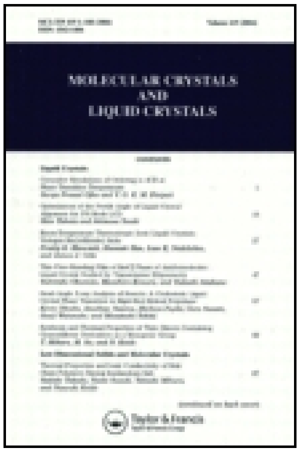

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Dielectric Studies on Strongly Polar Discotic Liquid Crystals

Geetha G. Nair [a] , S. Krishna Prasad [a] , S. Kumar [a] & M. Manickam [a]

[a] Centre for Liquid Crystal Research, P.B. No. 1329, Jalahalli, Bangalore, 560 013, India

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Dielectric Studies on Strongly Polar Discotic Liquid Crystals

GEETHA G. NAIR, S. KRISHNA PRASAD*, S. KUMAR and M. MANICKAM

Centre for Liquid Crystal Research, P.B. No. 1329, Jalahalli, Bangalore - 560 013, India

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We report dielectric investigations on the fourth and fifth homologues of the series 1-nitro-2,3,6,7,10,11-hexaalkoxytriphenylene. A hexagonally ordered columnar mesophase (D_{ho}) is exhibited by both the compounds but the fourth homologue shows in addition, a more ordered mesophase at lower temperatures. The dielectric constants observed are high compared to the values observed in other discotic materials. In the frequency range studied (1 Hz – 1 MHz) one relaxation mode is observed in the D_{ho} phase which can perhaps be correlated with a glass transition. A strong reduction in the magnitude of the relaxation frequency and an associated increase in the dielectric strength of the mode are observed at the transition from D_{ho} to the lower temperature phase. The data in the two-phase region of this first-order transition are also presented.

Keywords: Polar discotics; columnar mesophase; dielectric spectroscopy; alkoxy triphenylene

INTRODUCTION

Calamitic liquid crystals composed of strongly polar molecules have been extensively studied. These studies have led to the observation of a variety of interesting phenomena, *viz.*, reentrance [1], smectic A polymorphism [2] *etc.* In contrast, investigations on strongly polar disc-like molecules are scarce. The main reason for this is that such compounds were not available till recently [3, 4]. In this paper we report dielectric dispersion measurements on two asymmetrically-substituted mono-nitro triphenylene homologues.

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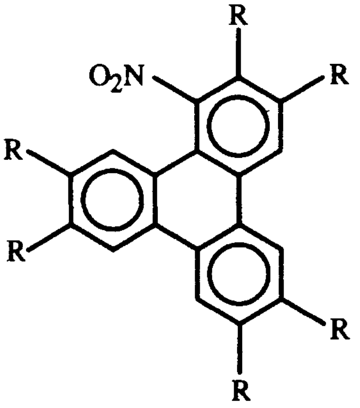
* Corresponding author.

EXPERIMENTAL

Experiments have been carried out on the 4th and 5th homologues of 1-nitro-2,3,6,7,10,11-hexaalkoxytriphenylene, the molecular structure of which is shown below



where $R = OC_nH_{2n+1}$ with $n = 4$ and 5.

Details regarding the synthesis of these compounds have been described elsewhere [5].

We expect the presence of the nitro group which has a very strong dipole moment to be reflected in the dielectric properties especially in the value of the dielectric constant. The transition temperatures for the two compounds (which for short we will refer to as C_nMNTP) determined in the cooling cycle by optical microscopy as well as Differential Scanning Calorimetry (DSC) are

$$C_4MNTP: \quad \text{Iso} \xrightarrow{141.3^\circ C} D_h \xrightarrow{47.7^\circ C} D_x$$

$$C_5MNTP: \quad \text{Iso} \xrightarrow{140^\circ C} D_h$$

While C_5MNTP shows only one mesophase, C_4MNTP exhibits two mesophases. In both the compounds the optical texture observed in the mesophase immediately below the isotropic phase is the mosaic texture characteristic of the hexagonal columnar mesophase. In case of C_4MNTP, across the second transition, the change in the texture is very subtle and observable only on careful examination.

