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Experimental Studies on a Terminally Non-Polar Reentrant Nematogenic Mixture

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(February 17, 1988; in final form June 10, 1988)

We present here the results of our x-ray, high pressure and dielectric studies on a reentrant nematogenic mixture of *n*-dodecyl-4-(4-ethoxybenzylideneamino)- α -methylcinnamate and 4-*n*-heptyloxyphenyl-4-(4-ethylcyclohexanoyloxy)benzoate, neither of which possesses a strongly polar end group. The layer spacing measurements show that the smectic A phase is probably of the partially bilayer type. While the pressure-temperature diagram of this mixture is similar to that observed for strongly polar reentrant systems, the dielectric results show some significant differences.

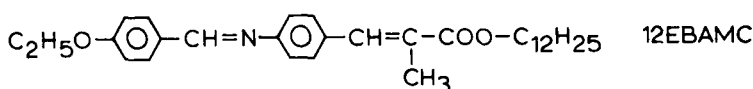
Keywords: terminally non-polar systems, reentrant nematogens

1. INTRODUCTION

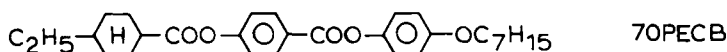
Recently, Pelzl *et al.*¹ observed reentrant nematic behavior in a binary system consisting of terminally non-polar compounds, *i.e.*, compounds without a nitro or cyano end group. Since then a number of phase diagrams involving such materials have been reported^{2–4} which exhibit the reentrant nematic phase. However, except for some preliminary x-ray studies^{1,3} no detailed physical studies have been carried out on terminally non-polar reentrant systems so far. In this paper, we present the results of our x-ray, high pressure and dielectric studies on a binary mixture of *n*-dodecyl-4-(4-ethoxybenzylideneamino)- α -methylcinnamate or 12EBAMC and 4-*n*-heptyloxyphenyl-4-(4-ethylcyclohexanoyloxy)benzoate or 70PECB, both compounds being terminally non-polar.

2. MATERIALS AND EXPERIMENTAL DETAILS

The chemical formulae of the compounds are given in Figure 1 along with their transition temperatures. The phase diagram involving these compounds have al-



K 69 A 81 I



K 61.5 C (41.5) N 183 I

FIGURE 1 Chemical formulae for *n*-dodecyl-4-(4-ethoxybenzylidene-amino)- α -methylcinnamate or 12EBAMC and 4-*n*-heptyloxy-phenyl-4-(4-ethylcyclohexanoyloxy)benzoate or 70PECB. Their transition temperatures are also given.

ready been published.³ The reentrant nematic (N_{re}) phase is observed over a narrow range of concentration, *viz.*, 42 to 46% of 12EBAMC. We have chosen for our study the 44% mixture whose transition temperatures are isotropic–nematic:132.5°C, nematic–smectic A: 68°C and smectic A–reentrant nematic:42°C.

The x-ray diffraction experiments were carried out using a bent quartz crystal monochromator, the film being kept at its focus. A magnetic field of 0.4 T ensured the alignment of the sample. The relative accuracy in the determination of the layer spacing (*d*) in the A phase was $\pm 0.1 \text{ \AA}$. The pressure studies were conducted using a high pressure optical cell with sapphire windows. The phase transitions were detected by the optical transmission technique. Pressure was measured to an accuracy of $\pm 1.5 \text{ bar}$ and temperature to $\pm 100 \text{ mK}$. The dielectric constants were determined using an impedance analyzer. The sample, typically 100 μm thick, was aligned by a 1.5 T magnetic field. Further details of the different experimental techniques have been described elsewhere.^{5–7}

3. RESULTS AND DISCUSSION

The layer spacing (*d*) versus temperature plot is shown in Figure 2. It is seen that 'd' exhibits a small but continuous decrease with decrease of temperature through-

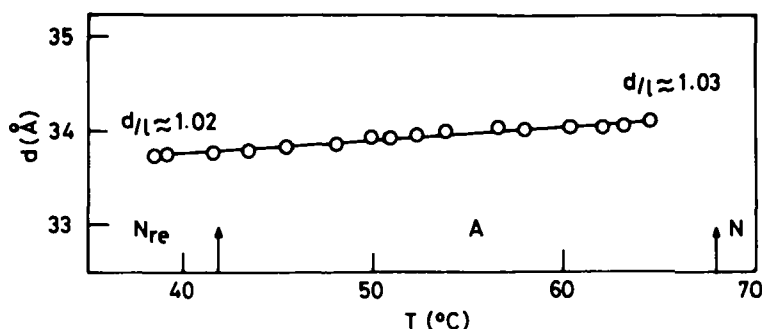


FIGURE 2 Temperature variation of the layer spacing (*d*) in the smectic A phase of 44 mol% mixture of 12EBAMC in 70PECB (see text).

out the A phase. The value of d/l , calculated using the average molecular length (l) of the mixture, comes out to be 1.03 at 65°C and 1.02 at 42°C. Thus it appears that the A phase of the reentrant nematic mixture is probably of the A_d kind although owing to the uncertainty in the determination of l , the possibility of its being a monolayer phase as reported in an earlier study³ cannot be completely ruled out.

