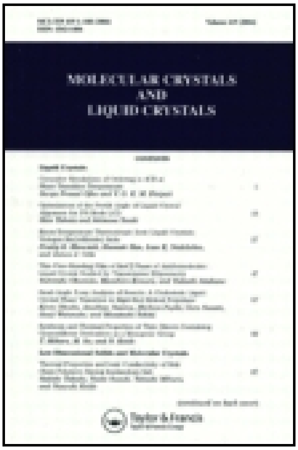

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^{14}N NMR Study of Order Fluctuations in the Isotropic Phase of Liquid Crystals

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^{14}N NMR Study of Order Fluctuations in the Isotropic Phase of Liquid Crystals

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Nitrogen-14 resonance lineshapes in the isotropic phase of a nematic (*p*-azoxyanisole) and of a smectic-A (diethylazoxybenzoate) liquid crystal have been studied using fast Fourier transform techniques. The temperature variation in linewidth is different in each sample, although both depend critically on the short range order fluctuations which exist about 10° to 15° into the isotropic phase. The experimental results for the isotropic phases of *p*-azoxyanisole and of diethylazoxybenzoate are explained in terms of short range order fluctuations of the nematic and of the smectic types, respectively.

INTRODUCTION

The application of NMR techniques in recent years to the study of dynamical properties of liquid crystals has proven very useful. Thus far, mainly proton and deuteron resonances have been used, owing to their abundances in liquid crystalline molecules and the relative ease of observing good resonant signals. In deuteron resonance work the molecules may be fully or partially deuterated, but the deuteration process is often difficult, expensive and time consuming. The main drawbacks in proton resonance work are the many inequivalent protons in each molecule and the intermolecular dipolar interactions, which complicate the analysis of the data. Recently ^{13}C resonance[1] has been used to study liquid crystals. The obstacles here are the low abundance of ^{13}C nuclei and the strong coupling between proton and ^{13}C nuclei. About five years ago, Cabane and Clark[2] reported the use of ^{14}N in the study of the liquid crystal *p*-azoxyanisole (PAA). Although ^{14}N is less abundant and more difficult to detect than protons it does undergo intramolecular quadrupolar relaxation, thus simplifying the identification of the relaxation mechanisms involved. Furthermore, liquid crystal impurities are less likely to affect the data since ^{14}N has short relaxation times. Cabane and Clark[2,3] applied boxcar integration to the free induction decay (FID) signal to obtain the ^{14}N absorption line spectrum. Because of the experimental difficulties involved in observing ^{14}N resonances in liquid crystals and the time involved in obtaining a good signal-to-noise (SN) ratio with boxcar integration no attempt has been made to reproduce the ^{14}N results or to use ^{14}N NMR in the study of other liquid crystals. Recently, we have employed fast Fourier transform (FFT) spectroscopy[4] to study both proton and deuteron lineshapes, and spin-lattice relaxations in liquid crystals. This technique is superior to conventional c.w. methods, as the pulsed FID signal can be accumulated quickly to the desired SN ratio before transforming to the frequency domain.

In this paper we report on our ^{14}N FFT spectra for the isotropic phase of the nematic liquid crystal PAA and of the smectic-A liquid crystal diethylazoxybenzoate (DEAB). ^{14}N linewidth measurements are used to show the existence of short range order fluctuation parameters of the nematic type[5] (Q) and of the smectic type[6] (Ψ) in the isotropic phase of PAA and of DEAB, respectively.

EXPERIMENTAL METHODS

The liquid crystals PAA and DEAB were obtained from Eastman Kodak. PAA was used without further purification, while DEAB was recrystallized four times in ethanol. All samples were sealed in a vacuum by the freeze-melt method. The clearing temperatures (T_c) of our PAA and DEAB samples are respectively ~133 and ~122°C.

The ^{14}N wide-line spectra at a Larmor frequency of 4.334 MHz were obtained with a Bruker B-KR 322s pulsed spectrometer equipped with a Bruker BNC-12 FFT accessory. The external field was "locked" at 14.09 KG with a Bruker B-SN 15 stabilizer accessory. The magnetic field was made as homogeneous as possible by trimming with shim coils. The 90° pulse width for ^{14}N was typically between 15 and 20 μs. The temperature of a sample was measured with a thermocouple immersed in the liquid crystal and maintained by an air flow with a temperature gradient across the sample of about 0.5°C.

The FFT spectra for PAA and DEAB were obtained from averaging about 20,000 and 40,000 FID signals, respectively. All spectra show a single line.

