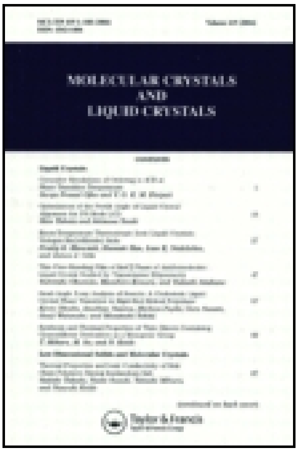

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Study of Molecular Dynamics In the Hexatic S_F Phase of TBDA: Comparison with Results from the Crystal S_G and the S_C Phases

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Version of record first published: 24 Sep 2006.

To cite this article: J. L Figueirinhas , C. Cruz , A. C. Ribeiro , Nguyen Huu Tinh & M. Vilfan (1991): Study of Molecular Dynamics In the Hexatic S_F Phase of TBDA: Comparison with Results from the Crystal S_G and the S_c Phases, Molecular Crystals and Liquid Crystals, 206:1, 45-53

To link to this article: http://dx.doi.org/10.1080/00268949108037717

Mol. Cryst. Liq. Cryst., 1991, Vol. 206, pp. 45–53
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Printed in the United States of America

Study of Molecular Dynamics in the Hexatic S_F Phase of TBDA: Comparison with Results from the Crystal S_G and the S_C Phases†

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(Received November 18, 1990; in final form March 13, 1991)

The molecular dynamics in the smectic C, F and G phases of the compound TBDA is studied by proton NMR relaxation. The spin-lattice relaxation time T_1 was measured for several temperatures spanning the three mesophases in the frequency range of 4–80 MHz. Measurements of the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ were also performed at a field of 4.9 Gauss and for the same set of temperatures. The results were analyzed in terms of the potential contributions of the different molecular motions for the relaxation process; namely reorientations, translational self-diffusion and for the S_C phase smectic layer undulations also.

INTRODUCTION

The hexatic mesophases in liquid crystalline compounds have been the object of wide interest in the last ten years. The short range positional order and the long range bond orientational order found in these phases through X-ray studies,[1] distinguished them clearly from both the smectic in plane liquid-like phases where these two types of order are short range (like S_C), and the crystal smectic phases

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† This work was presented at the 13th International Liquid Crystal Conference, Vancouver, B.C.

where these two types of order are long range (like S_G). Based on these properties the hexatic phases were identified with 3D analogs of the 2D hexatic phase predicted by the 2D melting theory by Halperin and Nelson,[2] leading also to a general identification scheme[3] between the liquid crystalline mesophases and the phases in the Halperin and Nelson theory.

An important point in mesophase characterization is the molecular dynamics, not yet fully analyzed in the hexatic phases. In this study using spin-lattice relaxation, we analyze the molecular dynamics to obtain a better picture of the differences in molecular behaviour between the hexatic smectic F phase and the smectic G and C phases. Spin-lattice relaxation measurements as a function of Larmor precession frequency were performed in the C, F and G phases in one compound from the series of the terephthalydene-bis-4-*n*-alkylanilines, respectively TBDA where the three phases are easily accessible.

EXPERIMENTAL

The compound terephthalidene-bis (4, *n*-decylaniline), TBDA exhibits five different mesophases.

$$\begin{array}{lcccccccccccc} K & \longrightarrow & S_G & \longrightarrow & S_F & \longrightarrow & S_I & \longrightarrow & S_C & \longrightarrow & S_A & \longrightarrow & I \\ T(^\circ C) & 71.9 & & 115 & & 148.7 & & 155.7 & & 189.6 & & 191.5 & \end{array}$$

The transition temperatures obtained from the Reference 4 were checked with a polarizing optical microscope equipped with a Mettler FP5 heating stage. The molecular structure is shown in Figure 1. The NMR sample was prepared by sealing 0.3 grams of material in a degassed 10 mm NMR tube. The spin-lattice relaxation time T_1 measurements were carried out in a Bruker SXP/4-100 MHz spectrometer using the standard inversion recovery sequence (π-τ-π_2, acq.). $T_{1\rho}$ was measured at 56 MHz by the spin locking method with a B_1 of 4.9 Gauss. The sample temperature was regulated within ±1°C by a B-ST 100 controller using nitrogen circulation. The measurements at each frequency where performed raising first the sample temperature to the isotropic phase in the presence of the magnetic field followed by a slow cooling to the highest desired temperature.

