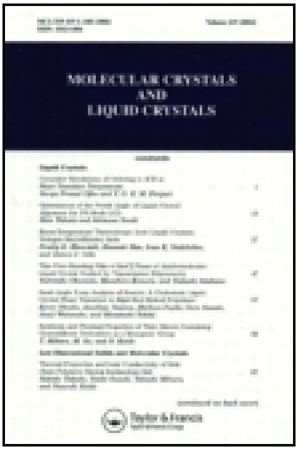

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Freedericksz Transition Studies of Solutions of Side Chain Polymer Liquid Crystals in Low Molar Mass Mesogens†

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A series of side chain liquid crystal polymer solutions using a low molar mass mesogen as the solvent have been studied by optical microscopy, the Freedericksz transition and dielectric constant measurements. The optical microscopy was used to establish that all the solutions were nematic and to determine their phase transitions. The samples were aligned homeotropically or with a planar texture and Freedericksz transition measurements were carried out using magnetic and electric fields. The apparatus and method used are described in detail. The dielectric constants were determined using a capacitance bridge method. From these measurements it was established that k_{11}, k_{33}, k_{33}/k_{11} and $\Delta\epsilon$ all decrease with increasing polymer concentration. The maximum polymer concentration used was 19.5% w/w and all the solutions were stable and homogeneous. It was also shown that the polymer appears to decrease the amount of antiparallel ordering exhibited by the cyano terminated nematogens. The results are discussed in terms of the important polymer features.

INTRODUCTION

Thermotropic polymer liquid crystals have evoked considerable interest recently because of their potential application to new technologies. For example, main chain thermotropic polymers would appear to have great potential for use in the production of ultra-high

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modulus fibres whilst the side chain systems have an equal potential for use in novel electro-optic displays. In the current paper we will be concerned with the latter types of polymer.

Side chain polymer liquid crystals have been recently reviewed in some detail by Finkelmann and Rehage[1] and also by Shibaev and Platé.[2] Essentially these systems consist of long flexible or semi-flexible polymer backbones with pendant mesogenic moieties attached at convenient positions along the backbone. The nature of the backbone (i.e. poly -acrylate, -methacrylate or -siloxane), the degree of side chain substitution and the length of the decoupling side chain spacer group all serve to alter the macroscopic molecular flexibility as well as the type of mesophase observed and its transition temperatures. The nature of the side group itself will also clearly have a part to play in determining the latter properties in particular. Electro-optic effects have been demonstrated in nematic side chain polymer liquid crystals although their response times were slow and the operating temperatures about 100°C above ambient.[3,4] Clearly these conditions are not convenient, although as pointed out[5] such materials may be used to effect storage of optical information below the polymer's glass transition temperature (Tg). We have recently reported methods[6] whereby storage may be achieved more conveniently using smectic polymer liquid crystals. It would appear that in the pure state the main use of such materials will be in the production of slow response or storage devices. However, in this paper and the accompanying one by Sefton et al[7] we wish to report on a further, and we believe novel, use of side chain polymer liquid crystals.

We have dissolved a side chain polymer liquid crystal in a monomeric host in order to try and use the backbone flexibility and degree of coupling between the side group and backbone to change the macroscopic elastic constants of the host without increasing the viscosity of the mixture to an unreasonably high value. In principle this should give a new method of engineering mixtures for display devices. Because of its high backbone flexibility, we have used a polysiloxane system with pendant cyano-biphenyl and benzoate ester side groups. This polymer was chosen because of its strong electro-optic response and also because it allowed us to use pentyl cyanobiphenyl as the monomeric host. This latter material is well known for its excellent chemical stability[8] and use in electro-optic displays.[9] All of the solutions, reported herein, exhibited nematic phases and we have observed no significant change in their properties over a twelve month period. In this paper we report on the optical microscopy, the dielectric anisotropy measurements and the evaluation of the Frank splay and bend elastic constants, obtained using the Freedericksz transition of polymer/monomer solutions up to a concentration of ~20% w/w. In the accompanying paper[7] we give details of the twist elastic constant-viscosity ratio (i.e. k_{22}/γ_1) and refractive index data of similar solutions.

EXPERIMENTAL

Material

The nematic monomeric liquid crystal host or solvent used in these studies was a 4-cyano-4'-n-pentyl biphenyl (5CB) which was provided

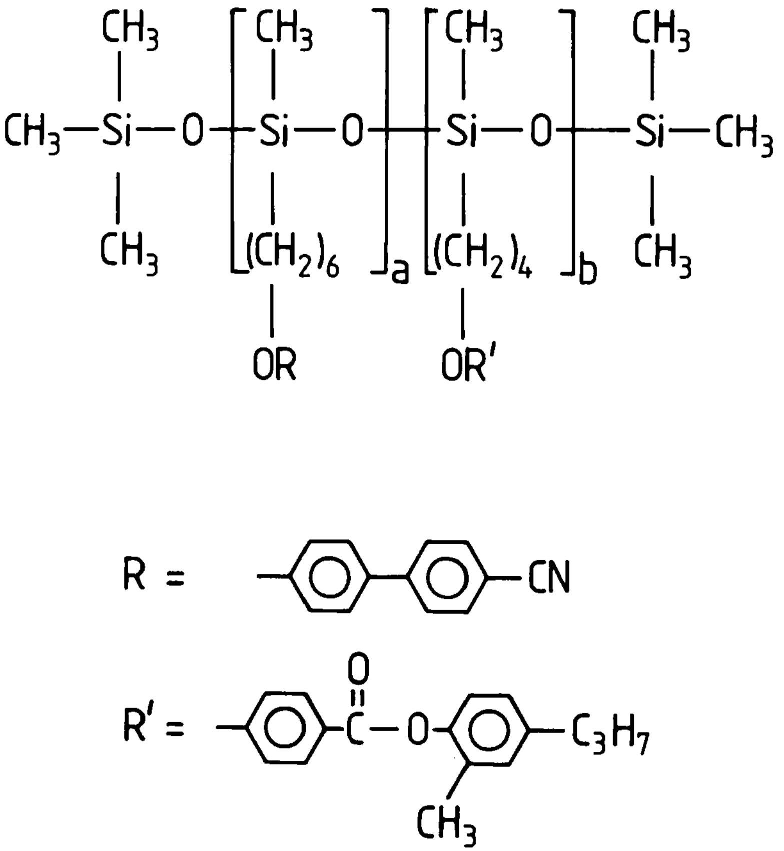


FIGURE 1 Chemical structure of the polysiloxane polymer liquid crystal PG296, where a = b = 25.

by BDH Ltd (Pool, Dorset, UK). This was used without further purification as its nematic to isotropic phase transition temperature (T_c) was within 0.05°C of that accepted for 5CB (i.e. T_c = 35.2°C). The polymer liquid crystal used as a solute was a polysiloxane system, Figure 1, containing 50 SiO units plus termination groups which was synthesised for us by Professor Gray and colleagues at Hull University.[10] This polymer had equal ratios of cyanobiphenyl and benzoate ester groups (i.e. a = b = 25) and in the pure state exhibits a smectic phase between 4°C (T_g) and 85.9°C (T_{SI}). The phase behaviour of this system, denoted PG296 for consistency with other published work, has been considered in some detail elsewhere.[11] The solutions were prepared by shaking at room temperature and, as discussed below, exhibited only nematic phases. Polymer/monomer solutions were studied up to a concentration of 19.5% w/w (weight of polymer/total weight of the solution). We verified from both refractive index measurements as a function of concentration[7] and optical microscopy that the solutions were homogeneous.