Figure 1 shows the DSC scans obtained for the two compounds on cooling from the isotropic phase. Corroborating the optical microscopy

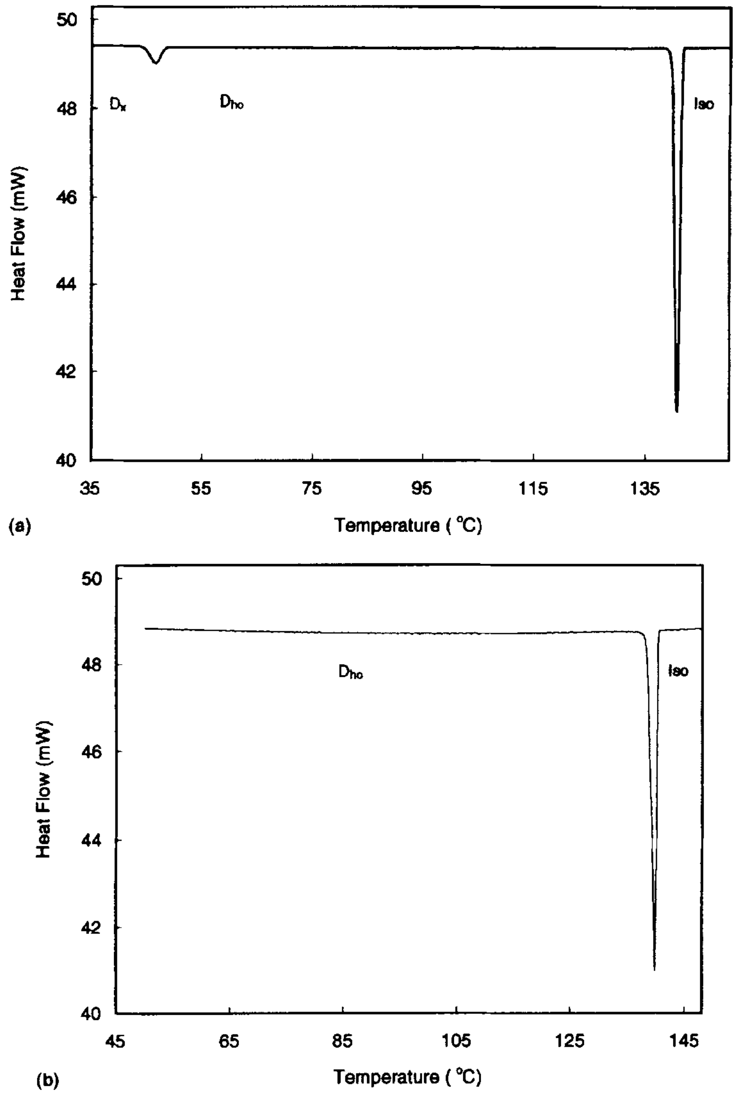


FIGURE 1 DSC trace obtained on cooling from the isotropic phase at a rate of 5°C/min for (a) $\mathrm{C_4MNTP}$ showing the Isotropic-D_h and $D_h - D_x$ transitions (the transition enthalpies are $\Delta H = 11.803\,\mathrm{J/g}$ and $1.124\,\mathrm{J/g}$ respectively) and (b) $\mathrm{C_5MNTP}$ exhibiting only the isotropic to D_h transition ($\Delta H = 9.469\,\mathrm{J/g}$). No crystallisation peak was observed for either of the compounds till room temperature. The D_h phase is identified as the hexagonally ordered columnar phase (D_{ho}) and the D_x, a highly ordered mesophase not yet fully characterised.

