Infrared Electroabsorption Spectroscopic Study of Association Structures of 5CB in the Solution, Isotropic Liquid and Nematic Liquid Crystal States

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The association structures of 4-*n*-pentyl-4'-cyanobiphenyl (5CB) in the solution, isotropic liquid, and nematic liquid crystal states have been studied by infrared electroabsorption spectroscopy. In a 0.5 mol dm^{-3} carbon tetrachloride solution, the determined value of dipole moment of 5CB (4.9D) agrees excellently with a literature value (4.85D) for monomer, indicating that the 5CB molecule exist as a monomer. Monomeric response of the 5CB molecule to the external field has also been found for the isotropic liquid state. For the nematic phase, marked deviation from the monomeric response has been found, showing the domain formation of the 5CB molecules. The size dependence of the domain response to the applied electric field has also been elucidated.

Study of molecular association is essential for understanding the properties of liquid crystals, since intermolecular interactions play major roles in the formation of the liquid crystal phase. Molecular association of 4-*n*-pentyl-4'-cyanobiphenyl (5CB, a prototype molecule forming nematic liquid crystal) has been studied in the bulk, in non-polar solvents and in inert matrices by infrared spectroscopy, calorimetry, dielectric measurement and light scattering.[1–4] X-ray diffraction study[5] suggested the domain formation of 5CB in the nematic liquid crystal phase. We have been studying the association structures of 5CB using Raman and infrared spectroscopy in diluted solutions.[6] Despite these intensive studies, the association structures of 5CB are not fully understood.

In the present study, we use infrared electroabsorption spectroscopy in order to shed more light on the association structures of 5CB in the solution, isotropic liquid and nematic liquid crystal states. We apply a sinusoidal wave of electric field to the sample and detect the change of the infrared absorption by the AC coupled technique using a lock-in amplifier.[7] Figure 1 shows the infrared absorption and electroabsoption spectra of 5CB in a 0.5 mol dm^{-3} carbon tetrachloride solution. Only the CN stretch band region is shown in the figure. The absorbance change ΔA of the CN stretch band of 5CB, whose transition moment is parallel to the permanent dipole moment, is given by the following formula;[7]

$$\Delta \mathrm{A}/\mathrm{A} = -\gamma^2/(\gamma^2 + 6) \qquad (1)$$

where A is absorbance, γ is the dipolar interaction parameter $\gamma = \mu E/kT$, μ is the dipole moment of 5CB, E is the applied electric field (V/m), k is the Boltzmann constant, and T is temperature. Using this equation, we are able to determine the value of dipole moment from the observed value of $\Delta A/A$, if the applied electric field E is known. In the present experiment, the acetone molecule was used as a standard for determining E. The dipole moment of acetone in a 0.5 mol dm^{-3} carbon tetrachloride solution was measured to be 2.2D using the same cell. The correction factor was obtained by comparing this observed dipole moment with the literature value($\mu = 2.72$D).[8] For 5CB in a 0.5 mol dm^{-3} carbon tetrachloride solution, a dipole moment of 4.9D is obtained. This value agrees excellently with the monomer dipole moment (4.85D) in the literature.[9] We therefore conclude that all the 5CB molecules exist as monomers in a 0.5 mol dm^{-3} carbon tetrachloride solution. A similar value, 5.0D, is also obtained for a 1.0 mol dm^{-3} carbon tetrachloride solution.

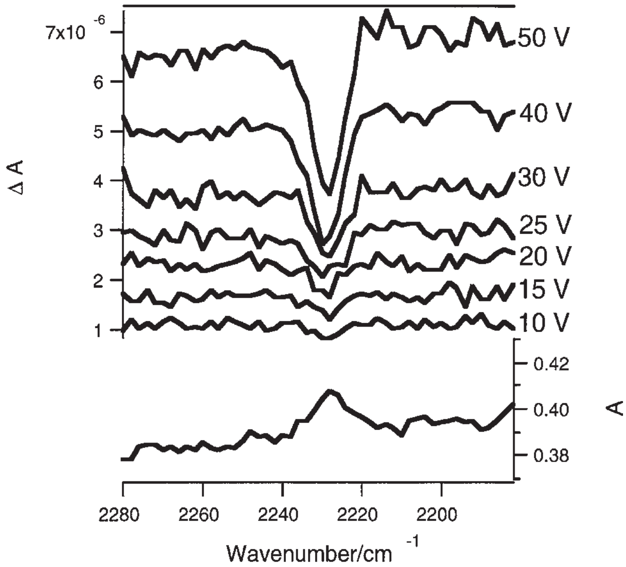

Figure 1. Infrared electroabsorption(upper) and absorption (lower) spectra of 5CB in carbon tetrachloride (0.5 mol dm^{-3}).

