electric field. Thus, it is very unlikely that exact simultaneous reorientation takes place during the course of the switching. Always one of the segments, a carbonyl group, a phenyl ring, or an alkyl chain responds earlier than the others. However, the differences in the initial response time might be very small among different segments. Probably, a few newly developed time-resolved IR systems allow one to detect such small differences.

Conclusions

The present study has showed that the multichannel asynchronous time-resolving system has great advantages in exploring repetitive fast phenomena like the dynamics of FLCs on switching the electric field. It has been found from the time-resolved IR spectra that the two C=O groups (both core and chiral parts) of FLC-1 respond first and then the alkyl chain and the mesogens follow. We currently investigate the initial response of different segments in the electric-field-induced dynamics for various FLCs by means of the new multichannel asynchronous FT-IR system and plan to report deeper insight into the electric-field-induced dynamic behavior of FLCs.

Acknowledgment. The authors thank K. Numahata and K. Nishimura (SOPAC Inc., Tachikawa, Japan) for their technical help.

References and Notes

- (1) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, *36*, 899.
- (2) Matsumoto, S.; Maruyama, A.; Hathi, H.; Kinoshita, Y.; Harai, H.; Ishikawa, M.; Kamagani, S. *Ferroelectrics* **1988**, *85*, 235.
- (3) Lagerwall, S. T.; Clark, N. A.; Dijon, J.; Clerc, J. F. *Ferroelectrics* **1989**, *94*, 3.
- (4) Dijon, J. in *Liquid Crystals, Application and Uses*; Bahadur, B., Ed.; World Scientific: Singapore, 1990; Vol. 1, p 305.
- (5) Walba, D. M. *Ferroelectric Liquid Crystals. In Advances in the Synthesis and Reactivity of Solids*; Lallouk, T. E., Ed.; JAI Press Ltd.: London, 1991; Vol. 1, p 173.
- (6) Goodby, J. W.; Blinc, R.; Clark, N. A.; Lagerwall, S. T.; Osipov, M. A.; Pikin, S. A.; Sakurai, T.; Yoshino, K.; Zeks, B. *Ferroelectric Liquid Crystals. Principles, Properties and Applications*; Gordon and Breach: Philadelphia, 1991.
- (7) Meyer, R. B. Paper presented at 5th International Liquid Crystal Conference, Stockholm, June 1974.
- (8) Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. *J. Phys. (Paris) Lett.* **1975**, *L69*, 36.
- (9) Toriumi, H.; Sugisawa, H.; Watanabe, H. *Jpn. J. Appl. Phys.* **1988**, Part 2 *27*, L935.
- (10) Gregoriou, V. G.; Chao, J. L.; Toriumi, H.; Palmer, R. A. *Chem. Phys. Lett.* **1991**, *179*, 491.
- (11) Sugisawa, H.; Toriumi, H.; Watanabe, H. *Mol. Cryst. Liq. Cryst.* **1992**, *214*, 11.
- (12) Urano, T.; Hamaguchi, H. *Chem. Phys. Lett.* **1992**, *195*, 287.
- (13) Takano, T.; Yokoyama, T.; Toriumi, H. *Appl. Spectrosc.* **1993**, *47*, 1354.