results, $\mathrm{C_5MNTP}$ shows only one peak which corresponds to Isotropic to D_h *transition* (Fig. 1b), $\mathrm{C_4MNTP}$ has an additional strong peak at lower temperatures (Fig. 1a). Neither of the two compounds were observed to crystallize from the melt till room temperature. Coverslip displacement test in the microscopy experiment confirmed that the low temperature phase, hereafter referred to as D_x phase, is not a crystalline phase. X-ray experiments show that the D_x phase is a three-dimensionally ordered phase while the D_h phase of both the compounds is the more frequently observed ordered hexagonal columnar (D_{ho}) phase [5]. It may be recalled that two types of 3D ordered discotic phases have been reported in the literature. A phase with a supra columnar helical order was observed by Heiney and co-workers in hexahexyl thio triphenylene [6]. More recently Glusen *et al.* [7] have reported what they term as a plastic columnar discotic phase in materials which have a chemical structure similar to our compounds. Although in the absence of detailed X-ray work we cannot, obviously, draw precise conclusions regarding the structure of D_x phase, it is possible that it is similar to the plastic phase observed by Glusen *et al.* [7].

Dielectric measurements were done in the frequency range of 1 Hz to 1 MHz using a frequency response analyser (Solatron FRA 1260). The samples were sandwiched between two aluminium coated glass plates and the thickness of the cell was defined using mylar spacers. The sample cell was placed in a hot stage whose temperature was controlled by an INSTEC temperature controller. The constancy of temperature during a frequency scan was better than 10 mK.

RESULTS AND DISCUSSION

Figure 2 is a plot of the dielectric constant ε' as a function of temperature at a constant frequency of 100 Hz for C_5MNTP and 10 Hz for C_4MNTP. To our knowledge, the dielectric constant observed here is the highest reported for any discotic material [7, 9]. While C_5MNTP shows a monotonic increase with decrease in temperature C_4MNTP has an abrupt increase at a temperature corresponding to the $D_{ho} \rightarrow D_x$ transition. The increase is to be expected as the D_x phase is more ordered than the D_{ho} phase. The small decrease observed at lower temperatures is, as we shall see later, due to a lowering of the relaxation frequency so much so that the frequency of measurement lies in the dispersion region.

Representative plots of ε'', the imaginary part of the dielectric constant at three different temperatures in the D_{ho} phase of C_5MNTP are given in Figure 3. A single relaxation is observed in the frequency range of measurement. These loss curves are broader than the ideal Debye relaxation and slightly asymmetric in shape. Therefore to extract the relaxation parameters

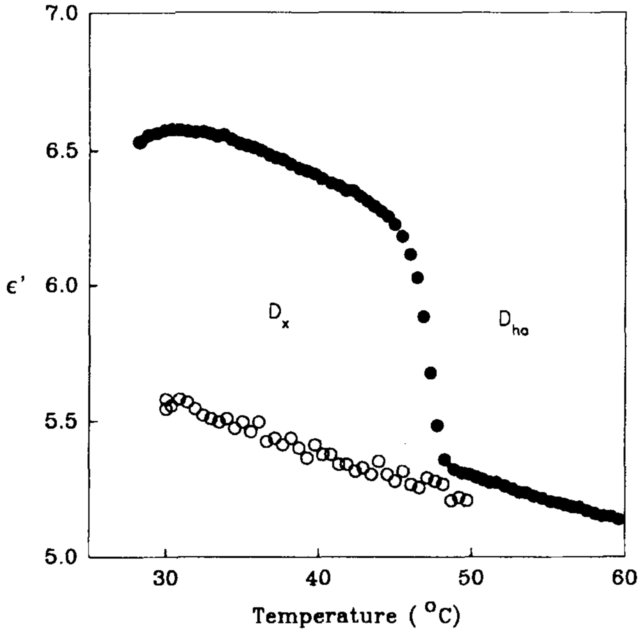


FIGURE 2 Temperature dependence of the real part of the dielectric constant ε' measured at 10 Hz for C_4MNTP (•) and at 100 Hz for C_5MNTP (o). In C_4MNTP a sharp increase in ε' is seen at temperatures corresponding to the D_{ho} to D_x transition; the slow decrease thereafter is due to the lowering of the relaxation frequency.

the empirical Havriliak – Negami (HN) function [10] was used to fit the data

$$\varepsilon(f) = \varepsilon_\infty + \frac{\Delta\varepsilon}{[1 + (if/f_R)^\alpha]^\beta} \tag{1}$$

Here f is the frequency of measurement, ε_∞ is the sum of the dielectric strengths of all the high frequency modes other than the one under consideration, $\Delta\varepsilon$ is the difference between low and high frequency dielectric constants and is a measure of the dielectric strength of the mode of interest, f_R is the characteristic relaxation frequency. The parameters α and β describe the width and asymmetric broadening of the relaxation curve. Solid lines in Figure 3 result from the best fit of the data to Eq. (1). At all temperatures both α and β were found to be close to 1.

