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Communication

Inversion of self-diffusion anisotropy by chemical substitution in smectic A liquid crystals as evidenced by PGSE experiment combined with a quadrupole-coil rotation

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Abstract

A technique of pulsed-field-gradient spin-echo (PGSE) NMR combined with a quadrupole-coil rotation was applied to the study of anisotropic self-diffusion in smectic A liquid crystals. Diffusion anisotropy was found to be inverted by chemical substitution of the terminal groups in homologous compounds: Namely, the diffusion across the layer is faster for the cyano compound, whereas the diffusion within the layer is faster for the trifluoromethoxy compound.

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1. Introduction to the experimental method

Pulsed-field-gradient spin-echo (PGSE) nuclear magnetic resonance is a powerful method for the study of dynamics in condensed matter [1] since it probes translational motion of molecules selectively, without being affected by vibrational or rotational motions. Because of this advantage it has been widely applied to the studies of dynamics of molecules in liquids or of rapidly diffusing species in disordered materials [1]. However, applications of this technique to strongly dipole-coupled spin systems with short T_2 or to the study of slow and anisotropic self-diffusion are still challenging works because combined techniques of line-narrowing, pulsing of sharp and intense field gradients (FG), and two-dimensional FG generation are necessary [2–7].

We reported a novel PGSE spectrometer [8] specifically designed for the measurements of slow and anisotropic self-diffusion, by realizing (i) intense and homogeneous FG of 12 T m^{-1} by a quadrupole coil and

a high quality current stabilizer, and also realizing (ii) a mechanism that each of the sample cell and the quadrupole coil is rotated from the axis of the external field. The diffusion anisotropy is measured in combination with the magic-angle orientation (MAO) technique.

This paper reports an application of this technique to discriminate the properties of two smectic A (S_A) liquid crystals. Experimentally obtained rotation patterns of the self-diffusion coefficient tensors revealed clear difference for the two liquid crystals.

The geometrical feature of the quadrupole coil is shown in Fig. 1. The coil current is applied along the y -axis and the coil is rotated about this axis. If the rotation angle of the quadrupole coil is denoted by ϕ , the FG components depend on ϕ in such a way that

$$\frac{\partial B_z}{\partial z} = \frac{2\mu_0 I}{\pi a^2} \sin 2\phi = \frac{2\mu_0 I}{\pi a^2} \cos \left(2\phi - \frac{\pi}{2} \right), \quad (1)$$

$$\frac{\partial B_z}{\partial x} = \frac{2\mu_0 I}{\pi a^2} \cos 2\phi = \frac{2\mu_0 I}{\pi a^2} \sin \left(2\phi - \frac{\pi}{2} \right). \quad (2)$$

Here, a is the coil radius, I is the coil current, and μ_0 is the vacuum permeability.

The translational self-diffusion in smectic A (S_A) liquid crystals is characterized by two independent diffusion coefficient tensor components, D_{\parallel} , the diffusion

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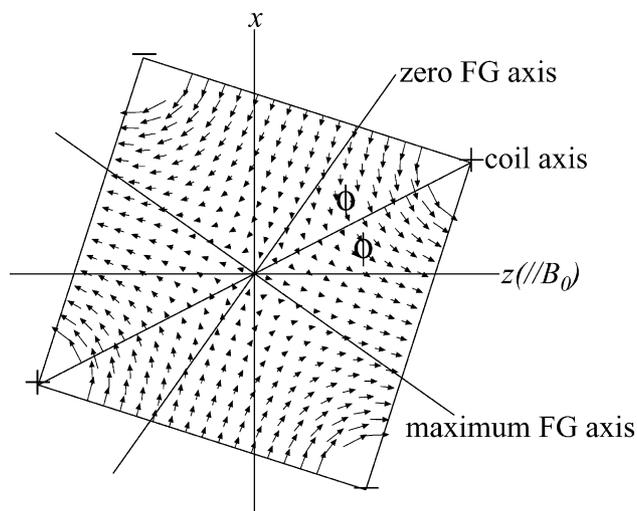


Fig. 1. The quadrupole coil. The main external field is applied along the z -axis. The quadrupole coil is placed so that the current leads are located along the y -axis crossing the xz -plane at equally distant four points on the circle of radius a . The signs $+$ and $-$ at the coil position indicate the directions of the current along $+y$ and $-y$, respectively. The coil rotation angle is denoted by ϕ . The two-dimensional distribution of the generated magnetic field is also shown by small arrows. Note that all the arrows on the axis at $2\phi - \pi/2$ from z (maximum FG axis) are parallel to the main external field, while the arrows are all perpendicular to z on the axis at 2ϕ from z (zero FG axis).

coefficient component parallel to the director (average orientation axis), and D_{\perp} , the component perpendicular to the director. In other words, D_{\parallel} describes the diffusion across the smectic layers, while D_{\perp} is related with the diffusion phenomenon within the layer.