Cell construction and alignment procedures

Cells were constructed from indium tin oxide coated glass slides using an inert polymer film (Du Pont's Kapton) for spacing and an epoxy

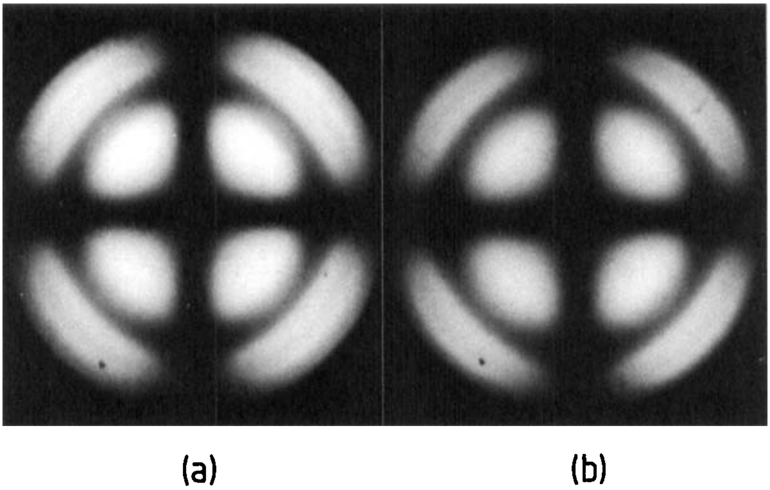


FIGURE 2 Conoscopic figures for (a) pure 5CB and (b) the 9.05% w/w solution. These figures were photographed with the samples held between crossed polars on the microscope stage. The microscope was equipped with a Bertrand lens and the samples were aligned homeotropically using lecithin as described in the text. T = 25°C.

See Color Plate I, Volume 131, nos. 3–4.

resin for sealing. Before alignment procedures were carried out and prior to construction, the indium tin oxide coated slides were cleaned ultrasonically in a detergent solution, rinsed in freshly distilled water and then blown dry with nitrogen. Great care was taken during cell construction to avoid possible contamination of the liquid crystalline solutions, and to this end the nematic-isotropic transition temperature was measured daily using a Mettler FP800 series hot stage, to confirm the stability of the cells and the material. In these studies a cell thickness of 40μm was used and this was reproducible to within ± 10%.

In order to determine the elastic constants and measure the dielectric constants by the methods used herein, we require good homeotropic and planar surface alignments. Homeotropic alignment was achieved by treating the surface with a lecithin solution (BDH-Egg Grade II at a concentration of 0.5% in chloroform). The wetted surface was then allowed to dry naturally. The quality of alignment was verified by optical conoscopy and is shown in Figure 2. The homeotropic alignment was equally good for the polymer solutions (Figure 2(b)) as for the pure 5CB (Figure 2(a)). Disclination free planar alignment, over the region of the cell used in these experiments (i.e. several mm^2) was achieved using a rubbed poly vinyl alcohol (PVA) surface layer. The PVA was applied from a 3% w/w solution (in distilled water), dried on a warm surface (~60°C) and then rubbed unidirectionally using a rayon velvet coated block. Cells made this way gave good planar alignment with low tilt angle, as monitored using crossed polarisers. It was also observed microscopically that fewer alignment non-uniformities occurred with increasing polymer concentration for the polymer/monomer solutions.

Phase behaviour

Phase transitions were determined optically using a Mettler F800 controller and FP82 hot stage. The nematic to isotropic transition temperatures were all determined on heating from the nematic phase at a uniform rate of 0.2°C/min. The crystalline to nematic phase transitions were determined on heating from the crystalline phase at 5.0°C/minute. The heating process was carried out in 1°C steps up to the melting point. Cooling was achieved by passing dry nitrogen, which had previously been cooled using a liquid nitrogen heat exchanger, over the sample on the microscope hot stage.

Elastic constant determination

The Frank elastic constants, k_{11} and k_{33} (i.e. splay and bend) have been determined using the Freedericksz transition technique.[12] Using the particular geometry for each case we have determined k_{11} and k_{33} using electric and magnetic fields respectively. The equivalence of the magnetic or electric field methods was established by Gruler et al.[13]

Our experimental arrangement is shown schematically in Figure 3. The HeNe laser (λ_0 = 632.8nm) was a Hughes Aircraft Corporation 10mW system with a ±0.3% intensity and polarisation stability. The polariser and analyser were Glan-Taylor polariser prisms (Electro-Optic Dev. Ltd. GT2). The photodiode was a fast linear response diode (Radiospares R. S. Components Photodiode BPX65) and its output was monitored and recorded using a BBC-B microcomputer adapted with a suitable interface. This interface also allowed the Bell 640 Incremental gaussmeter output to be monitored simultaneously. The microcomputer was connected on line to a PDP 11/34A mini-computer allowing fast data analysis and storage. The sample cell holder was home built from brass and thermally insulated with MI-CROTHERM lagging. A circulating silicone fluid system was used to control and maintain the sample temperature to a stability of ±0.01°C over a one hour period. A temperature range from −30°C to 150°C was available and was monitored at the sample, within 2mm of the laser beam, using a calibrated thermistor. The electro-magnet was built in the University and with a pole piece separation of 4cm gave fields up to 0.8T at the centre of the gap. Field inhomogeneities were less than 0.3% in the 1cm^3 central volume.

We have used the above experimental arrangement to measure both k_{11} and k_{33}. For small molecular distortions a suitable geometry may be chosen such that the expressions for the threshold fields contain only one elastic constant. For the magnetic field case the bend elastic constant is given by:

$$H_c = \frac{\pi}{d}\left[\frac{k_{33}}{\Delta\chi}\right]^{1/2} \tag{1}$$

where d is the thickness of the nematic layer and $\Delta\chi$ is the diamagnetic anisotropy. H_c is the threshold magnetic field needed to deform a homeotropic nematic layer, with the nematic director in the viewing direction and the magnetic field applied orthogonally to the director. This threshold field was determined optically by measuring the optical retardation between the ordinary and extraordinary components of the input laser beam for one traverse of the cell at a constant magnetic field. The optical retardation was then measured as a function of magnetic field and extrapolated to zero retardation in order to de-

