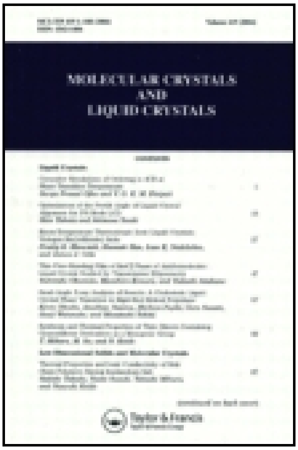

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Dynamic Behavior of a Hydrogen-Bonded Liquid Crystal Induced by the Orienting Film with a Large Dipole Moment

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Dynamic Behavior of a Hydrogen-Bonded Liquid Crystal Induced by the Orienting Film with a Large Dipole Moment

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Poly-(γ-benzyl-L-glutamate) molecules have been bonded covalently to a flat substrate *via* carbonyl end group to form an aligned dipole layer (CRA film). The authors have evaluated the electric influence of the CRA film on the dynamic change of the hydrogen-bonded liquid crystalline complex of 4-hexyloxybenzoic acid and 4-nonylpyridine (6OBA-9Py) by means of time-resolved infrared spectroscopy. Using the CRA film as an orienting film for 6OBA-9Py, the absorbance change of the complex when burst electric field was applied had many steps in response to the change of its sign. Moreover, the movement of the 6OBA-9Py complex was induced by an external electric field, not only in the direction of the complex long axis but also in that of the complex short axis. This characteristic dynamic behavior of the 6OBA-9Py complex was due to the weak hydrogen bonding.

Keywords: hydrogen bonding; CRA film; time-resolved infrared measurement; dynamic behavior; nematic; hydrogen-bonded liquid crystal

INTRODUCTION

Poly-(γ-benzyl-L-glutamate) (PBLG) molecules have been bonded covalently to a flat substrate *via* carbonyl end group to form an aligned dipole layer (PBLG-CRA film). Using this PBLG-CRA film as an orienting film for 4-pentyl-4'-cyanobiphenyl (5CB), the 5CB molecules in the vicinity of the CRA film can respond more rapidly to an applied electric field than in the case of using a rubbed polyimide film and they are responsive at frequencies in the MHz region.[1] The CRA film is considered to have a dynamic orienting force that can be switched off and on with the application and removal of the electric field.[2] However, the response of 5CB molecules in the bulk is scarcely accelerated because the 5CB molecules there are not influenced by the CRA film.

Kato and co-workers have reported that supramolecular liquid crystalline complexes can be obtained due to the molecular self-assembly of carboxylic acid and pyridine units through intermolecular hydrogen bonding.[3] The complex consisting of 4-alkoxybenzoic acid, operating as H-bonding donor, and 4-alkylpyridine, serving as H-bonding acceptor, shows a nematic phase near room temperature.[4] The intermolecular hydrogen bonding is of nonionic type with a double minimun potential energy, which is confirmed by infrared measurement.[5] Generally, if liquid crystals are themselves ionic compounds or if ionic impurities exist in a liquid crystal cell, the effective internal electric field is reduced owing to the formation of an electric double layer. However, since the hydrogen-bonded liquid crystalline complexes as described above are nonionic compounds, they are expected to be applicable as materials for nematic liquid crystal display devices.

The authors have reported that the hydrogen-bonded liquid crystalline complex of 4-hexyloxybenzoic acid and 4-nonylpyridine (6OBA-9Py) shows a nematic phase near room temperature and the complex in the vicinity of the CRA film responds more rapidly to an external electric field than in the case of using a rubbed polyimide film. Furthermore, the response of the complex in the bulk layer is also accelerated by the CRA film and it becomes responsive at frequencies in the MHz region. This dynamic behavior of the complex in the bulk layer is quite different from that of 5CB.[6]

In the present study, the authors have evaluated the electric influence of the CRA film on the dynamic change of the 6OBA-9Py complex by means of time-resolved infrared spectroscopy.

EXPERIMENTAL SECTION

Preparation of PBLG-CRA Film

PBLG-CRA film was preparaed by the method given in Ref 1.

Preparation of a Hydrogen-Bonded Liquid Crystal Cell

4-Nonylpyridine was prepared using the method of Comins and Abudullar.[7] The equivalent amounts of 4-nonylpyridine (9Py) and 4-(hexyloxy)benzoic acid (6OBA) were mixed, heated to the isotropic state, and then cooled to room temperature. The liquid crystal cell was prepared by a typical method. In order to clarify the contribution of the orienting film for 6OBA-9Py to the complex's response to an applied electric field, three kinds of liquid crystal cells were prepared as follows: Cell A and B employed the PBLB-CRA film as the orienting film for the complex. The opposite substrate for cell A was coated with a rubbed polyimide film (AL 1501 for thin film transistor (TFT) liquid crystal displays, JSR Corporation) that possessed a unidirectional static orienting force. As for cell B, the opposite substrate was coated with a nonrubbed polyimide film that did not possess an orienting force. Cell C had two rubbed polyimide films arranged antiparallel to each other. The cell gap was adjusted with a spacer powder of 6 μm which was mixed with an epoxy adhesive agent. 6OBA-9Py was injected into the cell in the isotropic state.