One can obtain a field-aligned S_A liquid crystal sample where the director lies along the field axis (z -axis) by applying a static magnetic field in the nematic (N) phase and then cooling gradually to the S_A phase. For such a sample, fine structures of the ^1H NMR line are caused mainly by the homonuclear pairwise dipolar interaction within the ring protons, and are not averaged because of the significant anisotropy in molecular rotation. Therefore the splitting of the dipolar doublet is proportional to $(3\cos^2\theta - 1)/2$, where θ is the angle between the director and the z -axis. One can therefore eliminate the dipolar splitting by turning the sample axis so that the director makes the magic-angle (Θ_M) from the z -axis (MAO). The effect of MAO is demonstrated in Fig. 2. Fig. 2a shows the free induction decay (FID) of the on-grown smectic A liquid crystalline sample CBOOA, namely, at $\theta = 0$, and Fig. 2b shows the FID at $\theta = \Theta_M$. See Section 4 for the acronyms of the compounds and the liquid crystalline phases. It is understood that the dipolar fine structure is eliminated and the line-narrowing is achieved by MAO.

If the diffusion measurement is carried out in the magic-angle configuration, $\theta = \Theta_M$, then the observed diffusion coefficient is given by

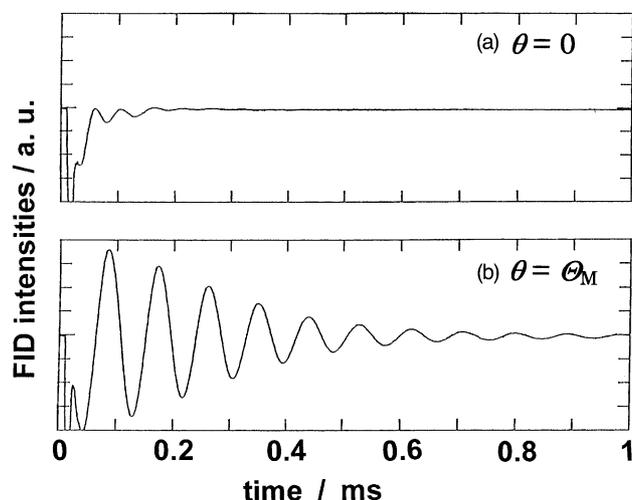


Fig. 2. Effect of magic-angle orientation (MAO). The upper trace (a) shows the free induction decay (FID) of CBOOA in the S_{Ad} phase at $\theta = 0$, namely, in the field-aligned condition. The lower trace (b) shows the FID after rotating the sample by magic-angle, namely, at $\theta = \Theta_M$.

$$\begin{aligned} D_{\text{obs}}(\phi) &= D_{\parallel} \sin^2(2\phi - \Theta_M) + D_{\perp} \cos^2(2\phi - \Theta_M) \\ &= \frac{1}{2}(D_{\parallel} + D_{\perp}) - \frac{1}{2}(D_{\parallel} - D_{\perp}) \cos(4\phi - 2\Theta_M). \end{aligned} \quad (3)$$

When the coil angle ϕ is varied, the $D_{\text{obs}}(\phi)$ oscillates with a period of $\pi/2$, with an amplitude of $(D_{\parallel} - D_{\perp})/2$. Eq. (3) tells that $D_{\text{obs}}(72.4^\circ) = D_{\parallel}$ if we place the quadrupole coil at the angle, $\phi = \Theta_M/2 + \pi/4 = 72.4^\circ$. If, on the other hand, we place the coil at $\phi = \Theta_M/2 = 27.4^\circ$, then we obtain $D_{\text{obs}}(27.4^\circ) = D_{\perp}$.