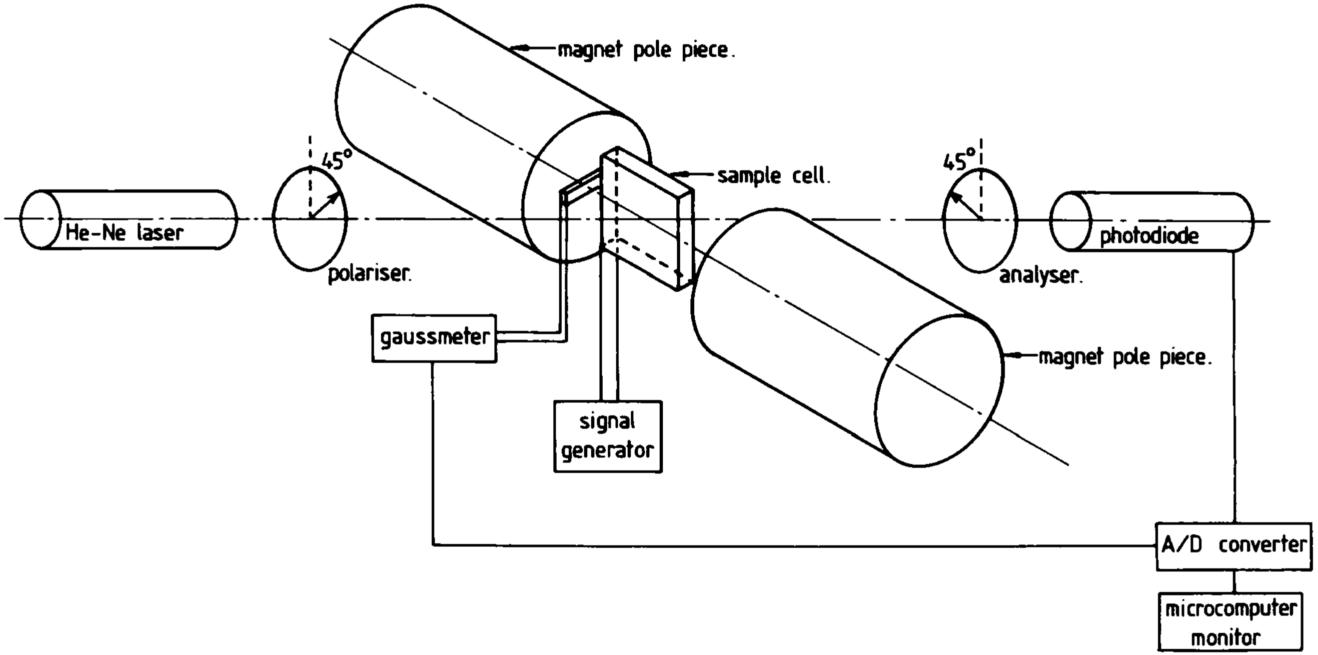


FIGURE 3 Schematic diagram of the experimental arrangement used for the Freedericksz transition measurements.

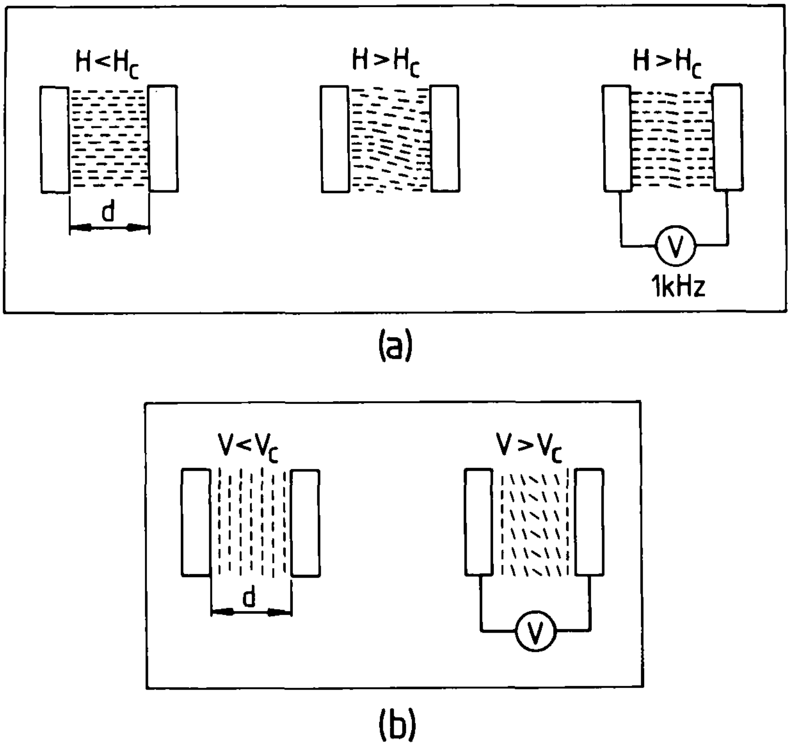


FIGURE 4 Schematic diagram of the molecular arrangement in the liquid crystal cell undergoing Freedericksz transition from (a) a hometropic alignment and (b) a planar alignment. In both (a) and (b) the probe laser beam passes from left to right through the cells. In (a) the magnetic field is applied transversely across the cell, i.e. in the vertical direction as drawn. In both (a) and (b) the electric field is applied in the direction of propagation of the probe beam.

termine H_c. $\Delta\chi$ can in principle be measured using a Faraday-Curie balance. However, we believe that this is an unnecessarily complicated technique and have used the method due to Schad et al[14] of balancing magnetic and electric fields. The latter method, outlined below, is probably quicker and more accurate than the Faraday-Curie method.

The basic principle of the Schad et al[14] method, shown from left to right in Figure 4a, is to apply a magnetic field transversely to a homeotropic aligned nematic sample (Figure 4(a) left). For $H > H_c$, a Freedericksz distortion of the cell occurs (Figure 4(a) centre). For a given magnetic field an opposing electric field is applied, in the original director direction, to counter the distortion caused by the magnetic field (Figure 4(a) right). Thus for a given value of H, a voltage V will be measured that just restores the initial conditions. Experimentally it is simpler to apply a fixed voltage V and determine the effective threshold magnetic field $H_c(V)$ necessary to cause the Freedericksz transition. For balancing fields, the relationship between $H_c(V)$ and V is given by:[14]

$$\left[H_c(V)\right]^2 = \left[H_c(O)\right]^2 + \frac{\epsilon_0 \Delta\epsilon}{|\Delta\chi|}\left[\frac{V}{d}\right]^2 \tag{2}$$

where $H_c(O) = H_c$ as defined in Equation 1, and $\Delta\epsilon$ is the dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ and the subscripts refer to parallel and perpendicular to the director respectively). Thus a graph of $[H_c(V)]^2$ versus V^2 allows $\Delta\chi.d^2/\Delta\epsilon$ to be determined. Since $\Delta\epsilon$ is measured, see below, for the k_{11} determination this method obviates the need for measuring $\Delta\chi$ and d separately. If d is measured accurately then $|\Delta\chi|$ is readily determined. In our measurements we varied V but used a fixed 1kHz a.c. frequency. V (which is an r.m.s. value) was measured using a true r.m.s. digital voltmeter accurate to ±0.5% at this frequency.