Data and Analyses

The temperature dependence of T_1 spanning the three mesophases for two working frequencies is shown in Figure 2. In Figure 3 is presented the temperature dependence of $T_{1\rho}$ for $B_1 = 4.9$ Gauss and $\nu_L = 56$ MHz. The frequency dependence of the relaxation rate $1/T_1$ in the different mesophases is given in Figures 4, 5 and 6.

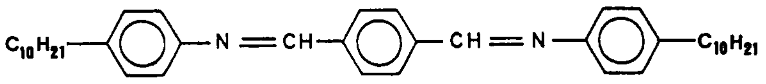

FIGURE 1 Molecular structure of the compound TBDA used in this study.

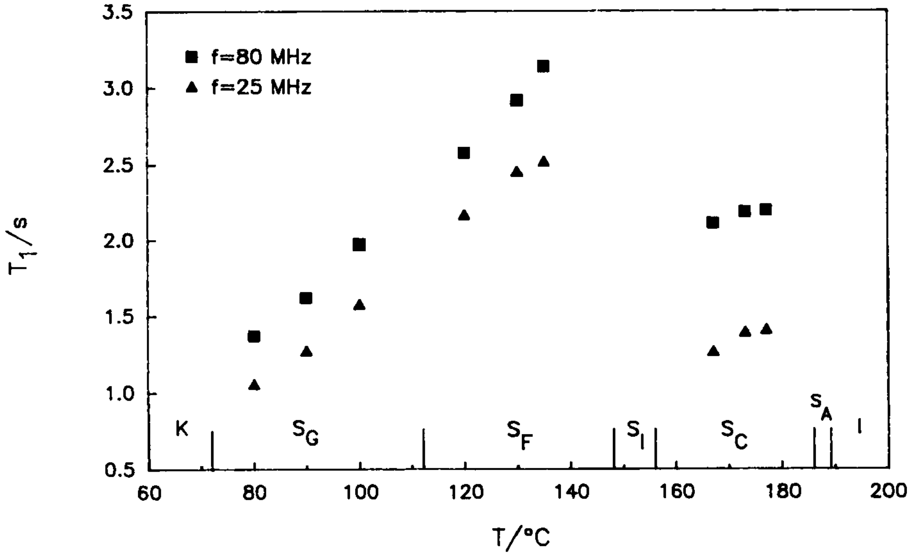

FIGURE 2 Temperature dependence of T_1 for Larmor frequencies spanning the mesophases analyzed.