The full-width at half-maximum intensity (Δ) for each line was obtained from the total sweep width used (20 KHz). Typical ^{14}N spectra had a SN ratio of 5 to 1.

THEORY

In this section we sketch de Gennes' theory of short-range orientational order in the isotropic phase of a nematic as applied to nuclear spin relaxation[7] and, by analogy, develop a theory for nuclear spin relaxation by short-range smectic order fluctuations in the isotropic phase of a smectic-A liquid crystal.

To describe the short range order in the isotropic phase of a nematic, de Gennes[5] introduced a tensorial order parameter Q. The free energy per unit volume is given, up to quadratic terms in Q, as

$$F = F_0 + \tfrac{1}{2}A(T)Q^2 + \tfrac{1}{2}L(\nabla Q)^2 \tag{1}$$

where L is a constant (slightly temperature dependent) describing the elastic coupling between two neighbouring molecules and

$$A(T) = a(T - T^*)^{\gamma'} \tag{2}$$

with $\gamma' = 1$ in the mean-field approximation and T^* a critical temperature for a second order phase transition slightly below the isotropic–nematic phase transition temperature T_c. In terms of Fourier components, the above free energy density becomes

$$F = F_0 + \tfrac{1}{2}VL(q^2 + \xi^{-2})|Q_q|^2 \tag{3}$$

where V is the sample volume, $\xi = (L/A(T))^{1/2}$ is the correlation length for the local anisotropy and q is the wave vector. Using the equipartition theorem, the amplitude of the qth fluctuation mode is given by

$$\langle |Q_q|^2 \rangle = \frac{kT}{LV}(q^2 + \xi^{-2}) \tag{4}$$

To discuss the dynamical properties, one writes a rate equation describing the relaxation of the local order with a correlation time τ. In a fluid at rest, this equation has the form of[5]

$$\frac{dQ}{dt} = -\frac{Q}{\tau} \tag{5}$$

The frictional forces responsible for relaxation are

$$\Phi \equiv -\frac{\partial F}{\partial Q} \equiv \frac{\nu\, dQ}{dt} \tag{6}$$

where ν is a phenomenological viscosity. ν has been found to vary as $\exp[W/T]$ with W being an activation energy. Using Eqs. (1) and (5) in (6), one obtains the relaxation time for the qth mode,

$$\frac{1}{\tau_{\mathbf{q}}} = \left(\frac{L}{\nu}\right)(q^2 + \xi^{-2}) = \left(\frac{1}{\tau_0}\right)(1 + q^2\xi^2) \tag{7}$$

with $\tau_0 = \nu\xi^2/L$. The frequency spectrum of this relaxation mode, whose amplitude is given by (4), is Lorentzian:

$$J_q(\omega) = \frac{kT}{\pi L(q^2 + \xi^{-2})}\frac{\tau_{\mathbf{q}}}{1 + \omega^2\tau_{\mathbf{q}}^2} \tag{8}$$

The nuclear spin-lattice relaxation rate $1/T_1$ is proportional to the spectral density at the nuclear Larmor frequency ω_L of all the relaxation modes, i.e.

$$\frac{1}{T_1} \propto, J(\omega_L) = \int 4\pi q^2 \, \mathrm{d}q J_q(\omega_L) \tag{9}$$

We limit our discussion here to the hydrodynamic ($q\xi < 1$) case of small Larmor frequencies ($\omega_L\tau_0 \ll 1$). Eq. (9) shows a critical temperature dependence:

$$\frac{1}{T_1} \propto, kT, \frac{\tau_0}{\xi L} = \frac{kT\nu\xi}{L^2} \tag{10}$$

In a smectic-A phase, molecules are stacked in a layered structure with their long axes parallel to the planar normal. de Gennes[6] defines an order parameter for the smectic-A phase as a complex quantity $\Psi(r)$, the modulus of which determines the density of the layers while the phase ϕ determines the position of the layers. In the smectic-A phase, the magnitude $|\Psi|$ of the density wave assumes a fixed value while ϕ may still fluctuate significantly. Furthermore a coupling exists between ϕ and the orientational order (director) fluctuations. In the isotropic phase of a smectic-A liquid crystal, Ψ vanishes on the average, but it does have short-range fluctuations in $|\Psi|$ inside the "cybotactic" groups. The free energy is given[6] as in (1) up to quadratic terms in $|\Psi|$ as

$$F = F_0 + A(T)|\Psi|^2 + \frac{1}{2M_v}\left(\frac{\partial\Psi}{\partial z}\right)^2 + \frac{1}{2M_T}\left[\left(\frac{\partial\Psi}{\partial x}\right)^2 + \left(\frac{\partial\Psi}{\partial y}\right)^2\right] \tag{11}$$