The thermal evolution of $\Delta\varepsilon$ and f_R for C_5MNTP are shown in Figures 4(a) and (b) respectively. A monotonic increase of $\Delta\varepsilon$ and lowering of f_R is observed (with decrease of temperature) over the entire range of

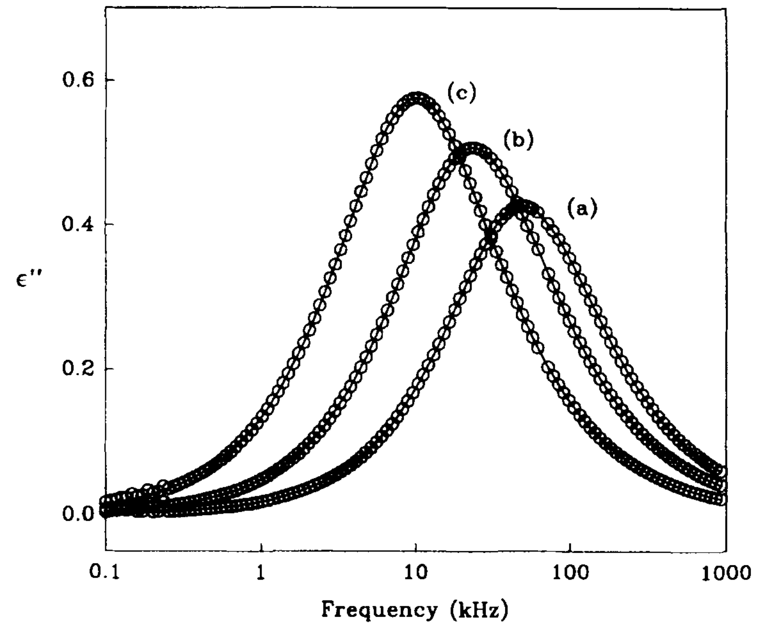


FIGURE 3 Dielectric loss curves obtained in the D_{ho} phase of C_5MNTP at three different temperatures: (a) 50°C, (b) 40°C and (c) 30°C. Notice that the maximum of ε'' increases and the corresponding frequency shifts to lower values as the temperature decreases. The circles are experimental data and the solid lines are fits to the HN expression (Eq. 1).

measurement. In similar asymmetrically substituted triphenylene compounds this type of a relaxation process has been attributed [8] to the hindered rotation of the molecular discs around the column axis and responsible for the glass transition observed at low temperatures. Our existing dielectric set up does not have provision to perform sub-ambient measurements. Therefore, we will not discuss this aspect of the relaxation process here.

The linear variation of f_R in the semilog plot (Fig. 4b) suggests that the behavior is Arrhenius-like and therefore should obey the expression.

$$f_R \propto \exp(-W/k_B T) \tag{2}$$

where k_B is the Boltzmann constant and W the activation energy.

A least-squares fit of the data to Eq. (2) is shown as a line in Figure 4b and does indeed describe the data very well. The calculated activation energy comes out to be 65 kJ/mole and is in good agreement with the values obtained in the D_{ho} phase of other materials [7].