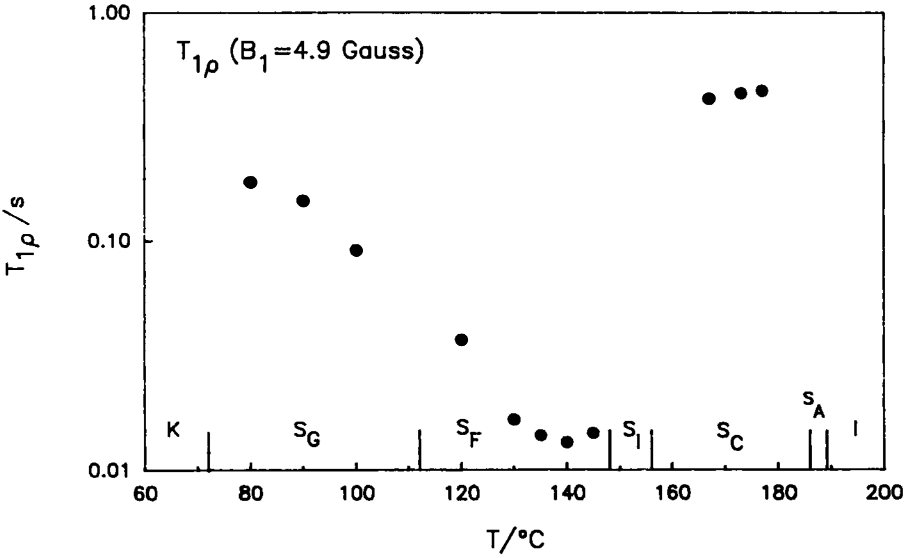

FIGURE 3 Temperature dependence of $T_{1\rho}$ for B_1 = 4.9 Gauss and ν_L = 56 MHz spanning the mesophases analyzed.

S_C phase. In the S_C phase three relaxation mechanisms were considered to explain the frequency dependence of the relaxation rate $1/T_1$:

$$1/T_1 = (1/T_1)_R + (1/T_1)_{SD} + (1/T_1)_{DF}. \tag{1}$$

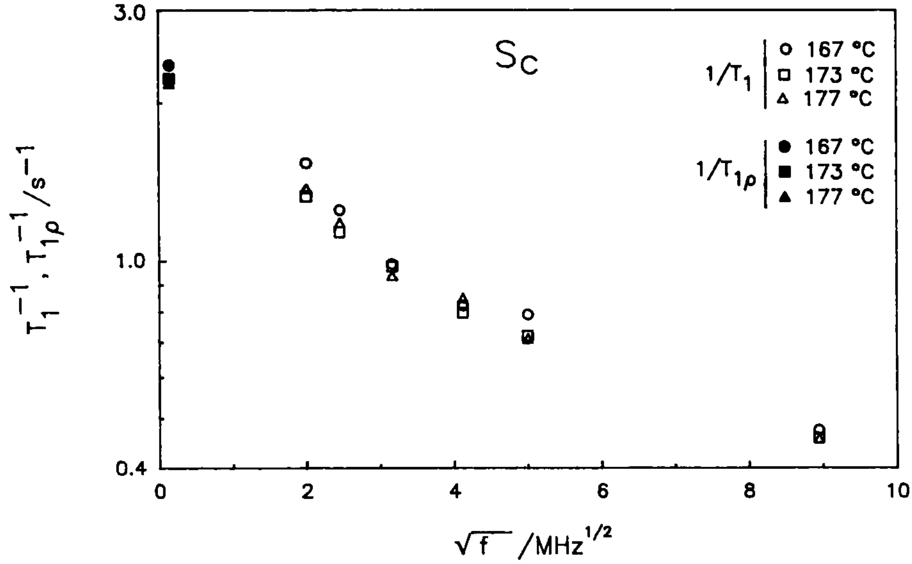

FIGURE 4 Frequency dependence of the relaxation rate $1/T_1$ in the S_C phase for the analyzed temperatures. The $1/T_{1\rho}$ points are indicated by filled symbols.