Director fluctuations have not been included. M_v and M_T are the principal components of the mass tensor along and perpendicular to the planar normal, respectively. For simplicity, it is assumed that $M_v \simeq M_T = M$. The amplitude of the qth fluctuation mode can be obtained from Eq. (11) as above,

$$\langle |\Psi_q|^2 \rangle = \frac{kT}{lV}(q^2 + \xi'^{-2}) \tag{12}$$

where $l = 1/M$ is related to an elastic constant for compression of the layers (slightly temperature dependent) and $\xi' = (l/2A(T))^{1/2}$ is the coherence length for a cybotactic group. Writing a rate equation for the relaxation of $|\Psi|$, we have as in Eq. (5)

$$\frac{\mathrm{d}|\Psi|}{\mathrm{d}t} = \frac{-|\Psi|}{\tau_m} \tag{13}$$

The frictional forces are

$$\Phi \equiv -\frac{\partial F}{\partial |\Psi|} \equiv \gamma \frac{\mathrm{d}|\Psi|}{\mathrm{d}t} \tag{14}$$

where γ is an effective viscosity for damping of the smectic order fluctuations. The relaxation time τ_m for the qth mode is easily shown to be

$$\frac{1}{\tau_m(\mathbf{q})} = \frac{l}{\gamma}(q^2 + \xi'^{-2}) = \frac{1}{\tau_m(0)}(1 + q^2\xi'^2) \tag{15}$$

The frequency spectrum of this relaxation mode is

$$J_q(\omega) = \frac{kT}{\pi l(q^2 + \xi'^{-2})} \frac{\tau_m(\mathbf{q})}{1 + \omega^2 \tau_m(\mathbf{q})^2} \tag{16}$$

In the same approximation as Eq. (10), one has

$$\frac{1}{T_1} \propto, kT \frac{\tau_m(0)}{\xi' l} = kT\gamma \frac{\xi'}{l^2} \tag{17}$$

One would therefore expect from Eqs. (10) and (17) that the nuclear spin relaxation rates are identical in the isotropic phases of a nematic and a smectic-A liquid crystal, unless the "viscosities" γ and ν have completely different temperature dependences. In the next section, we present some experimental ^{14}N data for PAA and DEAB in their isotropic phases and discuss the different temperature behavior.

RESULTS AND DISCUSSION

In Figure 1, we present the ^{14}N linewidth (Δ) measurements of PAA as a plot of the square of the inverse linewidth versus temperature. The inverse linewidth is proportional to the transverse spin relaxation time which has been

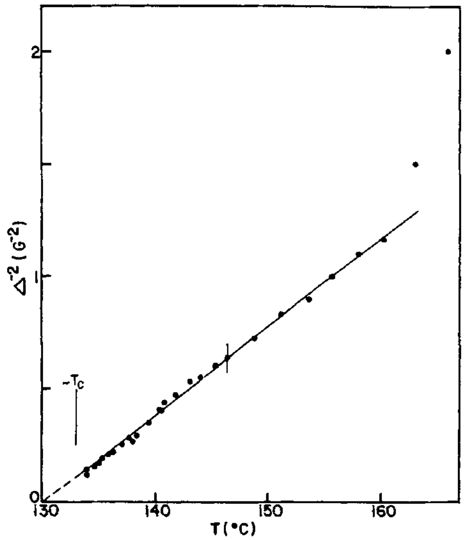

FIGURE 1 Inverse-square linewidth of ^{14}N resonance versus temperature in the isotropic phase of PAA.

shown to be equal to T_1 at 3 MHz in the isotropic phase of PAA.[7a] Our linewidth measurements would agree within experimental error with the earlier results of Cabane and Clark[2] if their definition of linewidth is indeed full-width at half-maximum intensity. It is seen that over the range of ~30° above T_c, the linewidth Δ reproduces the empirical relationship of Cabane and Clark,[2] i.e.

