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PRE-TRANSITIONAL EFFECTS IN THE ELECTRIC PERMITTIVITY OF CYANO NEMATICS

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ABSTRACT

Measurements we have made of electric permittivities have revealed new pre-transitional effects in nematics with cyano end groups. These effects have been found to be related to the discontinuity in the mean permittivity at T_{NI} observed for these nematics and they have been attributed to pre-transitional changes in the anti-parallel ordering.

INTRODUCTION

At the nematic to isotropic phase transition the long range nematic ordering vanishes; however, anomalous effects in certain physical properties reveal that residual short range nematic ordering persists well into the isotropic phase. These pre-transitional effects have been found to influence the isotropic values close to the clearing temperature (T_{NI}) of a number of physical properties[1], for example the magnetic birefringence, Kerr constant, nuclear spin lattice relaxation, light scattering and viscosity.[2] We report the new observation of pre-transitional effects in the electric permittivity of nematics with cyano end groups.

EXPERIMENTAL PROCEDURE

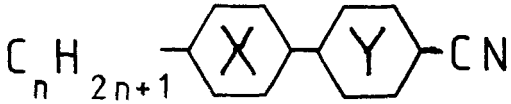
The isotropic permittivity (ε_{is}) was determined from the capacitance of a parallel plate cell measured empty and then full of liquid crystal. The capacitance was determined by an automatic bridge (HP4274A) using a 0.1 V to 5 V signal in the frequency range 100 Hz to 100 kHz. A guard ring was

incorporated in the cell to minimise fringing electric fields and the temperature was stabilized to 0.1°C. This enabled the measurement of ε_{is} to an absolute accuracy of 0.5% and a relative accuracy, for small changes in temperature (< 30°C) of 0.01%.

The permittivity components of the nematic phase ($\varepsilon_{\parallel}$, $\varepsilon_{\perp}$) were measured to within 0.5% using a similar technique.[3] $\varepsilon_{\perp}$ was obtained directly from low voltage measurements of a homogeneously aligned nematic layer and $\varepsilon_{\parallel}$ was estimated from high voltage measurements of the same cell, using a V^{-1} extrapolation.[4] The initial homogeneous alignment (with zero tilt) was achieved by the evaporation of 100 Å of silicon monoxide at 60° to the cell normal. Measurement of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ enabled $\bar{\varepsilon} = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$ to be obtained to an absolute accuracy of 1% and a relative accuracy of 0.5%.

MATERIALS

Table 1 shows the ring structures of the cyano nematics studied based on the following structure:



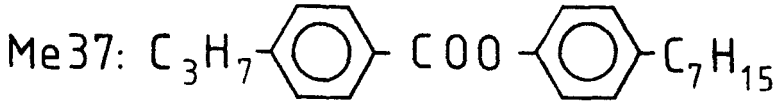
MATERIAL	X	Y
nCB		
nPCH		
nCCH		
nBCO		
5/7* PYR		
3/5/7† PDX		

TABLE 1

* 40m% n=5; 60m% n=7

† 30m% n=3; 40m% n=5; 30m% n=7

Also studied were the eutectic mixture E7 based on cyano-biphenyls, and the non-cyano di-alkylphenyl benzoate ester:



RESULTS AND DISCUSSION

The isotropic permittivity of 7CB measured at 1 kHz with a 5 V signal, is given as a function of $(T-T_{NI})$ in Figure 1 and the results show an anomalous decrease in ε_{is} with decreasing temperature just above T_{NI}. This anomalous behaviour of ε_{is}, which was not influenced by surface alignment, voltage, or frequency, was found to extend over 15°C to 20°C above T_{NI} and amount to $\approx 2\%$ of ε_{is}. A comparable effect below T_{NI} can be seen for $\bar{\varepsilon}$ in the nematic phase of 7CB. Figure 2, which presents ε_{is} for the CB homologues (n=5 to n=12), illustrates that although the effect is present in the isotropic phase of all the homologues, its magnitude depends on the alkyl chain length. These pre-transitional effects have also been observed in other nematics and the results for 3CCH, 3PCH, 3BCO, 5/7 PYR and 3/5/7 PDX are presented in Figure 3 in the form of $\varepsilon_{is}/\varepsilon_{is}$ (max) as a function of $(T-T_{NI})$, where ε_{is} (max) is the maximum isotropic permittivity observed at the peak. The results show a significant variation in the magnitude of these pre-transitional effects between the different nematics, with PCH showing the smallest effects and CB the largest.