The splay elastic constant was determined in the same apparatus as above but with a uniform planar surface alignment, Figure 4(b). In this case no magnetic field was applied and only a transverse electric field was used to perturb the nematic alignment. For this geometry the critical voltage V_c that just causes the Freedericksz distortion is related to the splay elastic constant by:

$$V_c = \pi \left[\frac{k_{11}}{\epsilon_0 \Delta\epsilon}\right]^{1/2} \tag{3}$$

We determined V_c from the optical retardation (as above) by varying V and extrapolating back to zero deformation.

The values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ were determined in collaboration with Drs. E. P. Raynes and M. J. Bradshaw of the RSRE (Malvern, U.K.). These dielectric constants were measured as a function of concentration and temperature using a capacitance bridge technique.[15] The measurements were performed using a 1kHz aligning electric field and the cell was constructed using a guard ring to avoid possible stray field effects. The values of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ were measured to an accuracy of better than 0.5% (ref 15). These values were then used in the determination of both k_{11} and k_{33}.

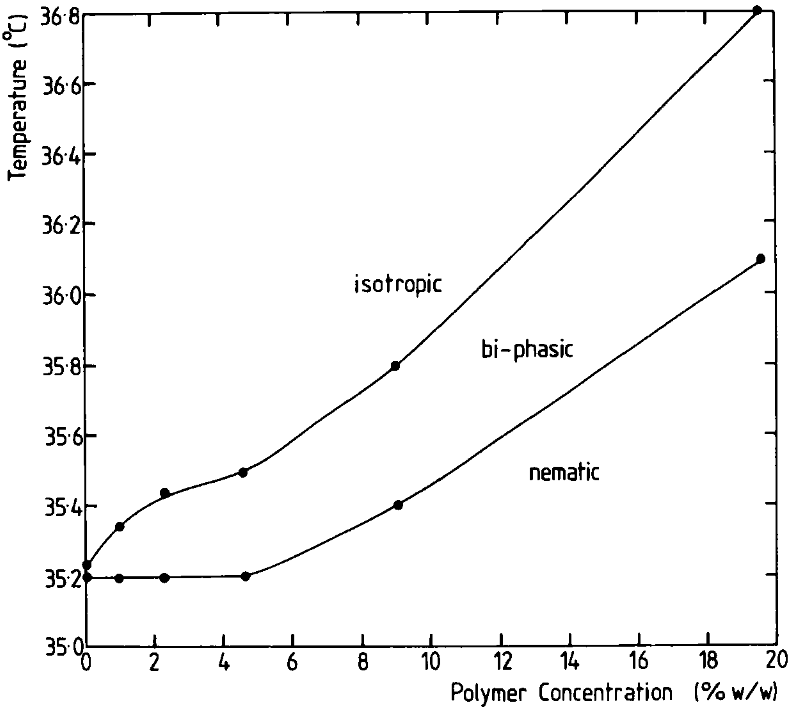


FIGURE 5 Partial phase diagram showing the nematic to isotropic transition as a function of concentration for the PG296/5CB solutions.

RESULTS AND DISCUSSION

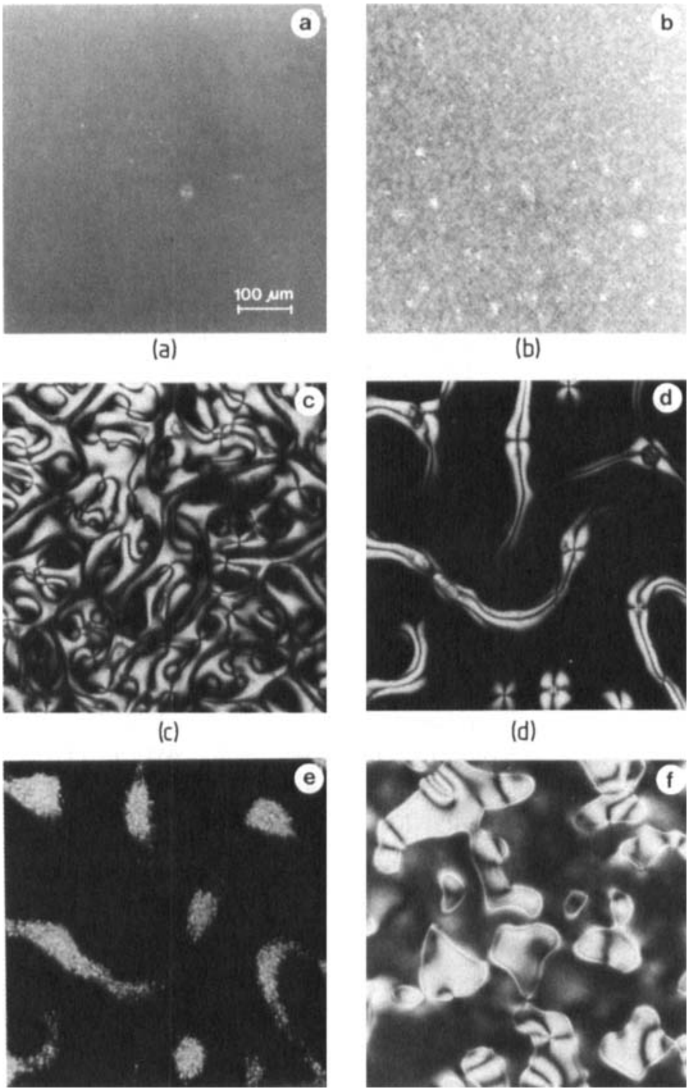
Phase behaviour

The behaviour of the nematic to isotropic phase transition with increasing polymer concentration is given in Figure 5. These data show two significant features. Firstly, the polymer causes the system to exhibit a stable biphasic region, although even for the 19.5% w/w solution this only spans a temperature range of 0.7°C. The second feature is the very gradual change in the clearing temperature with concentration. For example, for the 19.5% w/w solution T_c, taken as the mid-point of the biphasic region (see below), only increases by ~1.5°C with respect to pure 5CB. This is interesting since the pure polymer exhibits a smectic to isotropic phase transition[11] between 85°C and 113°C. A further feature of the addition of the polymer to 5CB is the large suppression of the crystallisation temperature (T_k). Pure 5CB has a T_k of 22°C although in a thin cell some supercooling may occur. At or above a concentration of 19.5% w/w we have not been able to observe T_k, for such a thin cell, even though our cooling stage has a lower limit of −60°C. For the 9.05% solution a value of T_k = 3.0°C was observed on heating from the crystalline state. No smectic phase transitions were observed with any of the solutions studied herein. This suggests that the addition of polymers to the monomers might be a convenient method for making wide temperature range nematic mixtures.