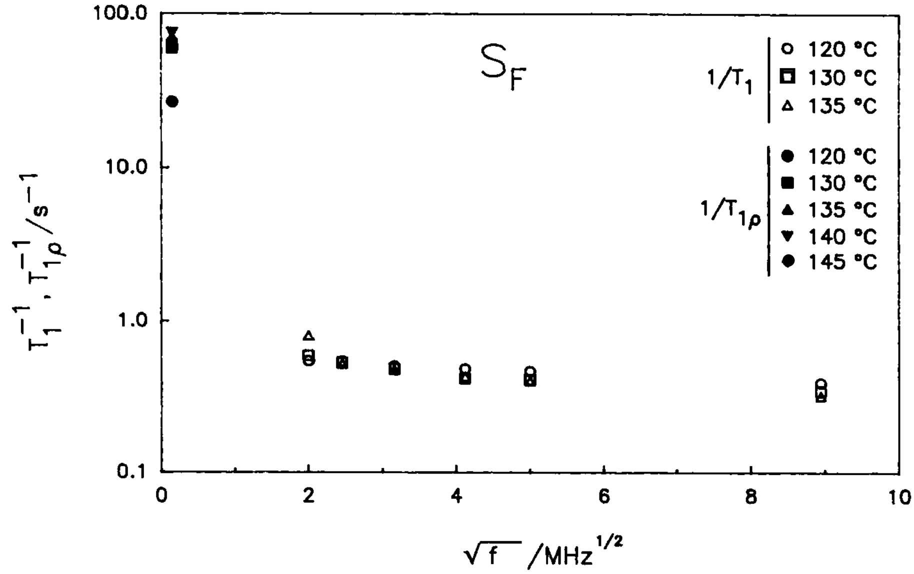

FIGURE 5 Frequency dependence of the relaxation rate $1/T_1$ in the S_F phase for the analyzed temperatures. The $1/T_{1\rho}$ points are indicated by filled symbols.

— Local molecular rotations and conformational changes of the aliphatic chains. In the frequency range of our measurements their contributions to the relaxation rate are reduced to a frequency independent term:

$$(1/T_1)_R = C \qquad (2)$$

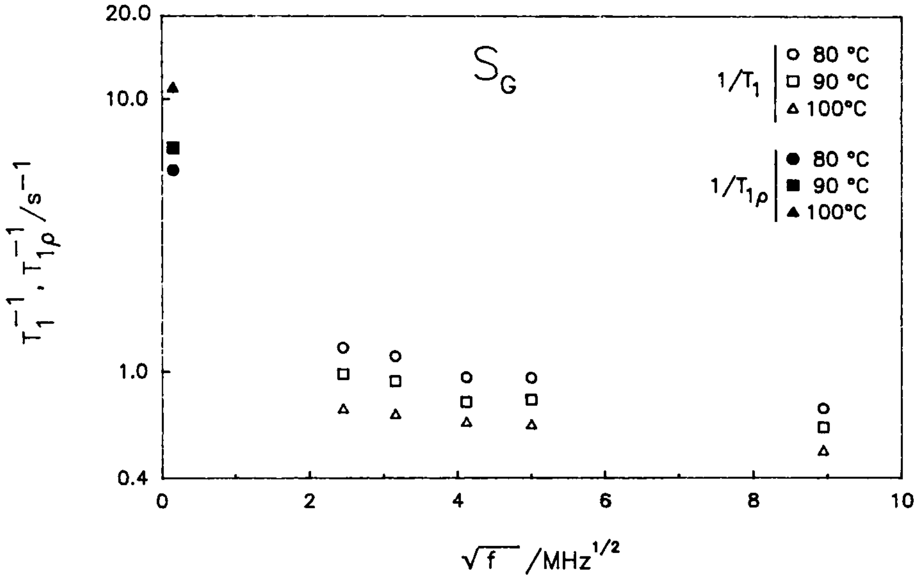

FIGURE 6 Frequency dependence of the relaxation rate $1/T_1$ in the S_G phase for the analyzed temperatures. The $1/T_{1\rho}$ points are indicated by filled symbols.

— Molecular translational self-diffusion described by the Zumer and Vilfan's theory[5] for smectics with liquid like layers.

$$(1/T_1)_{SD} = \frac{9}{8}\gamma^4\hbar^2 n \frac{\tau_\perp}{d^3} R\left(\omega\tau_\perp, \frac{\langle r^2_\perp\rangle}{d^2}, \frac{D_\parallel}{D_\perp}, \frac{\ell}{d}, \delta\right) \tag{3}$$

In Equation (3) we impose: $D_\perp/D_\parallel = 1$, $\ell/d = 5$ and $\langle r_\perp^2\rangle/d^2 = 1$. The values of $n = 5.36 \times 10^{22}$ spins/cm^3 and tilt angle $\delta = 26°$ were obtained from Reference 4, while d was assumed to be 7 Å, following earlier studies in the S_A and S_C phases of TBBA.[6] To test this value of d, fits to the experimental data were performed for values of d between 6.5 Å and 7 Å. The fits are seen to improve significantly with the increase in d.

