

Thermal Hysteresis in the Nematic Order of a PCH-3 Liquid Crystal

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Thermal hysteresis was observed, upon heating and cooling, in our proton nuclear magnetic resonance studies of the nematic phases in PCH-3 [trans-4 (4-propylcyclohexy) benzonitrile]. The microscopic nature of the hysteresis in this liquid crystalline material was revealed by our systematic measurements of the nematic order parameter and the spin-lattice relaxation.

Liquid crystals exhibit a mesophase in which rod-like molecules tend to be parallel. This liquid-crystalline state shows anisotropies in its optical, electrical, and magnetic properties [1,2]. While the general macroscopic properties of liquid crystals have phenomenologically been understood by using the elastic continuum theory of liquid crystals, their microscopic properties have not been well understood up to the present.

The p-disubstituted phenylcyclohexanes (PCH) are a new class of chemically stable, and colorless substances with low melting points, and with nematic liquid crystalline properties. Their nematic phase is characterized by a surprisingly low bulk viscosity in comparison to those of other liquid crystals. Since the bulk viscosity of liquid crystals is proportional to the flow viscosity and to the elasticity coefficients, a low threshold voltage and short switching times are to be expected for PCH liquid crystals [3]. As a consequence, they are considered particularly suitable for use in liquid-crystal displays.

The dynamics in liquid crystals have been studied by using nuclear spin-lattice relaxation time measurements [4-13]. Based on the collective modes of the fluctuation in the molecular order, Pincus first obtained the relation between the nematic mesophase and the nuclear spin relaxation by considering only the intramolecular dipole-dipole interaction between a pair of protons. According to his theory, the spin-lattice relaxation rate is represented as [4]

$$\frac{1}{T_1} = \omega_D^2 \left(\frac{kT}{K} \right) \left(\omega \left(D + \frac{K}{\eta} \right) \right)^{-1/2}, \quad (1)$$

where ω_D is the dipole frequency, K the Frank elastic constant, D the diffusion constant, η the viscosity, and ω the Larmor frequency. By including the high-frequency fluctuations about the preferred orientation as well as the collective fluctuations, Ukleja *et al.* [5] modified the

theory into the form

$$\frac{1}{T_1} = B \langle p_2 \rangle T \omega^{-1/2} \left(1 - (2\sqrt{2}/\pi) \left(\frac{\omega}{\omega_c} \right)^{1/2} \right), \quad (2)$$

where B is a constant including the apparent viscosity and the elastic constant, and ω_c denotes the higher cut-off frequency of the director fluctuation. In addition, $\langle p_2 \rangle$ represents the second-rank orientational order parameter.

In order to study the nematic order and its thermal hysteresis in liquid crystalline PCH-3, we made the ^1H NMR (nuclear magnetic resonance) lineshape and proton spin relaxation time measurements while heating and then cooling the sample through different phases. In this work, new light was thrown on the nature of the order and the local dynamics in this liquid crystal.

DSC (differential scanning calorimetry) measurements on our PCH-3 sample revealed phase transitions at around $T_N = 311$ K and $T_I = 317$ K on heating, corresponding to the solid-nematic and nematic-isotropic phase transition temperatures, respectively. On the other hand, the DSC peak corresponding to the nematic-solid transition disappeared on cooling, indicating that on cooling the nematic order persisted well below the isotropic-nematic phase transition.

The proton NMR measurements were performed at 45 MHz on a home-built pulsed spectrometer while heating and then cooling the sample through the phase transitions. The heating and the cooling were done slowly enough to ensure thermal equilibrium. The lineshape was obtained by Fourier transforming the free-induction decay (FID) signal. The spin-lattice relaxation time was measured using the inversion recovery method. The relaxation patterns were well fitted by a single-exponential form at all temperatures.

