Terahertz spectroscopy in smectic phases of a bent-core molecule

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The dynamics of a bent-core molecule in two smectic phases is studied using terahertz (THz) spectroscopy, which enables us to observe some rapid molecular motions and segmental motions reflecting intermolecular interactions. The isotropic liquid, liquid crystal and crystal phases of the bent-core liquid crystal P-8-PIMB are clearly distinguished by THz spectra. Unexpectedly, the transmittance in the B3 phase, which has been assigned to either a highly ordered smectic or crystal phase from results of x-ray diffraction analysis, is almost the same as that in the switchable liquid-crystalline B2 phase. This suggests that the molecular dynamics in the B3 phase is liquid-crystal-like on this time scale.

In the study of molecular dynamics, absorption peaks due to different vibrations of various chemical groups are observed in the middle infrared region, where information on intramolecular conformation and dynamics is obtained. On the other hand, collective macroscopic motions, such as co-operative molecular rotation and fluctuation, are observed in the millimeter-radio-wave region by nuclear magnetic resonance and high-frequency dielectric spectroscopy. Since the terahertz (THz) range corresponds to an intermediate regime, some rapid individual molecular motion and segmental motion reflecting intermolecular interactions are expected to be detected. Recently, THz spectroscopy has undergone significant development with the improvement in femtosecond pulse lasers and detectors, such as a bolometer. In this respect, time-domain far-infrared spectroscopy [1] and THz imaging [2,3] have been extensively studied.

The first study of the THz spectroscopy of liquid crystals was carried out and published twenty years ago. In that work, the far-infrared spectra of the crystal, nematic, isotropic, and solution phases of PAA and MBBA were measured, and the intermolecular modes in these phases were discussed [4]. Subsequently, only a very few studies of the THz spectroscopy of liquid crystals were carried out [5,6]. In the present paper, the application of THz spectroscopy to the analysis of a bent-core liquid crystal is reported. Particular attention is paid to the B3 phase, which is currently considered as one of the least known bent-core phases and is tentatively assigned to a highly ordered smectic or crystal phase. By comparing the spectra of the B3 phase with those in the other phases, i.e., B2, isotropic, and crystal, we discuss the difference in dynamics between the phases and conclude that the dynamics in the B3 phase is definitely different from that in the crystal phase, but is quite similar to that in the B2 phase.

The sample used was consisted of a prototype bent-core

molecule, P-8-PIMB [7], whose chemical structure and phase sequence are shown in Fig. 1. The sample was introduced into ~1.6° wedge-type sandwich cells with cell gaps from 0 to 188 μm to diminish the interference fringes. 100-μm-thick quartz plates were used as substrates of the cells. Among several THz spectroscopy techniques, we chose a FTIR spectrometer (Jasco FTIR660 plus) with a specific detector (Si bolometer). The wave number resolution was set to 2 cm^{-1} and the signal was accumulated 50 times. Far-infrared light was obliquely incident at 18° to diminish the interference fringes. The sample cells were set in a hand-made hotstage to control their temperature. Since the position at which temperature is monitored by a platinum thermoresister is slightly different from the sample position, the actual temperature is significantly different from the DSC data obtained. The transition temperature difference determined from the DSC data and texture observation is about 10 K. Hence, phase transition temperature in each cell was determined by texture observation.

Figure 2 shows the typical far-infrared (THz) transmittance spectra in each phase of P-8-PIMB. The transmittance T was normalized by the transmitted signal of an empty wedge cell T_0. Unfortunately, interference fringes are superimposed on the observed spectra despite the use of oblique incidence and wedge cells. Hence, all the transmittance spectra were renormalized by that of the sample cell at 50 °C (crystal phase). The normalized results are shown in Fig. 3. In the crystal phase, the transmittance is almost independent of temperature, although the transmittance between 40 and 80 cm^{-1} slightly decreases with increasing temperature. However, it drastically changes at the phase transition to the B3 phase; the decrease in transmittance from 20 to 80 cm^{-1} is clearly observed. This result suggests that the molecular motion corresponding to this frequency range would occur in the B3 phase. Strictly speaking, transmittance slightly de-
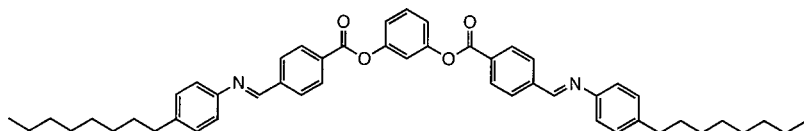
P-8-PIMB : Iso 158.1 B2 139.9 B3 72.2 Cryst.

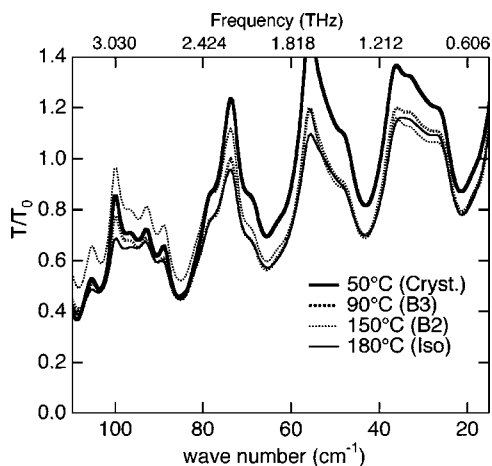FIG. 1. Chemical structure and phase sequence of P-8-PIMB.