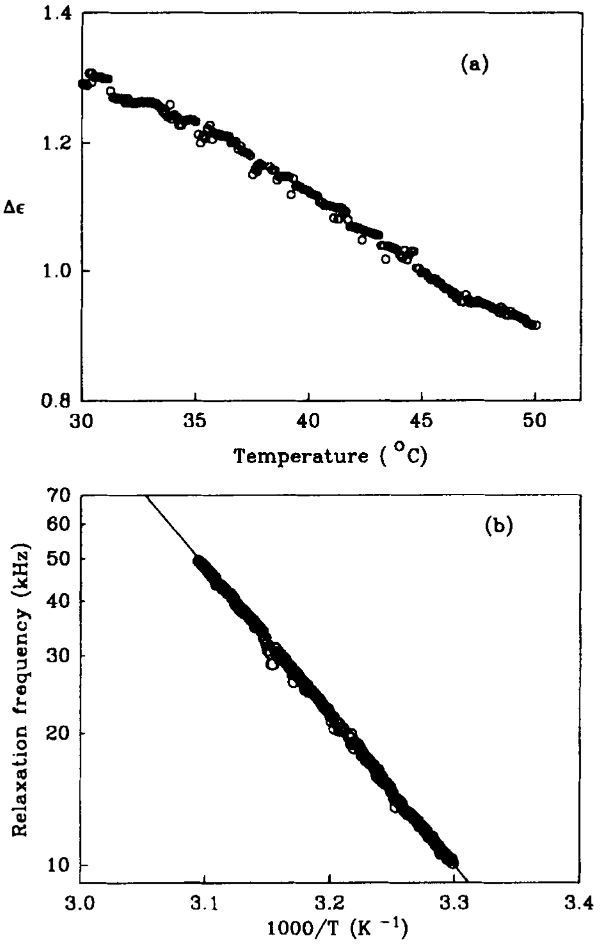


FIGURE 4 Thermal evolution of (a) the dielectric strength $\Delta\varepsilon$ and (b) the relaxation frequency for C_5MNTP. Circles represent the data obtained by fitting the loss curves to Eq. (1). The linear variation in the log (frequency) *versus* inverse temperature indicates Arrhenius behaviour. The "activation energy" responsible for this behaviour has been determined by fitting this data to Eq. (2) and turns out to be = 65 kJ/mol.

Figure 5 shows the ε'' *versus* frequency profiles in the D_{ho} and D_x phases and also in the transition region for the compound C_4MNTP. While only one peak is seen in each of the two phases, co-existence of two peaks is observed in the transition region. This is to be expected for the following reason. As seen in the DSC scan the D_{ho} to D_x transition is strongly first-order associated with a two-phase co-existence. Also the dielectric relaxation frequency changes significantly across the transition, enabling one to

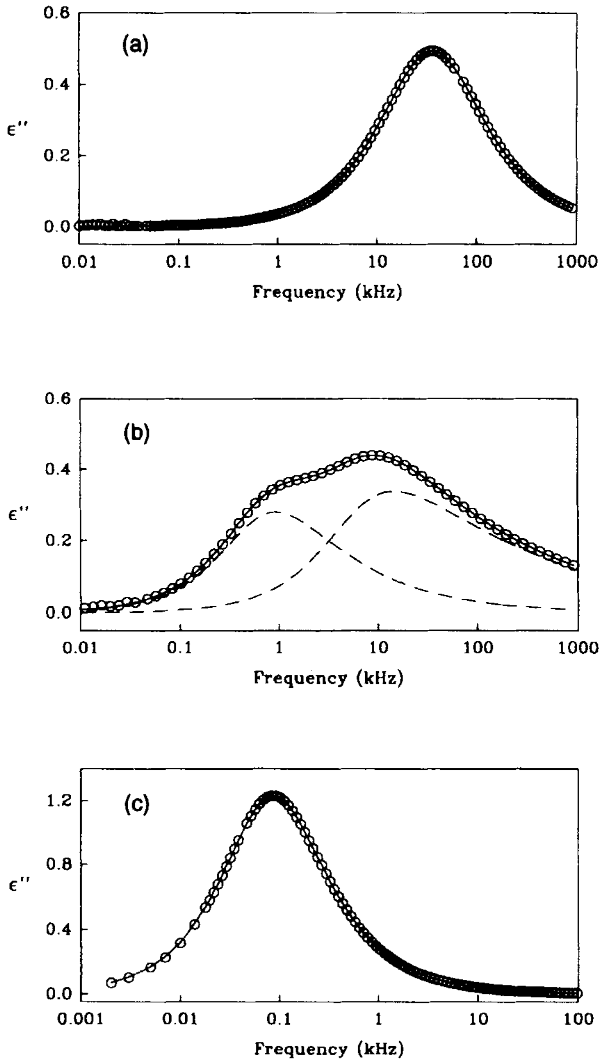


FIGURE 5 Representative plots of ε'' *versus* frequency for C_4MNTP in (a) the D_{ho} and (c) D_x phases. The profile in panel (b) shows the co-existence of peaks due to both the phases in the transition region indicating the transition to be first order. The solid lines through the experimental data (o) are fits to single HN functions in the D_{ho} and D_x phases and a sum of two HN functions in the co-existence region with the individual HN functions shown as dashed lines.