The P-T diagram of the mixture (Figure 3) is similar to those observed for strongly polar reentrant systems.⁶ The smectic A–nematic (A–N) phase boundary has an elliptic shape, the maximum pressure up to which the A phase exists being about 0.14 kbar. Another interesting feature of the P-T diagram is that the major axis of the elliptic shaped A–N phase boundary is seen to be parallel to the nematic–isotropic (N–I) phase line. This has been ascertained quantitatively by fitting the data for the A–N boundary to an ellipse and the N–I data to a straight line using a computer (shown as solid lines in Fig. 3). The tilt of the major axis of the elliptic A–N boundary is confirmed to be the same ($\sim 85^\circ$) as that of the N–I line. This indicates the existence of strong coupling between smectic and nematic ordering. Evidence of such a coupling has already been demonstrated in reentrant systems composed of terminally polar materials.⁸

Figure 4 shows the variation of the static dielectric constants (ϵ_{\parallel} and ϵ_{\perp}) and the dielectric anisotropy ($\Delta\epsilon$) in the N, A_d and N_{re} phases. It is seen that the dielectric behavior is different from what is generally seen in strongly polar reentrant systems—in particular $\Delta\epsilon$ shows a pronounced decrease with decrease of temperature

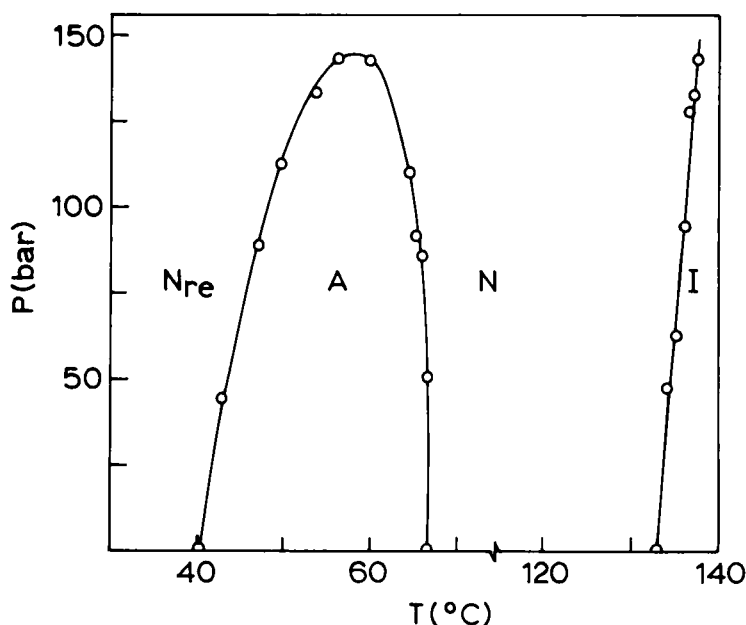


FIGURE 3 Pressure-temperature (P-T) diagram of the 44 mol% 12EBAMC–70PECB mixture. The solid curves are obtained by the computer fits of the A–N and N–I data to the equations of an ellipse and a straight line respectively.

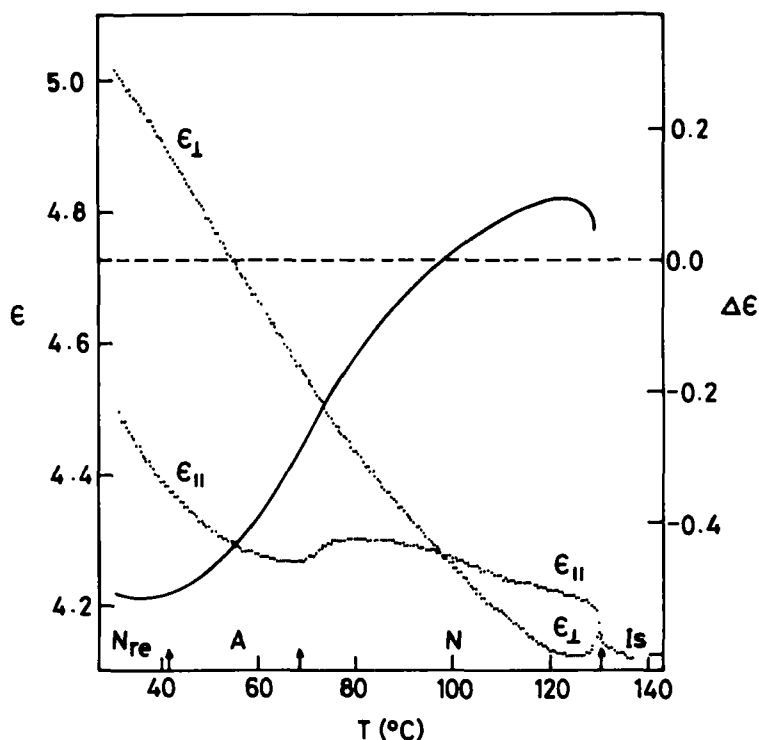


FIGURE 4 Variation of the static dielectric constants ($\epsilon_{||}$, ϵ_{\perp}) and dielectric anisotropy ($\Delta\epsilon$) in the different phases of the 44 mol% mixture of 12EBAMC in 70PECB.

leading to a sign reversal (see Figure 4) which is in striking contrast to the continuous increase of $\Delta\epsilon$ observed in strongly polar materials.⁹⁻¹¹ The reason for this unusual temperature dependence of the dielectric properties is not yet clear to us.

Although the occurrence of reentrant nematic phase in terminally non-polar systems has been explained by Dowell¹² on the basis of a molecular lattice theory, further experimental studies on more such systems are necessary for a better understanding of the reentrant nematic phenomenon.

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