Figure 1 shows the second-moment measurements on heating and then cooling the sample. On heating, the solid-nematic and nematic-isotropic phase transitions are well reflected in the characteristic manner with a marked discontinuity at T_N . On cooling, on the other hand,

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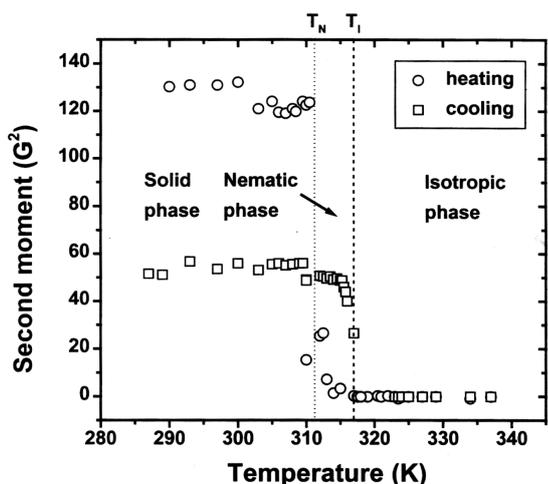


Fig. 1. Temperature dependence of the second moment on heating and then cooling.

while a relatively small change takes place at T_N , a discontinuity is noticed at T_I . No further hysteresis is observed on reheating.

In contrast to the cases of the solid and the isotropic phases, the proton NMR lineshape in the nematic phase showed a splitting which was characteristic of a liquid crystalline order. The line splitting δH arises from the dipole-dipole interaction of the adjacent benzene ring protons and disappears at the nematic-isotropic transition. The nematic order parameter S is given by $S = (1/2) \langle 3 \cos^2 \theta - 1 \rangle$, where θ is the angle between the instantaneous and the average direction of the molecular axis. The order parameter S can be found from the split-

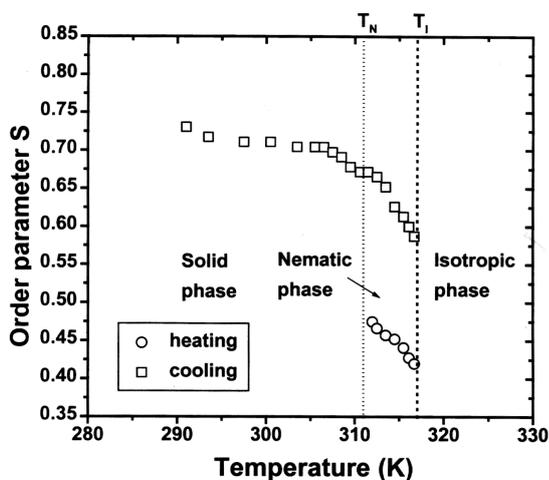


Fig. 2. Temperature dependence of the nematic order parameter obtained from line splitting on heating and then cooling.

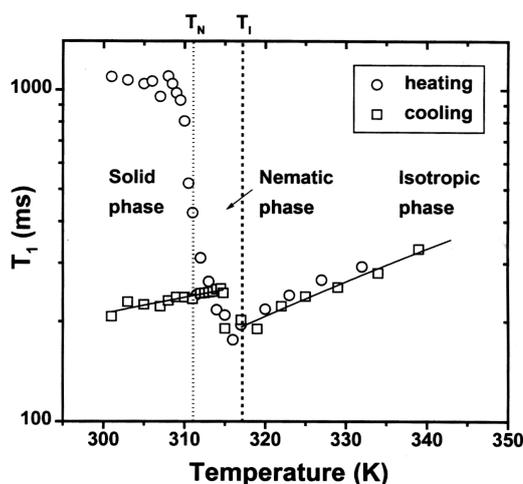


Fig. 3. Temperature dependence of the spin-lattice relaxation time (T_1) for heating and then cooling. The solid lines represent fits based on the activation mechanism.

ting δH by using the relation $\delta H = 4\alpha(\frac{3}{2} \cos^2 \phi - \frac{1}{2})S$, where α is $\frac{3}{2}\mu_H r^{-3}$ (r being the distance between the ortho protons) and ϕ is the angle between the para axis of a ring and the major molecular axis [9]. The value of α was calculated to be 1.44 G, and that of r to be 2.45 Å. A value for ϕ was also estimated from the molecular model.