Evaluation of response of 6OBA-9Py to an applied electric field

The block diagram of the system for AC-coupled dispersive time-resolved infrared spectroscopy is given in ref 8. It consists of a dispersive infrared spectrometer, a photoconductive MCT detector, an ultra low noise preamplifier, a main amplifier, a digital sampling oscilloscope, and a computer. The preamplifier is AC-coupled to the MCT detector and amplifies only the AC signal induced by the applied electric field generated by a multifunctional synthesizer and an amplifier. High sensitivity of 10^{-6} in the absorbance change, which is sufficiently high for precise observation of the orientation of liquid crystal molecules, is achieved with a time resolution of 10 μs. The digital sampling oscilloscope is used for the measurement of the time response of a certain infrared band at a fixed wavenumber which corresponds to an individual motion of the corresponding functional group.

RESULTS AND DISCUSSIONS

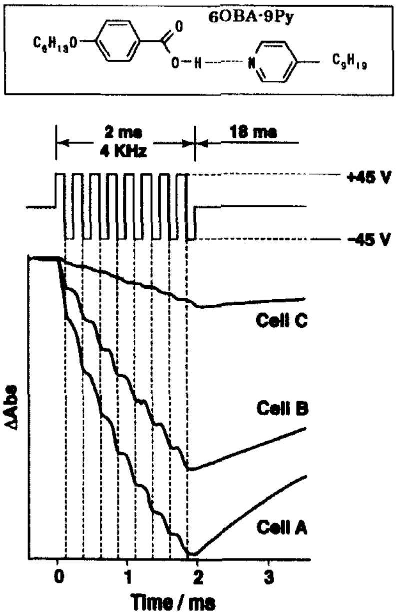

FIGURE 1 Absorbance change at 1605 cm-1 to burst electric fields of 2ms width in the cases of using cells A, B, and C.

The dynamic behavior of the individual functional group can be observed separately by the time-resolved infrared measurement. Common time responses to an applied electric field were measured for functional groups in the rigid part of the liquid crystal molecule, indicating that they move synchronously in the electric field like a rigid rod.[8] In the case of 6OBA-9Py complex, the ring mode (CC stretch) of the phenol and pyridine units (1605 cm^{-1}) was selected as the probe to monitor the motion of the complex in the direction of the complex long axis. The time-resolved infrared measurement was carried out, keeping the cell temperature at 52 °C. The complex exhibited a stable nematic phase at that temperature.

The movement of 6OBA-9Py complex in the bulk layer can be monitored by measuring the time response of the 1605 cm^{-1} band to the applied electric field of much higher voltage than the threshold voltage. Figure 1 shows the absorbance change of 6OBA-9Py complex to burst electric field of 2ms width (+45 V: -45 V=1:1, repetition rate 4 kHz, interval of burst electric field 18 ms). The movement of the complex was estimated to be no more than several degrees in angle. The absorbance change of cell A was about 1.4 times as large as that of cell B and 6.6 times as large as that of cell C at the same voltage. Interestingly, the response curves of the complex had many steps in response to the polarity change of the electric field. In particular, the steps in the response curve became large and sharp when the CRA film was used as the orienting film.

Generally, nematic liquid crystal molecules which have large dipole moment are located in positions symmetrically inverted to each other so as to minimize unfavorable dipolar repulsion and are responsive to an applied electric field mainly due to dielectric anisotropy ($\Delta\varepsilon$). In the case of 5CB, the response curve to burst electric fields was very smooth and no steps could be observed even when the CRA film was used. Therefore, the authors consider that the structural strain of 6OBA-9Py complex was generated in the dynamic state and responded to an external electric field due to its induced dipole moment, and the characteristic dynamic behavior was assisted by the dipole moment of the CRA film

In order to clarify the dynamic change of the 6OBA-9Py complex in response to an applied electric field, the authors chose the cell C which had two rubbed polyimide films arranged antiparallel to each other. The dichroic ratio was estimated to be about 4:1 based on the ring mode (CC stretch + CH bend) of the phenol group (1165 cm^{-1}), which was measured by FT-IR spectroscopy (Bio-rad FTS-60A) with a resolution of 4 cm^{-1} at 52 °C. The dichroic ratio of the complex is higher than that of 5CB in the same cell.