The monomeric response of the 5CB molecule to the applied electric field also manifests as a quadratic dependence of ΔA on E, as is expected from Equation (1). We first performed an experiment for a 1.0 mol dm^{-3} carbon tetrachloride solution, for which a nice quadratic dependence of ΔA on E was obtained (Figure 2), in harmony with the dipole moment measurement. We then proceeded to temperature controlled experiments for neat 5CB. For the isotropic liquid, the measured ΔA changes linearly with E^2 (Figure 3-a). This result shows that the response of the isotropic liquid is predominantly due to monomer 5CB. For the nematic phase (Figures 3-b and 3-c), deviation from the quadratic dependence is evident; the observed points are fitted with exponential functions for guide to eyes in Figures 3-b and 3-c. 5CB molecules in the nematic phase are thought to form domains and the interaction of the liquid crystal with the applied electric field occurs through the polarizability anisotropy of the domain rather than the dipole moment of the molecule. It is highly likely that the deviation from the quadratic dependence of ΔA on E is due to the domain formation in the nematic phase. Above the

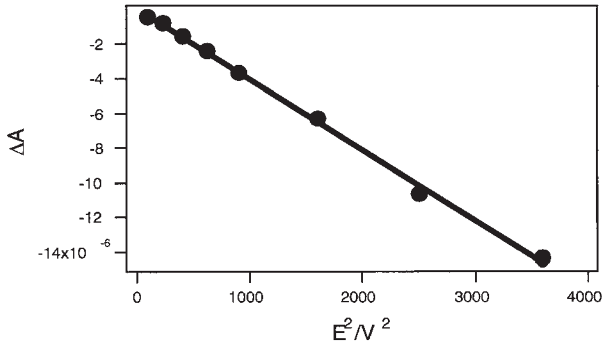

Figure 2. Relation between the absorption change ΔA and the square of the electric field E^2 for 5CB in carbon tetrachloride (1.0 mol dm^{-3}).

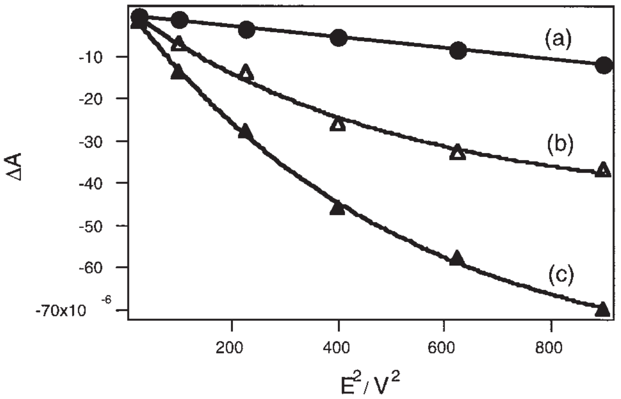

Figure 3. Relation between the absorption change ΔA and the square of the electric field E^2 for neat 5CB. (a) isotropic phase (48-51 °C), (b) nematic phase (28-32 °C), (c) nematic phase (22-25 °C).

nematic-isotropic transition point, the size of domain decreases and the 5CB molecules start to respond to the applied electric field as monomers. However, not all the 5CB molecules can respond as monomers. In fact, the dipole moment calculated from Equation (1) is 5.8D for the isotropic liquid state, which is significantly larger than the monomer value. The apparent larger dipole moment is indicative of the contribution of the domain response to the observed ΔA signal.

Figure 4 shows the temperature dependence of $\Delta A/A$ of 5CB at a constant electric field (20 V). The in-phase signal (●) and the out-of-phase signal (▲) are shown separately. The in-phase signal has the same phase as that of the applied sinusoidal electric field, while the out-of-phase signal has the 90 ° shifted phase. When the signal has the same phase as that of the applied electric field, only the in-phase signal is detected. The out-of-phase signal appears only when the response has a delay from the applied field. As seen in Figure 4, the in-phase and out-of-phase signals show different behaviors with temperature. The in-phase signal continuously decreases across the nematic-isotropic phase transition, while the out-of-phase signal suddenly disappears above the transition temperature. This observation is successfully interpreted in terms of the size dependence of the domain response. While the intensity change with temperature can also be explained by temperature dependent order parameter in the nematic liquid crystal state, the delayed response is more likely to be related to the domain size. With increasing temperature, the domain size decreases and the response becomes faster giving smaller out-of-phase signal. Above the transition temperature, the domain size is small enough to follow the applied electric field without delay. The remaining small-size domains cause the in-phase signal which is larger than that expected from the monomer response. As temperature further increases in the isotropic liquid state, the domain size becomes still smaller and the monomer response starts to dominate, as already shown in Figure 3-a.

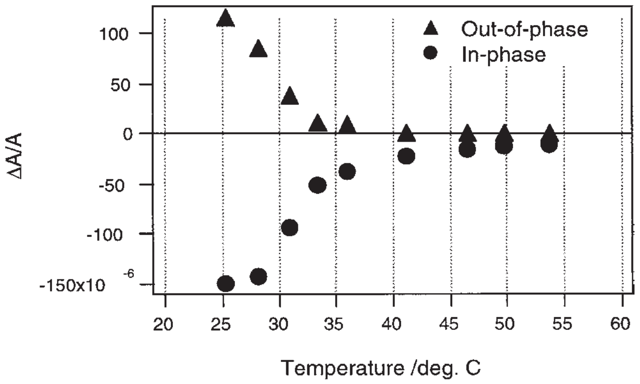

Figure 4. Temperature dependence of $\Delta A/A$ of neat 5CB at 20 V. ▲; out-of-phase signal, ●; in-phase signal.

In this way, the present study has provided direct spectroscopic evidence for the association structures of 5CB molecules in the solution, isotropic liquid and nematic liquid crystal states and their distinct response behaviors to the applied external electric field.

References and Notes

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