2. Results

The ϕ -rotation patterns of the self-diffusion coefficients are shown in Fig. 3 for CBOOA (open circles, the cyano derivative) and TFOBOOA (filled circles, the trifluoromethoxy derivative). The experiment was conducted at 77°C (S_{Ad} phase) for CBOOA and at 95°C (S_A phase) for TFOBOOA.

A most striking fact is that the phases of the sinusoidal angular oscillations are inverted between the two compounds. Namely, $D_{\parallel} > D_{\perp}$ for CBOOA, whereas $D_{\parallel} < D_{\perp}$ for TFOBOOA. Both results are reproduced well by Eq. (3) and thus the values of D_{\parallel} and D_{\perp} are determined by fitting. The results are summarized in Table 1 and the sinusoidal curves in Fig. 3 are drawn by these fitted values. The observed diffusion anisotropy for CBOOA, $D_{\parallel}/D_{\perp} = 2.1$, means that diffusion across the layers is faster than that within the layer, while for TFOBOOA the fact, $D_{\parallel}/D_{\perp} = 0.35$, means that diffusion within the layer is much faster.

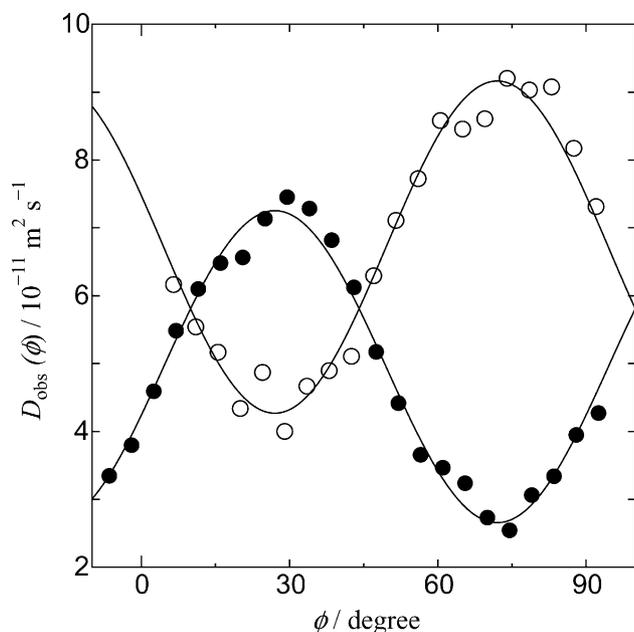


Fig. 3. Angular rotation pattern of the anisotropic self-diffusion coefficient components for CBOOA (○) and TFOBOOA (●). The experiment was conducted at 77 °C (S_{Ad} phase) for CBOOA and at 95 °C (S_A phase) for TFOBOOA. The solid curves are drawn by Eq. (3) with the parameters given in Table 1. The experimental data at the angles of 72.4° and 27.4° correspond, respectively, to D_{\parallel} and D_{\perp} .

Table 1
Observed self-diffusion coefficient components

Compounds	Substituents	D_{\parallel} (m ² s ⁻¹)	D_{\perp} (m ² s ⁻¹)	D_{\parallel}/D_{\perp}
CBOOA	CN	9.2×10^{-11}	4.2×10^{-11}	2.1
TFOBOOA	CF ₃ O	2.5×10^{-11}	7.2×10^{-11}	0.35

3. Discussion

It is interesting that only the replacement of the terminal polar group brings about a drastic change in the diffusion properties. Generally, the relationship $D_{\parallel}/D_{\perp} > 1$ has been observed for nematic liquid crystals and the typical value of D_{\parallel}/D_{\perp} is two [7]. On the other hand, the relationship, $D_{\parallel}/D_{\perp} < 1$, has been observed for smectic liquid crystals with distinct layer structures. The present experimental results show that the S_{Ad} structure of CBOOA is highly disordered like the nematic phase from the viewpoint of diffusion, while TFOBOOA has a liquid crystalline phase with a conventional S_A structure.