The textures observed with the polymer solutions were typical of low molar mass nematogens with the exception of the existence of the biphasic region. Photographs of the microscopic observations of a homeotropically aligned sample of the 9.05% w/w solution are presented in Figure 6. The cycle starts with the nematic sample at a temperature 0.6°C below the start of the biphasic region, Figure 6(a). The sample was then heated at 0.2°C per minute through the biphasic region, Figures 6(b)–(d), and became totally isotropic at 35.8°C. The black areas in the photographs correspond to the isotropic phase. The sample was then heated a further 0.2°C into the isotropic phase and then cooled rapidly, in 15 seconds, back to the starting temperature. Shortly after cooling commenced, the biphasic appearance of the sample returned, Figure 6(e), followed by the nematic phase, Figure 6(f). The alignment of the nematic phase, unlike pure 5CB, did not return directly to a homeotropic state. As figure 6(f) shows the nematic sample exhibited unstable regions of planar alignment which persisted for several minutes before the texture relaxed back to the homeotropic state. This alignment hysteresis was typical of the polymer solutions. Finally, for comparison we have presented the textures observed on melting pure 5CB, Figure 7. In this figure there is a temperature gradient from left to right of 0.02°C. The left hand side of the figure shows the isotropic phase whilst the right hand shown the homeotropic texture. It is worth stressing that for both the homeotropic and planar alignment techniques all of the polymer solutions exhibited good alignment with a slight improvement in quality for the most concentrated solutions.

Elastic constant determination

Using the method due to Schad et al[14] of counteracting magnetic and electric fields, we have determined $\Delta\chi . d^2/\Delta\epsilon$ for all of our samples. Typical data is given for $[H_c(V)]^2$ versus V^2 for pure 5CB at various temperatures in Figure 8. As seen from Equation 2, the slope of these graphs give $\Delta\chi . d^2/\Delta\epsilon$ and from Figure 8 it is evident that this term is only very weakly temperature dependent. Between 12.7°C and 2.1°C below T_c the slope only alters by ~2% in keeping with the data for



(a) (b) (c) (d) (e) (f)

FIGURE 6 Optical photo micrographs of the homeotropically aligned 9.05% w/w polymer solution on heating into the isotropic phase (a)-(d) and cooling into the nematic phase (e) and (f). All photographs were taken through crossed polars and the magnification is indicated by the scale bar in (a); (a) shows the homeotropic texture at 34.8°C, (b), (c) and (d) show the sample transforming through the biphasic region to the isotropic phase (black regions) and (b), (c) and (d) correspond to temperature of 35.5, 35.6, and 35.7°C respectively, (e) and (f) show the texture on cooling rapidly to 34.8°C in the nematic phase. The planar texture shown in (f) relaxes back after several minutes to a homeotropic alignment as in (a).

See Color Plate II, Volume 131, nos. 3–4.

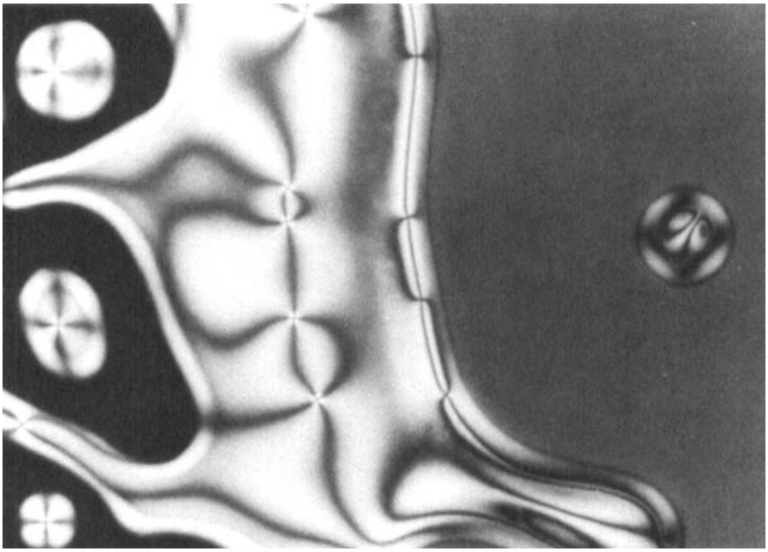


FIGURE 7 Optical photomicrograph of pure 5CB. The photograph was taken through crossed polars and the sample held near to its clearing temperature T = 35.2°C so that there is a decreasing temperature gradient of 0.02°C across the photograph from left to right. The black regions correspond, therefore, to the isotropic phase. The width of the sample area shown is approximately one millimeter.

See Color Plate III, Volume 131, nos. 3–4.

7CB presented by Schad et al.[14] Similar straight line graphs were recorded for all of the polymer solutions with a slightly increased change in slope, i.e. 4% for the most concentrated solutions over the same temperature range. Using these data and the values of $\Delta\epsilon$ measured independently (see below) the elastic constants k_{11} and k_{33} were determined as a function of temperature for pure 5CB and various concentrations up to 19.5% w/w, Figures 9 and 10 respectively. In these and subsequent figures T_c is taken as the middle of the biphasic region for the polymer solutions and not the temperature at which the last biphasic structure disappears. This mid-point was the highest temperature at which a Freedericksz transition could be observed in any of our samples and therefore such a T_c would seem to be a sensible choice for use in comparisons between the solutions and pure 5CB.

The results for pure 5CB are in good agreement with those presented by Bunning et al,[16] who compared their data to those of Karat and Madhusudana[17] (after scaling), and with Bradshaw et al.[18] The repeatability of the method was good. The points lying on the $T_c - T = 10.5°C$ line in figure 8 are taken from two measurements on the same cell separated by several hours and several thermal cycles. The

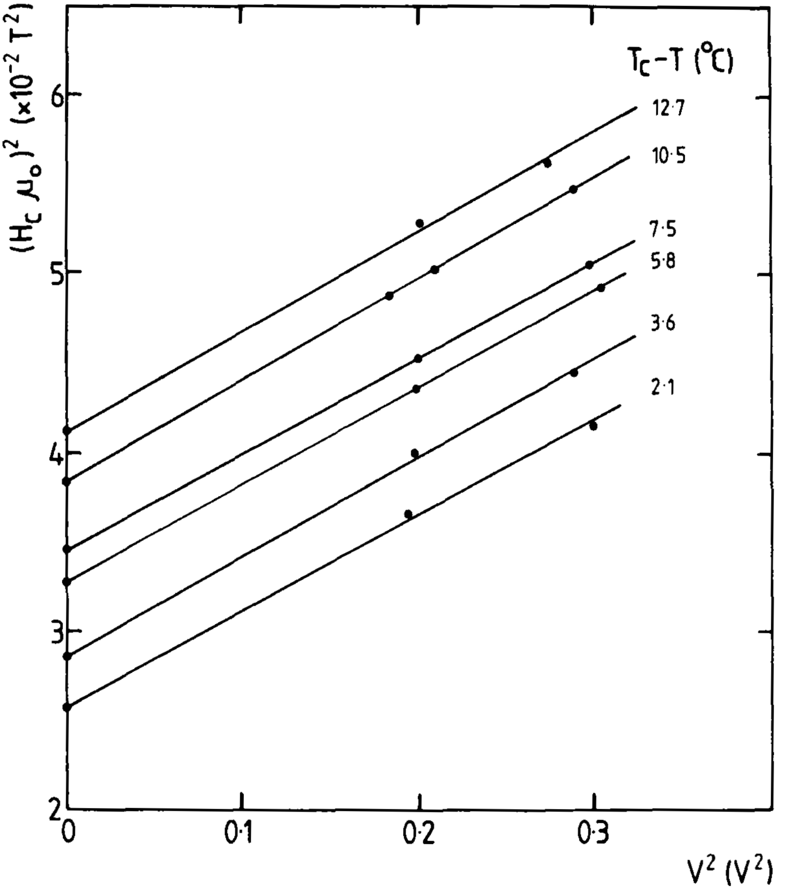


FIGURE 8 Variation of the threshold magnetic field $[H_c]^2$ as a function of the crossed r.m.s. electric field V^2 for pure 5CB at several reduced temperatures, T_c = 35.2°C and f = 1kHz.

cell by cell repeatability was also good and the k_{11} data for pure 5CB, Figure 9, comprises data taken for three different cells.