— Director fluctuations, in particular layer undulations described by a contribution $(1/T_1)_{DF}$ proportional to ω^{-1}.[7]

Within the S_C phase the relaxation rate is quite insensitve to the temperature. The theoretical expressions for T_1^{-1} and $T_{1\rho}^{-1}$ according to the proposed relaxation mechanisms were simultaneously fitted to the experimental data. The best fit of the frequency dependence of the relaxation rates T_1^{-1} and $T_{1\rho}^{-1}$ for $T = 173°C$ is shown in Figure 7. Translational self-diffusion is seen to be the dominant relaxation mechanism for frequencies below 62 MHz and the fit implies the values $\tau_\perp = 1.81 \times 10^{-9}$ s and $D_\perp = 6.77 \times 10^{-11}$ m^2 s^{-1}. The contribution of the director fluctuations is only relevant below 1 MHz. The low cut-off frequency for the hydrodynamic modes associated with the layer undulations must be below 20 kHz, as indicated by the $T_{1\rho}$ measurement. This observation is in agreement with previous

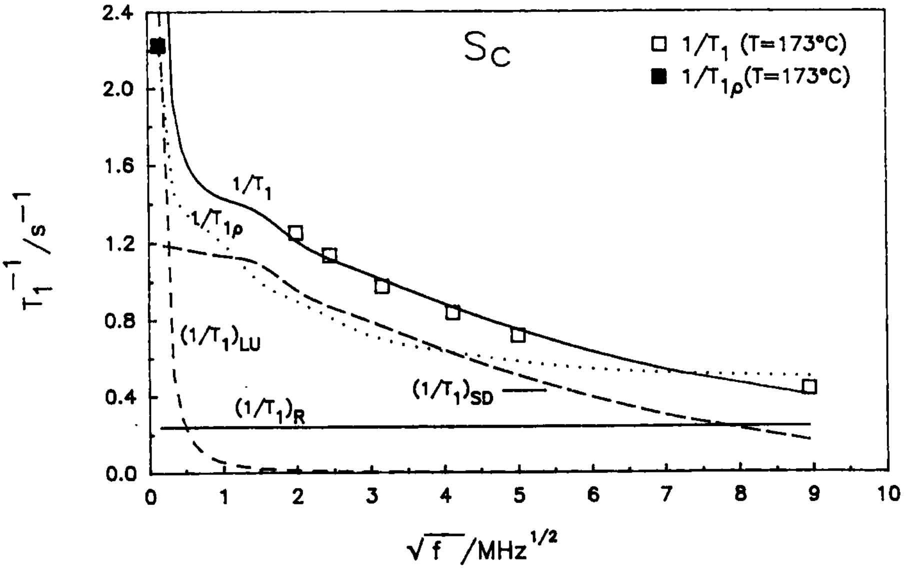

FIGURE 7 Frequency dependence of the relaxation rate $1/T_1$ in the S_C phase at $T = 173°C$. The solid line corresponds to the best theoretical fit to the $1/T_1$ data points. The dotted line is the $1/T_{1\rho}$ theoretical curve for $\nu_L = 56$ MHz. The different contributions in $1/T_1$ are also displayed.

results for S_A phases.[8] Local molecular reorientations show a contribution compatible with correlation times for these motions of the order of 10^{-11} s.

S_F phase. In the S_F phase two relaxation mechanisms were proposed to explain the frequency dependence of the relaxation rate:

$$1/T_1 = (1/T_1)_R + (1/T_1)_{SD}$$

— Local molecular rotations and conformational changes of the aliphatic chains. In the frequency range of our measurements these contributions are reduced to frequency independent terms again:

$$(1/T_1)_R = C$$

— Molecular translational self-diffusion described by the Zumer and Vilfan's theory[9] for hexatic phases (case c-dynamical disorder of the layer stacking).

$$(1/T_1)_{SD} = \frac{9}{8}\gamma^4 h^2 \frac{\eta}{d^3}\tau_\perp Q(\omega\tau_\perp, D_\perp/D_\parallel, \ell/d, a/d, \delta) \qquad (4)$$

In Equation (4) we impose: $D_\perp/D_\parallel = 2$, $\ell/d = 5$, $a/d = 0.5$, $n = 5.60 \times 10^{22}$ spins/cm^3 and $\delta = 22°$. The n and δ values were obtained from Reference 4, while d was estimated from the $T_{1\rho}$ data as shown below.