Generally, the intermolecular interaction is dominant along the short axis for liquid crystalline molecules of a rod-like shape. This explains the emergence of the S_A phase at low temperature, because the layer structure guarantees the energetic stabilization caused by the side-by-side intermolecular interactions. On the other hand, at higher temperatures, entropic terms that describe translational motions become important in the free energy

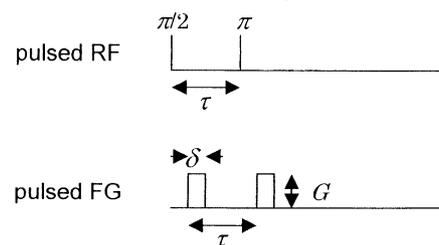
expressions of liquid crystalline phases. The conventional S_A structure becomes unstable at high temperature because the translational motions are more or less restricted to within the layers. This is because the N phase, which is characterized by the entropic gain by three-dimensional diffusion and the energetic loss by reduced lateral interactions, dominates at high temperature.

The S_{Ad} structure found for the cyano derivative (CBOOA) is a variation of the S_A liquid crystal, where a partially interdigitated structure has been reported [9]. Interdigitation takes place because of strongly polar and conjugated nature of the cyano group. This intermolecular correlation obstructs the formation of rigid layers, and will be the origin of the nematic-like diffusion as observed in the present experiment. It is thus expected that the S_{Ad} phase of CBOOA becomes unstable at low temperature, because of high translational entropy and less intermolecular interactions. The peculiarities caused by the strongly polar and conjugated nature of the terminal cyano group are related also with the various interesting properties of CBOOA, such as absence of higher order reflection in the X-ray diffraction in the S_{Ad} phase [10], anomalous critical phenomena at the nearly second order S_{Ad}/N phase transition [11], and the thermotropic reentrant phase transition, N–S_{Ad}–N, at high pressure [12].

4. Experimental

The instrumentation was reported in our previous papers [8,13]. The quadrupole coil was placed in an iron-cored electromagnet. The ¹H Larmor frequency was set at 55 MHz and a 16 channel versatile pulse generator

(a) two-pulse echo sequence



(b) three-pulse sequence (stimulated echo)

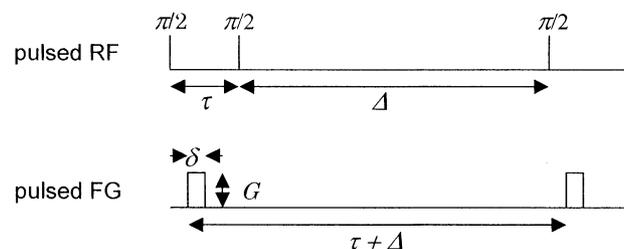


Fig. 4. Pulse sequences for (a) two-pulse spin echo, and (b) three-pulse stimulated spin echo. Pulse-modulated radio frequency (RF) fields and the field gradients (FGs) are shown schematically in each figure.

[13] was used. Spin-echo pulse sequences are shown in Fig. 4. The Stejskal–Tanner two-pulse method, $\pi/2-\tau-\pi-\tau$ [14] schematized in Fig. 4a, was used for CBOOA, while the three-pulse stimulated echo method, $\pi/2-\tau-\pi/2-\Delta-\pi/2-\tau$ [15] as in Fig. 4b, was used for TFOBOOA. Typically, the time intervals were set at $\tau = 2$ ms and $\Delta = 10$ ms. The echo intensities were recorded as functions of the FG intensities. The FG pulse balances were optimized by observing the spin echo of siloxane and the FG intensities were calibrated by measuring the scalar diffusion coefficients of water and glycerol for each method.

The line-narrowing by the method of MAO is shown in Fig. 2. The free induction decay (FID) signal in Fig. 2a is taken at the original orientation, $\theta = 0$, for the field-aligned S_{Ad} liquid crystal CBOOA. Fig. 4b shows the FID taken at $\theta = \Theta_M$ after the sample is rotated by Θ_M (the magic-angle). It is readily recognized that the dipolar structure is eliminated and the line-narrowing is achieved by MAO.

The samples were the two homologous liquid crystalline compounds, 4-Octyloxy-*N*-(4-substituted benzylidene)aniline (XBOOA; $X-C_6H_4-CH=N-C_6H_4-OC_8H_{17}$). The substituent is cyano ($X=NC$) for CBOOA [16] and is trifluoromethoxy ($X=CF_3O$) for TFOBOOA [17]. The phase transition sequence is I (isotropic)–N (nematic)– S_{Ad} (smectic Ad)–Crystal for CBOOA and I–N– S_A (smectic A)–Crystal for TFOBOOA. Here, S_{Ad} and S_A are both uniaxial smectic A phases.

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