Figure 2 shows the temperature dependence of the order parameter S obtained from the line splitting measurements when heating the sample above T_I and then cooling it. The figure shows that the nematic order is only found below T_I and that a thermal hysteresis in the local order is evident in the thermal history. On cooling, the splitting persists below T_N , which is in agreement with the DSC measurements. It is also to be noted, in contrast to what is generally assumed, that the order parameter has much greater values on cooling than on heating. In order to exclude the possibility that the thermal hysteresis in the nematic order parameter was obtained by thermal nonequilibrium on heating, as might be suspected, enough time, up to more than an hour, was allowed between measurements at different temperatures in the nematic phase, and the complete experiments were repeated several times on fresh samples and produced identical results.

The temperature dependence of the proton spin-lattice relaxation time (T_1) on heating and then cooling the sample is shown in Fig. 3. On heating, a rapid decrease around T_N , corresponding to active molecular motions such as fast rotational or translational diffusion, take place at the solid-nematic phase transition. The figure also shows a reversal in the slope at T_I , which corresponds to a relaxation by an Arrhenius-type activation mechanism with a single correlation time in the limit of $\omega\tau \ll 1$ in the isotropic phase.

On heating, the T_1 in the nematic phase is inversely proportional to temperature as in Eqs. (1) and (2) and as in other liquid crystals [5]. This is indicative of the dominant contributions of the orientational nematic order fluctuation and diffusion to the relaxation mechanism in the nematic phase. However, on cooling, the relaxation shows a much different pattern from that for heating. Specifically, while a discontinuity is observed at T_I , unlike in the case of heating, the relaxation pattern below T_I is quite similar to that above it except for the slope. In other words, the spin-lattice relaxation in the nematic phase on cooling appears to be dominated by an activation mechanism with a single correlation time, just as in the isotropic phase, except for the greater activation energy of 20 kJ/mol in comparison to that of 9 kJ/mol in the isotropic phase.

In conclusion, we have made a systematic proton NMR investigation of the PCH-3 liquid crystal. As a result, substantial differences were observed in the nematic order upon heating and upon cooling, and the nature of the molecular dynamics pertinent to the spin-lattice relaxation in the nematic phases was revealed. This work is expected to shed new light onto the nature of the order and the molecular motions in the nematic phase of this liquid crystalline system.

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REFERENCES

- [1] P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, 1974).
- [2] S. Chandrasekhar, *Liquid Crystals* (Cambridge University Press, Cambridge, 1992); S-W. Suh, S-D. Lee and J. S. Patel, *J. Korean Phys. Soc.* **29**, 399 (1996).
- [3] L. Pohl, R. Eldenschink, G. Krause and D. Erdmann, *Phys. Lett.* **60A**, 421 (1977).
- [4] P. Pincus, *Solid State Commun.* **7**, 415 (1969); K. W. Lee, C. E. Lee and J. K. Kang, *J. Korean Phys. Soc.* **28**, 383 (1995).
- [5] P. Ukleja, J. Pirs and J. W. Doane, *Phys. Rev.* **A14**, 44 (1976); C. H. Lee, C. E. Lee, J-I. Jin and C-K. Park, *J. Korean Phys. Soc.* **29**, 137 (1996).
- [6] J. W. Doane and D. L. Johnson, *Chem. Phys. Lett.* **6**, 291 (1970).
- [7] R. Blinc, D. L. Hogenboom, D. E. O'Reilly and E. M. Peterson, *Phys. Rev. Lett.* **23**, 969 (1969).
- [8] T. C. Lubensky, *Phys. Rev.* **A2**, 2497 (1970).
- [9] S. Miyajima, N. Nakamura and H. Chihara, *Mol. Cryst. Liq. Cryst.* **89**, 151 (1982).
- [10] C. L. Watkins and C. S. Johnson, Jr., *J. Phys. Chem.* **75**, 2452 (1971).
- [11] G. Klose, F. Volke, M. Hentschel and A. Mops, *Mol. Cryst. Liq. Cryst.* **90**, 245 (1983).
- [12] R. Lenk, *Fluctuations, Diffusion and Spin Relaxation* (Elsevier Science Publishers B. V., Amsterdam, 1986).
- [13] J. F. Martin, R. R. Vold and R. L. Vold, *J. Chem. Phys.* **80**, 2237 (1984).