The $1/T_{1\rho}$ temperature dependence shows a maximum for $T = 140°C$ with a value for $1/T_{1\rho} = 75\ s^{-1}$. The contribution to $1/T_{1\rho}$ from molecular reorientations is negligible when compared with the contribution from the translational self-diffusion. In Figure 8 is shown a fit of $(1/T_{1\rho})$ versus $\tau_\perp$ to the experimental values of $1/T_{1\rho}$ for different values of d. The maximum in $1/T_{1\rho}$ imposes as valid, the curve with $d = 6.40$ Å. From this fit the values $\tau_\perp$ and $D_\perp$ for the different temperatures are obtained and are given in Table I. The temperature dependence of $\tau_\perp$ and $D_\perp$ can be well described by an Arrhenius type law with an activation energy of 123

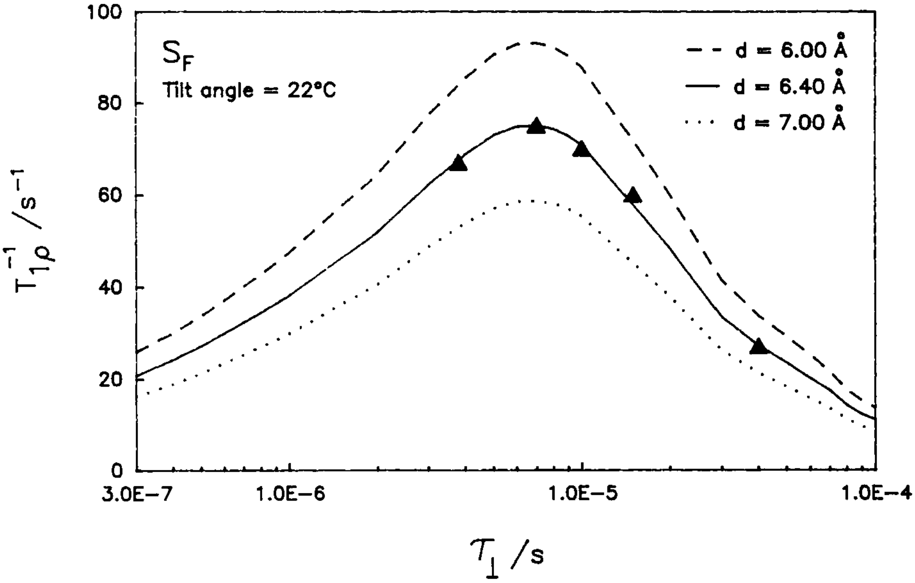

FIGURE 8 Fit of $1/T_{1\rho}$ versus $\tau_\perp$ in the S_F phase for $B_1 = 4.9$ Gauss. The lines represent the theoretical curves for different values of d. In the theoretical curves only translational self-diffusion was considered as relaxation mechanism since the contribution of local molecular rotations is negligible at this frequency.

TABLE I

T(°C)	$\tau_\perp$ (s)	$D_\perp$ ($m^2\ s^{-1}$)
120	3.9×10^{-5}	2.62×10^{-15}
130	1.35×10^{-5}	7.59×10^{-15}
135	9.7×10^{-6}	1.06×10^{-14}
140	6.4×10^{-6}	1.60×10^{-14}
145	3.6×10^{-6}	2.84×10^{-14}