As pointed out by Bunning et al,[16] the k_{33} data is very sensitive to misalignment errors. Misalignment of the sample relative to the laser beam and magnetic field causes the optical retardation versus applied field curve to deviate from a straight line near to H_c. This could cause some error in the determination of H_c. In the field compensating method the same problem arises in determining $\Delta\chi d^2/\Delta\epsilon$. However, in this case the sources of error tend to cancel each other out and, although great care was taken to align the probe laser beam orthog-

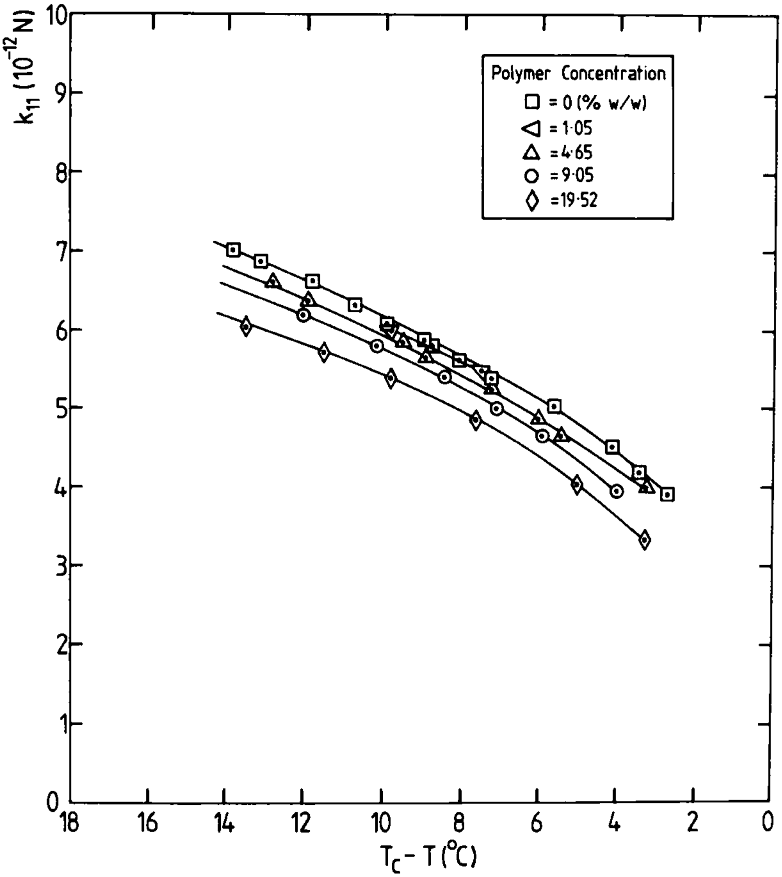


FIGURE 9 Splay elastic constants k_{11} as a function of the reduced temperature for various polymer concentrations. The inset key also gives the concentrations for the PG296/5CB solutions referred to in Figures 10, 14 and 16.

onally to the applied fields, the compensating method is inherently less sensitive to such problems. Further, as the cell is not removed from the cell holder, all measurements are carried out at the same temperature, over the same surface area and at the same cell thickness.

From Figures 9 and 10 it is evident that addition of the polymer causes both elastic constants to decrease significantly with increasing polymer concentration. The variation of either k_{11} or k_{33} with temperature appears to be similar for the concentrations studied herein. To examine the concentration behaviour further we have re-examined

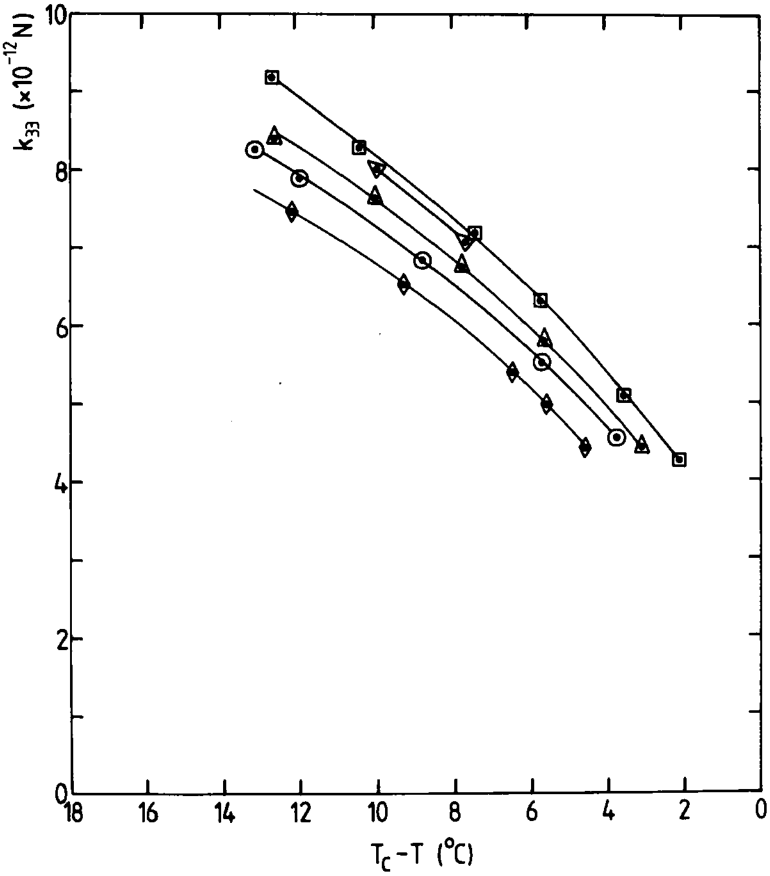


FIGURE 10 The bend elastic constant k_{33} as a function of the reduced temperature for the same concentrations of PG296 in 5CB as in Figure 9.

the data at fixed temperatures as a function of concentration, Figures 11 and 12. From these data it is clear that k_{11} and k_{33} both decrease smoothly with increasing polymer concentration. It is also evident that k_{33} decreases more markedly than k_{11}. This has important implications for multiplexing mixtures and is shown clearly in Figure 13 where k_{33}/k_{11} has been given as a function of concentration. Thus, it would appear that the polymer has an important influence on primarily the bend elastic constant. For the 19.5% w/w solution, k_{33} decreases by ~20% relative to 5CB at 25°C. Our recent preliminary results suggest that the relevant viscosity coefficient for the bend deformation increases by *circa* an order of magnitude for the same