It has been observed that these pre-transitional effects occur in all nematics with strongly polar end groups which exhibit a discontinuity in $\bar{\varepsilon}$ ($\delta\bar{\varepsilon}$) at T_{NI}, and they can be interpreted as a consequence of the anti-parallel local ordering which produces the discontinuity $\delta\varepsilon$.[5] On approaching T_{NI} from the isotropic phase there is a coupling between the developing short range nematic ordering and the intrinsic anti-parallel local ordering, resulting in increased anti-parallel correlation which reduces the molecular dipole moments' contribution to ε_{is}. Similarly, the increase in $\bar{\varepsilon}$ observed in the nematic phase can be attributed to a decrease in the anti-parallel correlation resulting from the rapidly reducing long range nematic ordering. For materials which do not exhibit a discontinuity in $\bar{\varepsilon}$ ($\delta\bar{\varepsilon}=0$) the anomalous decrease in ε_{is} is

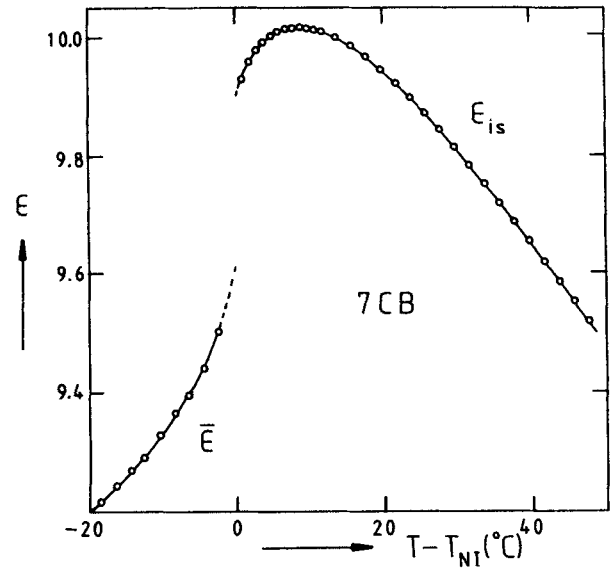


Figure 1. Permittivity of 7CB

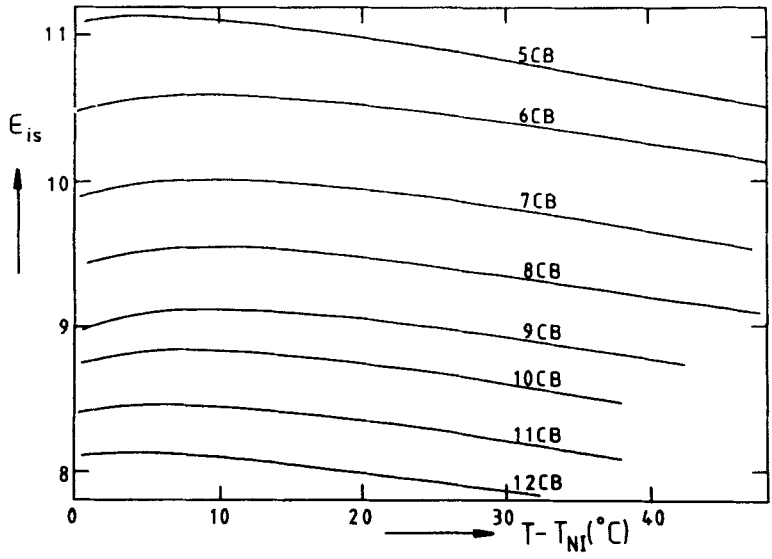


Figure 2. Isotropic Permittivities of Cyanobiphenyls

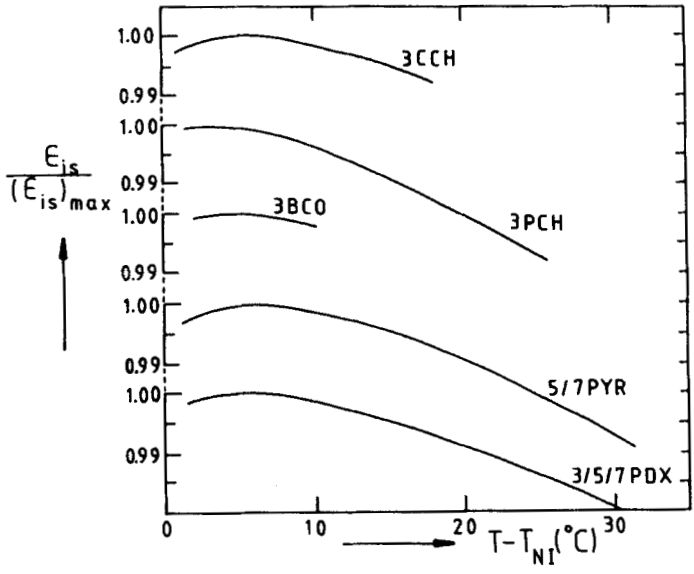


Figure 3. Isotropic Permittivities of Cyano Nematics

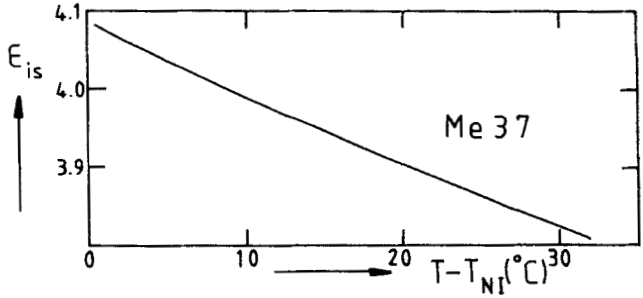