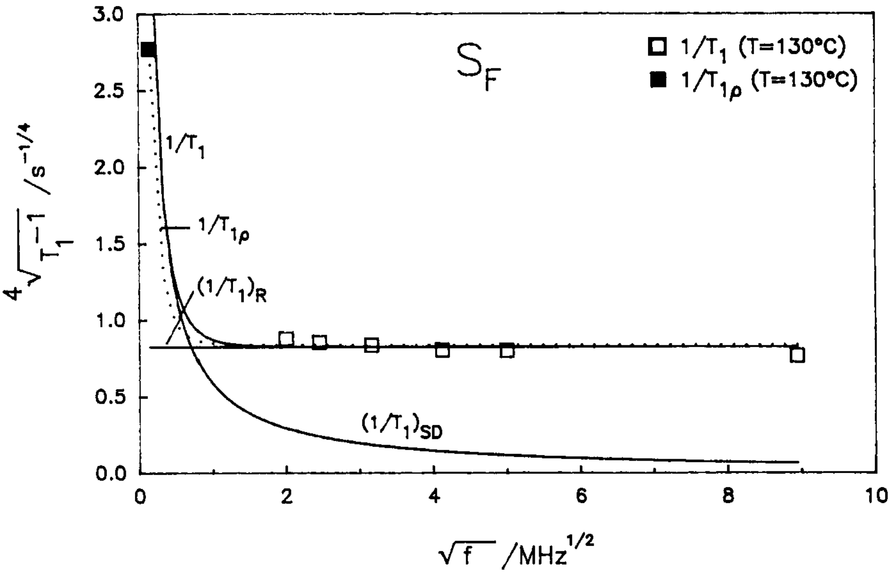

FIGURE 9 Frequency dependence of the relaxation rate $1/T_1$ in the S_F phase at T = 130°C. The solid line corresponds to the best theoretical fit to the $1/T_1$ data points. The dotted line is the $1/T_{1\rho}$ theoretical curve ν_L = 56 MHz. The different contributions in $1/T_1$ are also displayed.

kJ/mole. The values of $D_\perp$ obtained from the fits are several orders of magnitude below the values in the S_C phase. Similar differences were detected between the S_C and S_G phases of TBBA.[10] As the TBDA molecule is larger than TBBA, smaller diffusion constants should be expected.

In Figure 9 is given the best fit of the frequency dependence of the relaxation rates T_1^{-1} and $T_{1\rho}^{-1}$ for T = 130°C. Local molecular rotations and conformational changes of the aliphatic chains are seen to be the dominant relaxation mechanism in the high frequency region, while translational self-diffusion dominates in the low frequency region. The contribution from local molecular rotations and conformational changes of the aliphatic chains is $(1/T_1)_R = 0.458\ s^{-1}$ at T = 130°C. This mechanism is thermally activated with an activation energy of 8.7 kJ/mole.

S_G Phase. Two relaxation mechanisms were proposed to explain the frequency dependence of the relaxation rate in the S_G phase namely, molecular translational self diffusion described by the Vilfan and Zumer's theory for the smectic crystal phases[9] and local molecular rotations and conformational changes of the aliphatic chains, the later being dominant in high frequency limit. The measured values of $T_{1\rho}^{-1}$ one gets unrealistically large times associated with the diffusion process. In spite of the inexistence of diffusion measurements for this phase in TBDA, the huge values obtained for $\tau_\perp$ using the Vilfan and Zumer's theory,[9] point for the non-applicability of this theory in this case. One possible reason is the fact that this theory is not applicable when the correlation times for the diffusion process are of the order of the inverse of the dipolar coupling frequency as pointed out by

the authors. In the S_G phase of TBDA it is possible that the described situation is realized.

CONCLUSIONS

The results obtained for the S_C phase regarding the diffusion constant and the rotation correlation time are in good agreement with values from the literature for other S_C phases in particular those obtained for the S_C of TBBA.[6] It is also seen that layer undulations are only an effective relaxation mechanism in the kHz region. The relaxation data in the S_F phase can be well accounted for by the two proposed relaxation mechanisms. While the correlation time for local molecular rotations is of the same order of magnitude than in the S_C phase ($10^{-11}s$), the diffusion constant is several orders of magnitude smaller than the value in the S_C phase. Nevertheless the existence of a minimum of $T_{1\rho}$ versus T for T = 140°C is a strong indication that these values are correct. In the S_G phase no conclusion can be drawn regarding the diffusion constant.

Acknowledgment

We acknowledge JNICT for financial support (Project 871460) and FNCC for the use of computer facilities.

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