observe the co-existence of peaks due to both the phases in the transition region. In fact, such features have been seen in X-ray scattering [11] and spontaneous polarisation [12] experiments on materials exhibiting a first-order transition.

To get the relaxation parameters, the data collected at temperatures outside the transition region were analysed using a single HN function (Eq. 1). But in the co-existence region, to separate out the individual contributions of the two phases, we used a sum of two HN functions. In the D_{ho} phase the parameters α and β were close to a value of 1 just as for the compound C_5MNTP, but they decreased slightly on going to the D_x phase. For this reason, we have considered the relaxation frequency to be the frequency corresponding to the peak value of ε''.

Plots of $\Delta\varepsilon$ and f_R as a function of temperature are given in Figures 6(a) and (b) respectively for C_4MNTP. It is observed that the transition is accompanied by an upward jump in the magnitude of $\Delta\varepsilon$ and a concomitant downward jump in f_R—additional features characteristic of a first-order

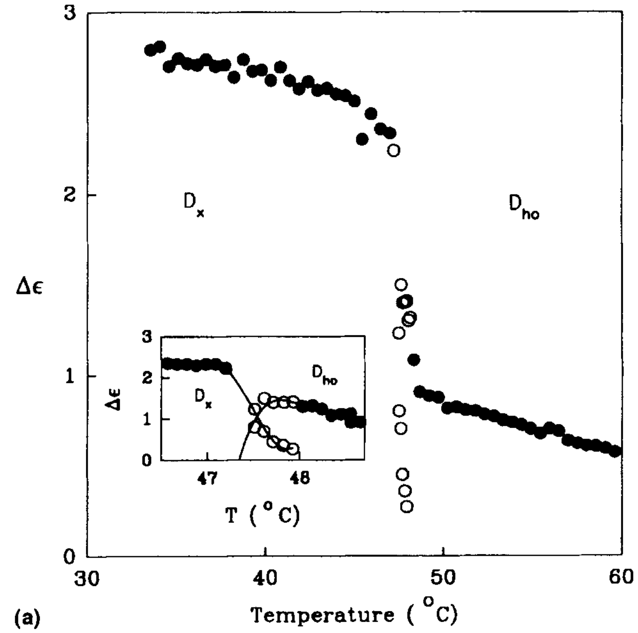


FIGURE 6 (a) Temperature variation of the dielectric strength for C_4MNTP, showing an abrupt increase across the D_{ho} to D_x transition. The data in the two-phase region are plotted as open circles. The inset presented on an enlarged scale shows the variation more clearly with a cross over in the values roughly in the middle of the co-existence region. The solid lines through the open circles are given merely as guide to the eye; (b) Relaxation frequency f_R *versus* temperature for C_4MNTP. f_R falls down by an order of magnitude as the material transforms from the D_{ho} to the D_x phase. Here again data in the vicinity of the transition are shown on an enlarged scale in the inset. In contrast to the behaviour seen for $\Delta\varepsilon$ in the 2-phase region the individual f_R values remain at approximately the same values prior to the transition, a feature to be expected. The activation energy values calculated by considering the data away from the transition yields 89 kJ/mol and 122 kJ/mol in the D_{ho} and D_x phases respectively.