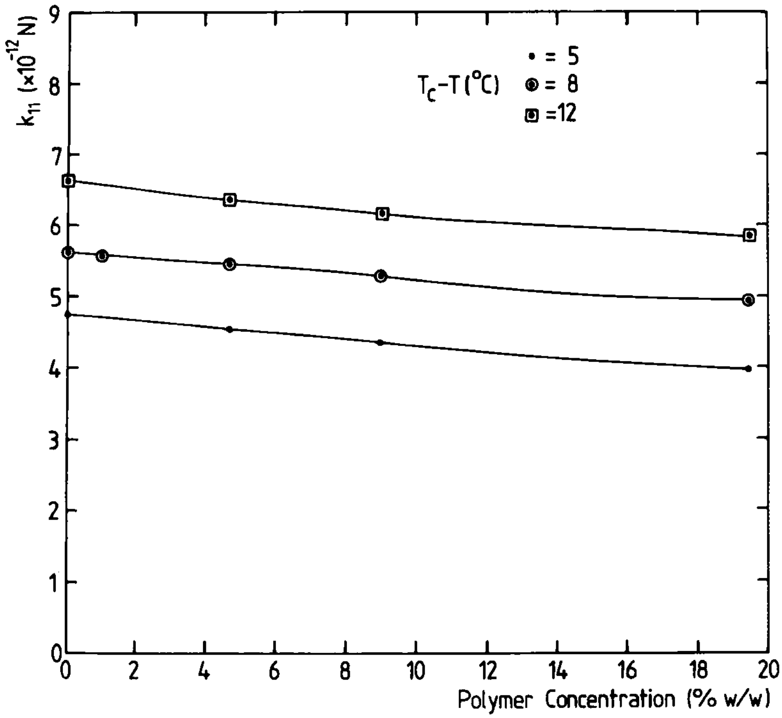


FIGURE 11 The splay elastic constant k_{11} as a function of concentration for three reduced temperatures.

concentration in comparison with 5CB. Using suitable thin cells this would suggest response times ≤200ms at modest applied voltages which would still be acceptable for many display devices.

Dielectric constants

Using the capacitance bridge method developed by Clark et al[15] we have measured the dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for pure 5CB and three of the solutions as a function of temperature, Figure 14. From these data it would appear that $\epsilon_{\parallel}$ is most affected by the increasing polymer concentration whilst $\epsilon_{\perp}$ only increases marginally. From these data we have calculated $\Delta\epsilon$ and this is shown in Figure 15 for various temperatures as a function of concentration. These initial results suggest that $\Delta\epsilon$ decreases linearly and slowly with increasing polymer concentration. We have used this fact when determining $\Delta\epsilon$ values used in the k_{11} and k_{33} calculations for the 1.05% w/w solution. The important observation from the present measurements is that the ratio

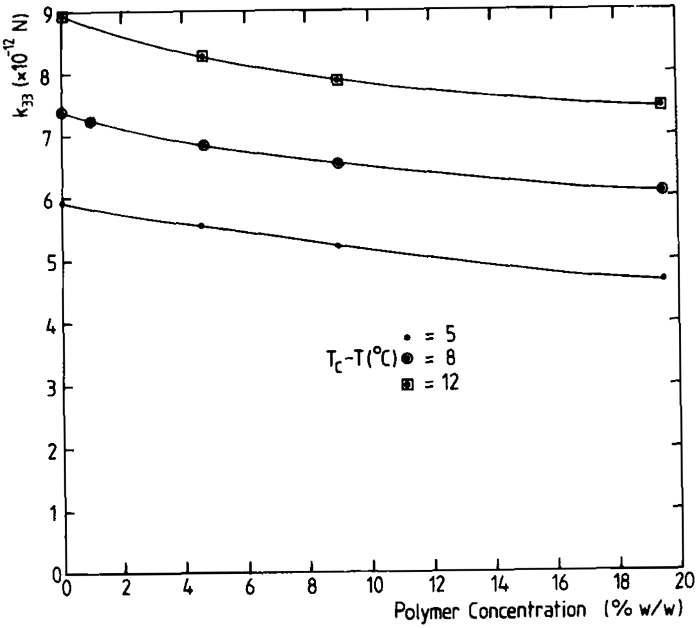


FIGURE 12 The bend elastic constant k_{33} as a function of concentration for three reduced temperatures.

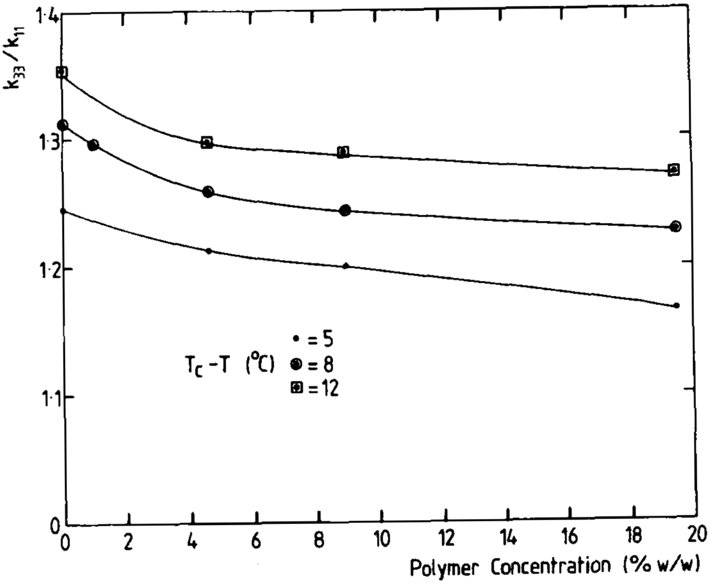


FIGURE 13 The bend/splay elastic constant ratio k_{33}/k_{11} as a function of concentration for three reduced temperatures. T_c for each solution is given in Figure 5.

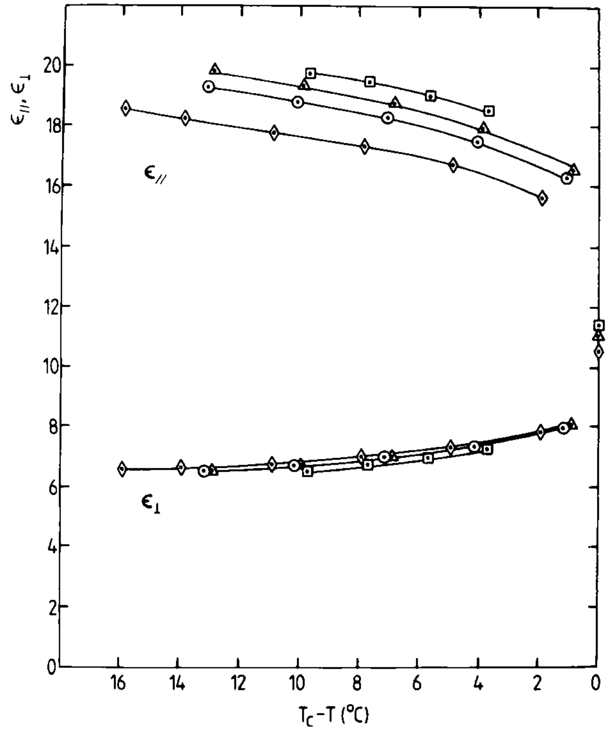


FIGURE 14 The dielectric permittivity $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ for pure 5CB and the polymer solutions as a function of reduced temperatures. The concentration key is given in Figure 9, and the subscripts ∥ and ⊥ refer to the nematic director direction.