Time-resolved infrared measurement was performed at several fixed wavenumbers using the polarized IR light, parallel or perpendicular to the rubbing direction. Figure 2 shows the absorbance change at (a) 1605 cm^{-1} and (b) 1165 cm^{-1} bands in response to burst electric field of 2ms width (voltage; 10V, 20V, 30V, plus : minus =1:1, repetition rate 4 kHz, interval of burst electric field 138 ms) at 52 °C. The resolution was 12 cm^{-1}. Although the absorbance change perpendicular to the rubbing direction was about one-hundredth as large as that parallel to the rubbing direction, it strongly suggests that the motion of the phenol unit and pyridine unit has the component in the direction of the complex short axis.

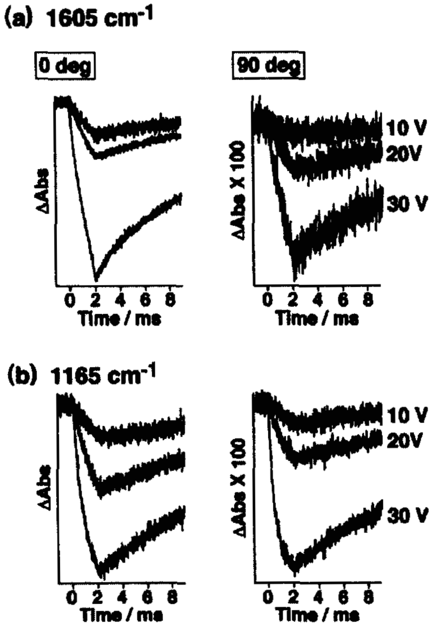

FIGURE 2 Absorbance change at (a) 1605 cm^{-1} and (b) 1165 cm^{-1} bands in response to burst electric field of 2ms width. 0 degree and 90 degree represent the rubbing direction and the direction perpendicular to that respectively.

Figure 3 shows the corresponding absorbance change at (a) 1850 cm^{-1} and (b) 1700 cm^{-1} bands when the electric field was applied. 1850 cm^{-1} band is assigned to the hydrogen bonding mode (OH stretch) between benzoic acid unit and pyridine unit.[5] The SN ratio was lower than that in the cases of 1605 cm^{-1} and 1165 cm^{-1} because the absorbance of the hydrogen bonding was much broader than the resolution. As for this band, the absorbance change perpendicular to the rubbing direction was observed similarly, which was about one-fiftieth as large as that parallel to the rubbing direction. On the other hand, the absorbance of the carbonyl stretching band (1700 cm^{-1}) scarcely changed even when the electric field of 30 V was applied.

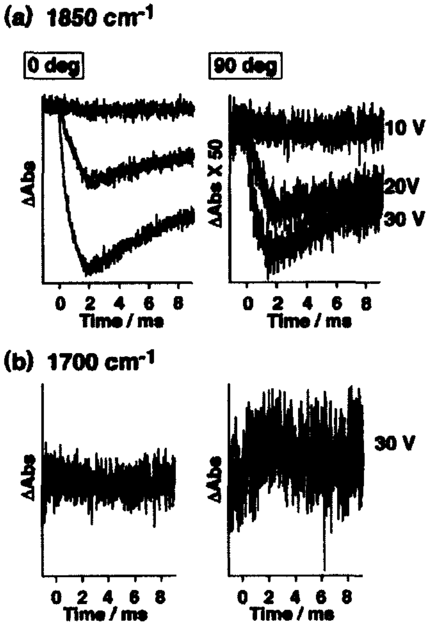

FIGURE 3 Absorbance change at (a) 1850 cm^{-1} and (b) 1700 cm^{-1} bands in response to burst electric field of 2ms width. 0 degree and 90 degree represent the rubbing direction and the direction perpendicular to that respectively.

CONCLUSION

The authors investigated the dynamic behavior of the individual functional group of 6OBA-9Py complex separately by the time-resolved infrared measurement. The complex showed dynamic behavior quite different to that of 5CB. The phenol unit, the pyridine unit, and the hydrogen bonding responded to an external electric field, not only in the direction of the complex long axis but also in that of the short complex axis. On the other hand, the motion of the carbonyl group was scarcely observed when the other parts of the complex had already started to move. These facts indicate that the structural strain of the complex was induced by an applied electric field and the complex could not be located in positions symmetrically inverted to each other when the electric field was applied. However, this induced dipole moment was considered to be small because the response curve of the complex was very smooth and distinct steps could not be observed in the case of the cell which had two rubbed polyimide films arranged antiparallel to each other. On the other hand, using the CRA film, the response curves of the complex had many steps in response to the polarity change of the electric field because the dipole moment induced by the electric field became large under the influence of the CRA film. Therefore, the authors conclude that the characteristic dynamic behavior of the 6OBA-9Py complex was caused by structural strain around the weak hydrogen bonding and was strongly assisted by the dipole moment of the CRA film.

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