Figure 4. Isotropic Permittivity of Me37

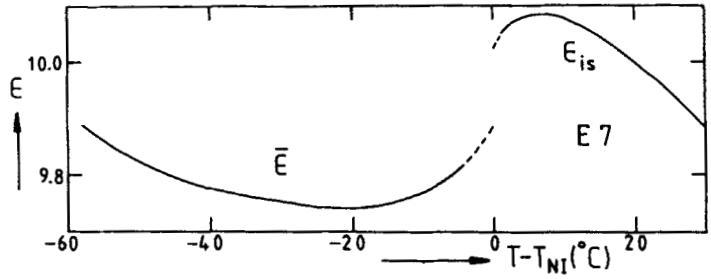


Figure 5. Permittivity of Cyanobiphenyl Mixture E7

not observed; this is illustrated in Figure 4 which shows ε_{is} as a function of $(T-T_{NI})$ for Me37. This observation can be attributed to these materials having no intrinsic anti-parallel local ordering in either the nematic or isotropic phases, and therefore the growth of the short range nematic order in the isotropic phase does not effect the mean permittivity.

The temperature dependence of $\bar{\varepsilon}$ and ε_{is} over a wide range of temperature is illustrated in Figure 5 by the permittivity of the cyanobiphenyl mixture E7. Well away (± 20°C) from T_{NI} it approaches the classical Debye T^{-1} dependence (as in Figures 1, 2 and 3), whereas close to T_{NI} the values are approximately independent of temperature. This suggests that the frequently quoted result that $\bar{\varepsilon}$ and ε_{is} are approximately independent of temperature in nematic materials with strongly polar end groups is true only close to T_{NI} and is a consequence of pre-transitional effects, whereas observation well away from T_{NI} leads to a quite different conclusion.

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