$$\Delta = 5.1(T - T^*)^{-\frac{1}{2}}\,{}^\circ\mathrm{K}^{1/2}G \tag{18}$$

with $T_c - T^* \sim 3°\mathrm{C}$. This empirical result is consistent with the prediction of Eq. (10) if it is assumed that the temperature dependence in Δ only comes from ξ which is proportional to $(T - T^*)^{-1/2}$ in the mean field approximation. Of course it is assumed that our ω_L satisfies the short correlation time limit. From Figure 1 it appears that the coherence length ξ does not tend to zero up to 30° above T_c. This is surprising since ξ has been measured directly and found to be equal to the molecular length at about 16° above T_c in the nematic *p*-methoxybenzylidene *p*-*n*-butylaniline (MBBA).[8] In order to properly[7a] analyse the ^{14}N linewidth data, the temperature dependence ($\exp[W/T]$) of the transport coefficient ν has to be included. Taking $W = 4 \times 10^3\,°\mathrm{K}$ for PAA,[9] our ^{14}N data is replotted at $(T^2/\Delta^2)[\exp 2W/T]$ versus temperature in Figure 2. According to Eq. (10), one should have

$$\left[\frac{T^2}{\Delta^2}\right]\exp\left[\frac{2W}{T}\right] \propto (T - T^*) \tag{19}$$

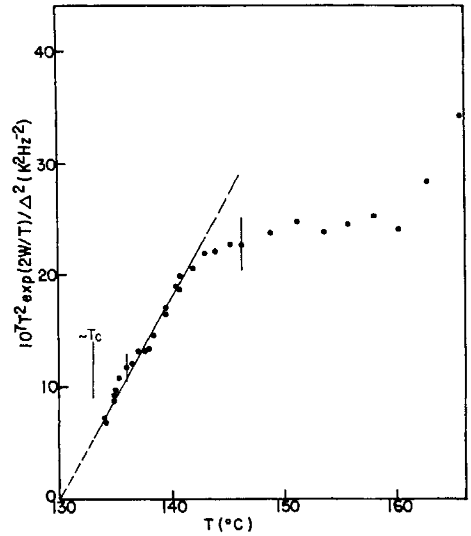

FIGURE 2 $T^2 \exp[2W/T]/\Delta^2$ versus temperature in the isotropic phase of PAA. $W = 4000$°K.

which is obeyed as long as ξ is nonzero. The plot reveals a deviation from linear behavior at $T \simeq 143$°C. This shows that ξ actually has a sharper cutoff than was implied in Figure 1. As far as NMR can tell, ξ already tends towards the molecular size (~ 20 Å) at 10° above T_c. Cabane[7a] has estimated ξ at T_c in PAA to be ~ 250 Å. Unfortunately ξ has not been measured directly by light scattering for PAA, although x-ray measurements have been reported.[10]

Above $T = 143$°C, the spin relaxation rate (Δ) is no longer due to short range orientational order fluctuations. If R_0 denotes any relaxation rate in addition to the short-range nematic order fluctuations, the observed linewidth can be written as

$$\Delta = \text{constant} \cdot T \exp\left[\frac{W}{T}\right]\xi + R_0 \tag{20}$$

Thus

$$\text{constant} \cdot \xi = \frac{\Delta - R_0}{T \exp[W/T]} \tag{21}$$

where $R_0/T \exp[W/T]$ is found to be a constant up to 160°C. The temperature dependence of ξ is shown in Figure 3 as a plot of $(\Delta - R_0)/T \exp[W/T]$ versus $(T/T^* - 1)^{-1/2}$ with $T^* = 130$°C. Using the estimated value of 250 Å for ξ at T_c for PAA, one obtains roughly

$$\xi \sim 22\left(\frac{T}{T^*} - 1\right)^{-1/2} \text{Å} \tag{22}$$

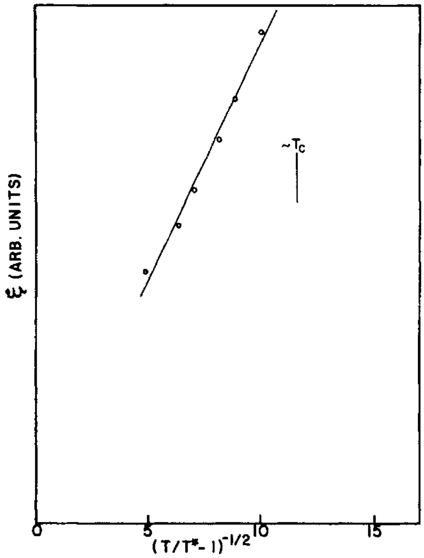

FIGURE 3 A plot of coherence length ξ versus $[(T/T^*) - 1]^{-1/2}$ where $T^* = 403°$K.