FIG. 2. Typical transmittance spectra of P-8-PIMB in each phase. Transmittance T is normalized by that of the empty cell, T_0.

creases with increasing temperature within the B3 phase.

On the other hand, at the phase transition from B3 to B2, transmittance intensity and spectral shape hardly change, and remain unchanged within the B2 phase. Therefore, we conclude that the molecular dynamics corresponding to this frequency range is almost the same in the B2 and B3 phases. At the phase transition to the isotropic liquid phase, the spectral shape markedly changes again. The transmittance intensity at

wave numbers larger than 50 cm^{-1} increases compared with those in that B2 and B3 phases. Moreover, at wave numbers larger than 80 cm^{-1}, the transmittance intensity is larger than that in the crystal phase. Although the scattering from microdomains with sizes comparable to the wavelength of far-infrared light is considered to contribute to the decrease in transmittance in the B2 and B3 phases, the result for the isotropic liquid supports the notion that the decrease in transmittance in the B2 and B3 phases is caused by the absorption due to molecular motions, and not due to such scattering.

In summary, it has been shown that three phases (liquid, liquid crystal, and crystal) exhibit different molecular dynamics in the THz region. At $\sim$80–100 cm^{-1}, the absorption in the B2, B3, and crystal phases is stronger than that in the isotropic liquid phase, being assigned to rapid molecular motions related to intermolecular interactions, due to the appearance of macroscopically anisotropic order in the three phases. On the other hand, the absorption at $\sim$40–80 cm^{-1}, which is observed in the isotropic, B2 and B3 phases, corresponds to a liquid-like molecular motion under weak and isotropic interactions with neighboring molecules. The most important result concerns the spectrum in the B3 phase. The B3 phase has been believed to be either a highly ordered smectic phase or a crystal phase because of a two-dimensional in-plane order, as observed by wide-angle x-ray diffraction [7–10]. However, the present result suggests that the molecular dynamics of the B3 phase on the THz scale is
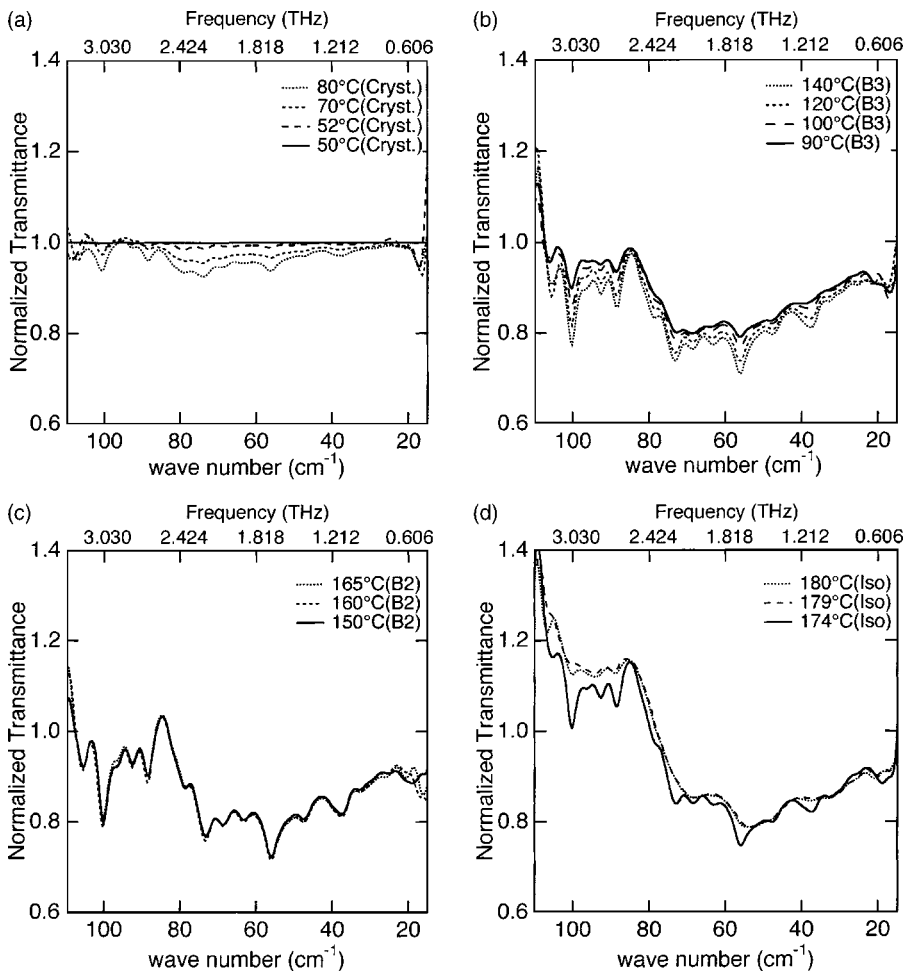

FIG. 3. Normalized transmittance spectra at various temperatures of P-8-PIMB in the (a) crystal, (b) B3, (c) B2, and (d) isotropic liquid phases. Normalization was carried out by dividing each spectrum by that at 50 °C.

not crystal-like but liquid-crystal-like. For the dynamics of the B3 phase, Salfetnikova *et al.* [11] carried out dielectric measurements, and insisted that it is improbable that the B3 phase is a classical crystalline modification from a dynamical point of view. Our results support their interpretation though the frequency ranges in their work and ours are different. The assignment of each THz transmittance peak to a particular molecular dynamics could not be realized, and is a subject for future study. For this purpose, it is necessary to measure the spectra of homologous series of compounds and compare the results in light of molecular dynamics calculation.

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