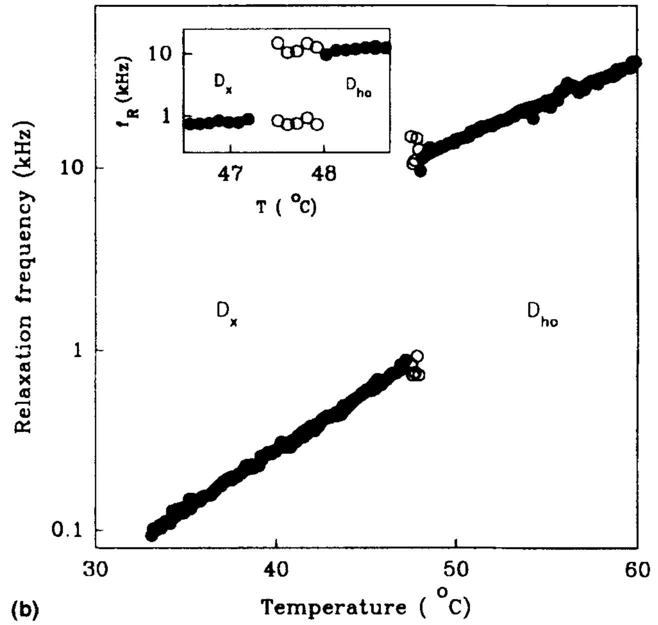


FIGURE 6 (Continued).

transition. Similar enhancement in $\Delta\varepsilon$ and decrease in f_R have been observed across the transition from D_{ho} to plastic columnar phase, although separation of individual contributions in the co-existence region has not been reported. Further, the changes observed in C_4MNTP are orders of magnitude larger than the ones reported for the case of D_{ho}-plastic phase transition [7]. Calculating the activation energies using the data away from the transition we find that in the D_{ho} phase $W = 89$ kJ/mole which is higher than the value got for the D_{ho} phase in C_5MNTP. In the D_x phase we get a higher value $W = 122$ kJ/mole, a trend to be expected as it is more ordered than the D_{ho} phase and therefore the rotations of the molecule are more hindered.

Experiments are underway to carry out measurements below room temperature to find out whether the relaxation phenomenon observed is indeed associated with a glass transition.

Acknowledgements

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References

[1] See *e.g.*, P. E. Cladis, *Mol. Cryst. Liq. Cryst.*, **165**, 85 (1988).

[2] F. Hardouin, A. M. Levelut, M. F. Achard and G. Sigaud, *J. Chim. Phys.*, **80**, 53 (1983); R. Shashidhar and B. R. Ratna, *Liquid Crystals*, **5**, 421 (1989).

[3] N. Boden, R. J. Bushby and A. N. Cammridge, *Mol. Cryst. Liq. Cryst.*, **260**, 307 (1995).

[4] J. A. Rego, S. Kumar and H. Ringsdorf, *Chem. Mater.*, **8**, 1402 (1996).

[5] S. Kumar and M. Manickam, *Mol. Cryst. Liq. Cryst. Lett.*, **309**, 291 (1998); S. Kumar, M. Manickam, V. S. K. Balagurusamy and H. Schonherr (under preparation).

[6] P. A. Heiney, E. Fontes, W. H. De Jeu, A. Riera, P. Carrol and A. B. Smith, *J. Phys. France*, **50**, 461 (1989).

[7] B. Glusen, W. Heitz, A. Kettner and J. H. Wendorff, *Liquid Crystals*, **20**, 627 (1996); B. Glusen, A. Kettner and J. H. Wendorff, *Mol. Cryst. Liq. Cryst.*, **303**, 115 (1997).

[8] S. U. Vallerien, M. Werth, F. Kremer and H. W. Spiess, *Liquid Crystals*, **8**, 889 (1990); H. Groothues, F. Kremer, D. M. Collard and C. P. Lillya, *Liquid Crystals*, **18**, 117 (1995).

[9] T. J. Philips, J. C. Jones and D. G. McDonnell, *Liquid Crystals*, **15**, 203 (1993).

[10] S. Havriliak and S. Negami, *J. Polym. Sci.*, **C14**, 99 (1966).

[11] S. Krishna Prasad, D. S. Shankar Rao, S. Chandrasekhar, M. E. Neubert and J. W. Goodby, *Phys. Rev. Lett.*, **74**, 270 (1995).

[12] S. Krishna Prasad, Geetha G. Nair and S. Chandrasekhar, *J. Mater. Chem.*, **5**, 2253 (1995).