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NMR SPIN-LATTICE RELAXATION STUDY IN THE NEMATIC PHASE OF BUTYLCYANO-PHENYLCYCLOHEXANE

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NMR Spin-Lattice Relaxation Study in the Nematic Phase of Butylcyano-Phenylcyclohexane

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The NMR spin-lattice proton relaxation dispersion $T_1(\nu_L)$ of the liquid crystal butylcyano-phenylcyclohexane are studied over several decades of Larmor frequencies at different temperatures in the nematic mesophase. The results show that the order fluctuation of the local nematic director contribution to $T_1(\nu_L)$ undergoes a transition between two power regimes: from $T_1(\nu_L) \propto \nu_L^{1/2}$ to ν_L^{α} ($\alpha \approx 1/3$) on going from low to high Larmor frequencies.

Keywords: Liquid crystals; Molecular dynamics; NMR

I. INTRODUCTION

Liquid crystals have suscited the interest of numerous studies due to their unique characteristic of behaving as an isotropic liquid or having collective motions in different time scales [1]. Field-cycling NMR relaxometry [2] has been widely used to probe reorientational molecular motions through the dispersion of the spin-lattice relaxation time ($T_1(\nu_L)$). In thermotropic liquid crystals at Larmor frequencies higher than 10^6-10^7 Hz individual mechanisms of relaxation, as molecular self diffusion and rotations dominate the relaxation. Self diffusion modulates the intramolecular dipolar interactions by reorientation's of individual molecules with respect to the external Zeeman magnetic field while they are translationally diffusing through the liquid crystalline

locally oriented domains. In addition, the inter spin vector can rotate with the whole molecule.

For frequencies below 10^5-10^6 Hz collective molecular motions govern the relaxation. Cooperative molecular interactions create microscopic domains with an orientational order, within each domain a local director is defined. Thermally stimulated fluctuations of this local director produce orientational order fluctuations (ODF) [1] that can be represented by overdamped elastic modes propagating in a spherical way in the nematic mesophase.

The discrimination of different NMR relaxation mechanisms is based on the identification of characteristic frequency dispersion laws of spin-lattice relaxation. The most known examples of ODFs are the square-root law ($T_1(\nu_L) \propto \nu^{1/2}$) for the nematic mesophase [3] and the linear law ($T_1(\nu_L) \propto \nu^1$) in smectics [4,5].

In this work we measured $T_1(\nu_L)$ in butylcyano-phenylcyclohexane (4-PCH) in the nematic mesophase at different temperatures within the range of 10^3Hz $<\nu_L<$ 10^8Hz. In addition to the $T_1(\nu_L) \propto \nu^{1/2}$ regime, the data behavior shows an anomalous dispersion law of $T_1(\nu_L) \propto \nu^{\alpha}$ (with $\alpha \approx 1/3$) in the range of $3 \cdot 10^4$-$3 \cdot 10^7$ Hz.

II. EXPERIMENTAL

Butylcyano-phenylcyclohexane liquid crystal was purchased to Merck Co., recrystallized and purified by local fusion in the solid state. Glass sample holders were filled under vacuum and sealed.

The measurements of the longitudinal proton relaxation dispersion was performed by means of a home-built fast field-cycling [7] NMR spectrometer for frequencies in the range 10^3Hz$<\nu_L<10^7$Hz and by a conventional NMR spectrometer in the range 10^6Hz$<\nu_L<10^8$Hz. The random error of the individual T_1 points is less than 10% after appropriate signal averaging, and the sample temperature has been controlled with an accuracy of at 0.2 °C.

Figure 1 shows the spin-lattice relaxation profile at 29 and 31°C. At both temperatures the typical nematic behavior of $T_1(\nu_L) \propto \nu_L^{1/2}$ is seen between 10^2Hz and $3 \cdot 10^4$Hz. The plateau in $T_1(\nu_L)$ is reached for frequencies below $\nu_c = 5 \cdot 10^3$Hz. This low-frequency cut-off is associated with a coherence length, $\xi_c = \sqrt{2\pi K/(\eta \upsilon_c)}$, of $8.5 \cdot 10^3$Å for 29°C and $8 \cdot 10^3$Å for 31°C. The values for the effective viscosity, η, and elastic

constants, K_i, measured by Schad *et al.*[9] were used in the calculation of ξ_c. A transition from the $\nu_L^{1/2}$ regime to a $\nu_L^{0.35}$ regime occurs at ν_t=3.4·10^{4}Hz for 29^{0}C and ν_t=3.1·10^{4}Hz for 31^{0}C and is present until 3·10^{6}Hz, where individual relaxation mechanisms (IM) composed by rotations over the long axis of the molecules and self diffusion dominate T_1.

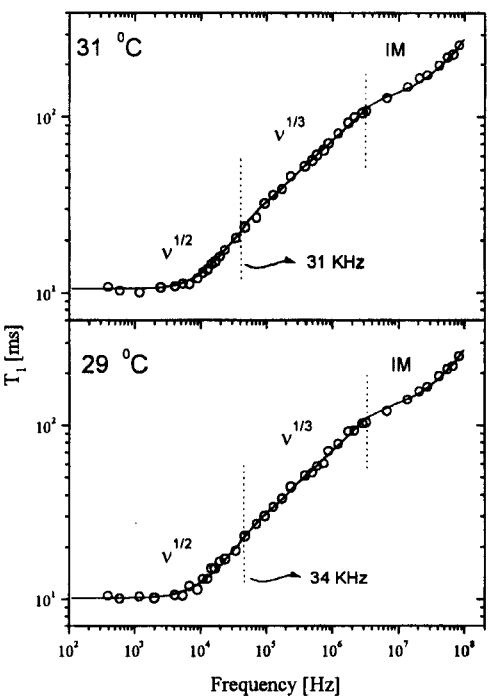

FIGURE 1: $T_1(\nu_L)$ for 29 and 31^{0}C. The typical square-root law is present at both temperatures below 3.4·10^{4}Hz and 3.1·10^{4}Hz respectively. For frequencies higher than 3·10^{6}Hz individual relaxation mechanisms (IM) dominate T_1.

III. DISCUSSION

In Figure 1 it can be observed that for frequencies higher than ν_t the values of T_1 fall below the continuation of the $\nu_L^{1/2}$ curve, this indicates that there exists another mechanism contributing to the relaxation rate. As the frequency domain where this process takes place is larger than that of 3D-ODF, a smaller coherence length for it should be expected, this is, short range molecular interactions are expected. Bending of the molecules could generate different modes of collective fluctuation of the local director and might be favored in this compound because of its low viscosity. This is in agree with Fig. 1 which shows that with increasing temperature, this is, decreasing viscosity, the frequency range for this process is larger.

An adequate theoretical frame explaining this process is material for future research. A change in the free energy expression involving an elastic constant that accounts for the proposed will change the mean square amplitude of the modes of the elastic waves that waves that represent the ODF's [10] which in turn leads to a change in the spectral density which determines the exponent in the power law.

Actually we are measuring similar compounds in the nematic and the smectic phase to gain knowledge in how the structure of the compounds affects the spin-lattice relaxation.

IV. ACKNOWLEDGMENTS

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