- (14) Sasaki, H.; Ishibashi, M.; Tanaka, A.; Shibuya, N.; Hasegawa, R. *Appl. Spectrosc.* **1993**, *47*, 1390.
- (15) Urano, T.; Hamaguchi, H. *Appl. Spectrosc.* **1993**, *47*, 2108.
- (16) Shilov, S. V.; Okretic, S.; Siesler, H. W. *Vibr. Spectrosc.* **1995**, *9*, 57.
- (17) Masutani, K.; Sugisawa, H.; Yokota, A.; Furukawa, Y.; Tasumi, M. *Appl. Spectrosc.* **1992**, *46*, 560.
- (18) Masutani, K.; Yokota, A.; Furukawa, Y.; Tasumi, M.; Yoshizawa, A. *Appl. Spectrosc.* **1993**, *47*, 1370.
- (19) Czarnecki, M.; Katayama, N.; Satoh, M.; Watanabe, T.; Ozaki, Y. *J. Phys. Chem.* **1995**, *99*, 14 101.
- (20) Katayama, N.; Czarnecki, M. A.; Satoh, M.; Watanabe, T.; Ozaki, Y. *Appl. Spectrosc.* **1997**, *51*, 487.
- (21) Katayama, N.; Sato, T.; Ozaki, Y.; Murashiro, K.; Kikuchi, M.; Saito, S.; Demus, D.; Yuzawa, T.; Hamaguchi, H. *Appl. Spectrosc.* **1995**, *49*, 977.
- (22) Shilov, S. V.; Skupin, H.; Kremer, F.; Gebhard, E.; Zentel, R. *Liq. Cryst.* **1997**, *22*, 203.
- (23) Czarnecki, M. A.; Okretic, S.; Siesler, H. W. *J. Phys. Chem. B* **1997**, *101*, 374.
- (24) Shilov, S. V.; Okretic, S.; Siesler, H. W.; M. A. Czarnecki, *Appl. Spectrosc. Rev.* **1996**, *31*, 82.
- (25) Hide, F.; Clark, N. A.; Nito, K.; Yasuda, A.; Walba, D. M. *Phys. Rev. Lett.* **1995**, *75*, 2344.
- (26) Kim, K. H.; Ishikawa, K.; Takezoe, H.; Fukuda, A. *Phys. Rev. E* **1995**, *51*, 2166.
- (27) Jin, B.; Ling, Z.; Takanishi, Y.; Ishikawa, K.; Takezoe, H.; Fukuda, A.; Kakimoto, M.; Kitazume, T. *Phys. Rev. E* **1996**, *53*, 4295.
- (28) Kim, K. H.; Miyachi, K.; Ishikawa, K.; Takezoe, H.; Fukuda, A. *Jpn. J. Appl. Phys., Part 1* **1994**, *33*, 5850.
- (29) Verma, L.; Zhao, B.; Jiang, S. M.; Shen, J. C.; Ozaki, Y. *Phys. Rev. E* **1997**, *56*, 3053.
- (30) Verma, A. L.; Zhao, B.; Terauchi, H.; Ozaki, Y. *Phys. Rev. E* **1999**, *7*, 1868.
- (31) Nagasaki, Y.; Yoshihara, T.; Ozaki, Y. *Phys. Chem. Chem. Phys.*, in press.
- (32) Palmer, R. A.; Manning, C. J.; Caho, J. L.; Noda, I.; Dowrey, A. E.; Marcott, C. *Appl. Spectrosc.* **1991**, *45*, 12.
- (33) Uhmman, W.; Becker, A.; Taran, C.; Siebert, F. *Appl. Spectrosc.* **1991**, *45*, 390.
- (34) Palmer, R. A.; Chao, J. L.; Dittmar, R. M.; Gregoriou, V. G.; Plunkett, S. R. *Appl. Spectrosc.* **1993**, *47*, 1297.
- (35) Masutani, K.; Numahata, K.; Nishimura, K.; Ochiai, S.; Nagasaki, Y.; Katayama, N.; Ozaki, Y. *Appl. Spectrosc.* **1999**, *53*, 588.
- (36) Nagasaki, Y.; Masutani, K.; Katayama, N.; Yoshihara, T.; Numahata, K.; Nishimura, K.; Ochiai, S.; Ozaki, Y. *Int. J. Vibr. Spectrosc.* **1999**, *3*, 5.
- (37) Iwata, K.; Hamaguchi, H. *Appl. Spectrosc.* **1990**, *44*, 1431.
- (38) Yuzawa, T.; Kato, C.; George, M. W.; Hamaguchi, H. *Appl. Spectrosc.* **1994**, *48*, 684.
- (39) Yoshihara, T.; Kiyota, Y.; Shioto, H.; Makino, T.; Mochizuki, A.; Inoue, H. *17th ILCC* **1998**, 1–74.