If this is correct, the minimum ξ at which ^{14}N linewidth measurements can detect short-range order fluctuations in PAA is about five molecular lengths. The minimum ξ value is greater than can be attained by proton work in MBBA.[11]

^{14}N linewidth measurements for DEAB are presented in Figure 4 in an identical manner to PAA in Figure 1. Clearly these two plots differ distinctly, indicating that the ^{14}N linewidth in the isotropic phase of DEAB behaves differently due to its lower temperature phase being a smectic-A. To show the critical temperature behavior of DEAB, the ^{14}N data is replotted as Δ/T versus temperature in Figure 5. Again the observed linewidth is written as a sum of two relaxation rates, the contributions from short-range smectic order fluctuations and from molecular rotations (R_0), as

$$\Delta = \text{constant } T\gamma\xi' + R_0 \tag{23}$$

The coherence length ξ' for the smectic density wave tends towards the molecular length at ~138°C which is 16° above the clear point. Above 138°C (up to 150°C), the ^{14}N linewidth (R_0) does not seem to depend on temperature. Subtracting this constant R_0 from Δ, one obtains the relaxation rate due to the short-range smectic order fluctuations. Since $\xi' \propto (T - T^*)^{-1/2}$ in the mean field approximation, one has

$$\text{constant} \cdot \gamma = \frac{\Delta - R_0}{T}\left(\frac{T}{T^*} - 1\right)^{1/2} \tag{24}$$

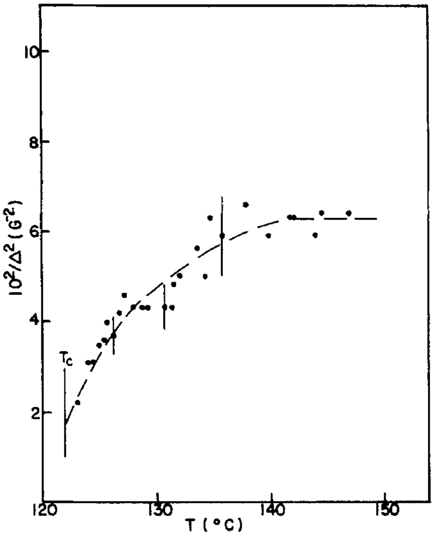

FIGURE 4 Inverse-square linewidth of the ^{14}N resonance versus temperature in the isotropic phase of DEAB.

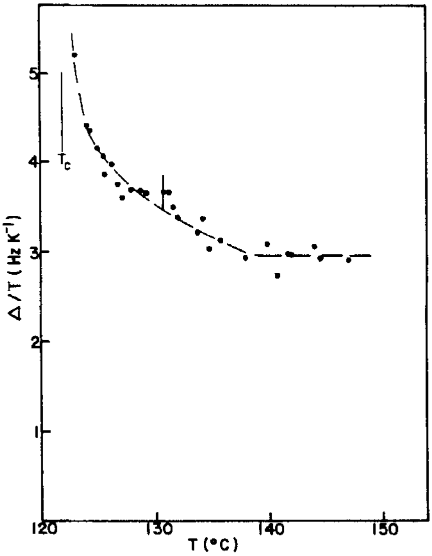

FIGURE 5 Δ/T versus temperature in the isotropic phase of DEAB.

where T^* is slightly below T_c and is not known. In our earlier proton work[12] with DEAB, we determined $T_c - T^* \sim 1°C$. Using this approximation, the temperature dependence of γ is shown in Figure 6. Its behavior varies slightly with different T^*. The present ^{14}N data for DEAB precludes a precise determination of both the critical exponent of γ and T^* due to the large scatter. However the temperature variation in γ (Figure 6) agrees qualitatively with the early viscosity measurements[13] for DEAB and seems to substantiate our proton study.[12]

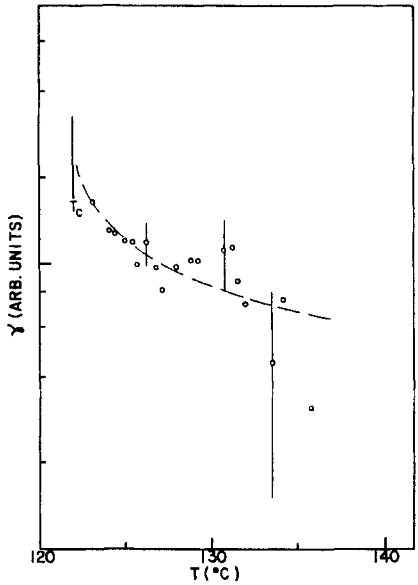

FIGURE 6 Temperature dependence of viscosity in the isotropic phase of DEAB derived from eq. (24) (see text).

In conclusion, we have shown that ^{14}N NMR measurements can lead to direct observation of short range order fluctuations in the isotropic phase of liquid crystals. It appears that short-range order of the nematic and of the smectic types have correlation times with different critical temperature dependences. The FFT technique can alleviate some of the difficulties in observing ^{14}N signals in liquid crystals.

Acknowledgements

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