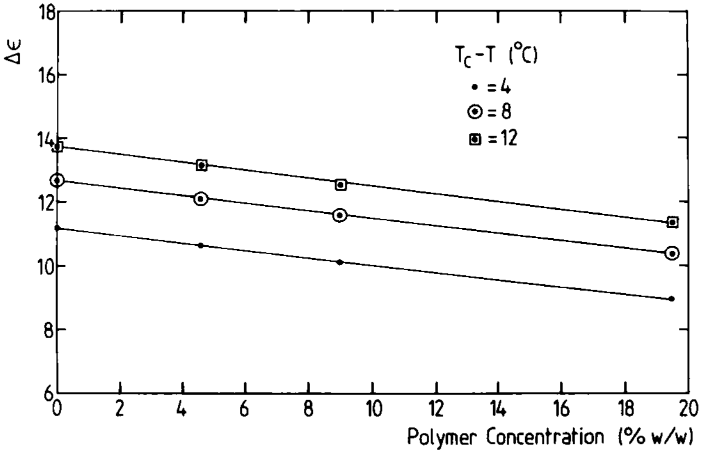


FIGURE 15 The dielectric anisotropy, $\Delta\epsilon$, as a function of concentration for three reduced temperatures. T_c for each solution is given in Figure 5.

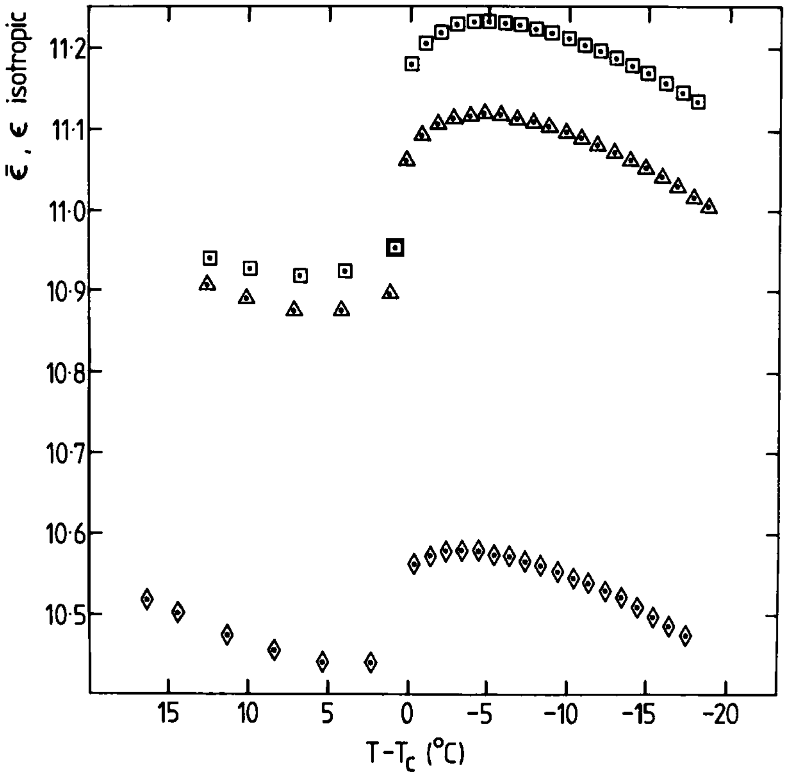


FIGURE 16 Mean dielectric permittivity $\bar{\epsilon}$ in the nematic phase and $\epsilon_{\mathrm{isotropic}}$ phase as a function of reduced temperature for pure 5CB and the 4.65 and 19.5% w/w solutions.

$\Delta\epsilon/\epsilon_{\perp}$ will decrease with increasing polymer concentration. For example, this ratio drops to ~1.6 for the 19.5% w/w solution in comparison with a value of 2.3 for pure 5CB at 25°C. This is a desirable feature for mixtures to be used in multiplexed display devices.

For pure 5CB and two polymer solutions (4.65 and 19.5% w/w) we have extended the dielectric constant measurements into the isotropic phase. The data are presented in Figure 16. In this figure $\bar{\epsilon} = (2\epsilon_{\perp} + \epsilon_{\parallel})$ in the nematic phase, whilst $\epsilon_{\mathrm{isotropic}}$ refers to the dielectric permittivity in the isotropic phase above T_c. From Figure 16 it is evident that the polymer solutions as well as pure 5CB show antiparallel ordering or pretransitional effects in the isotropic phase. Such data has previously been reported by Bradshaw et al for a series of cyano terminated nematic compounds.[19] It is known from X-ray diffraction measurements that the repeat distance for the 'quasi-smectic' ordering in 5CB is ~1.4 molecular lengths[20] and to affect regions containing ~100 molecules. Similar effects were observed for the two polymer solutions, Figure 15; for example $\bar{\epsilon}$ became discontinuous at T_c. For the polymers, however, the jump from $\bar{\epsilon}$ to $\epsilon_{\text{isotropic}}$ decreases by a factor of two for the highest polymer concentration in comparison with pure 5CB. Further, the absolute values of $\bar{\epsilon}$ and $\epsilon_{\text{isotropic}}$ also decrease with increasing polymer concentration. Whilst the 5% drop in $\bar{\epsilon}$ and $\epsilon_{\text{isotropic}}$ probably only reflects addition of material with a low dielectric constant (evident from the chemical structure, Figure 1), the large change in discontinuity suggests a marked reduction in the degree of antiparallel ordering. Intuitively this is correct since the size of the polymer with 50 side chain moieties will be of the order as that of the antiparallel regions of correlation and, therefore, well able to perturb their structure. This suggests a further interesting X-ray study.

CONCLUSIONS

We have established that side chain polysiloxane liquid crystals may be added to a low molecular weight nematogen to alter a number of parameters pertinent to the performance of the nematogen in a display device. Firstly, despite the dissimilarity between the chemical structures of the polymer side group moieties and the host nematogen, all of the solutions, up to a concentration of at least 20% w/w, were homogeneous and stable. We believe that this is due to the strongly dipolar side group terminations. Secondly, for all solutions studied, both lecithin and rubbed polyvinyl alcohol could be used to effect homeotropic and planar alignment respectively. The quality of alignment appeared to increase with increasing polysiloxane content. Thirdly, we have shown that increasing polymer concentration decreases k_{11}, k_{33}, k_{33}/k_{11} and $\Delta\epsilon/\epsilon_{\perp}$ in comparison with pure host monomer. The decrease in these constants are regular with increasing polymer concentration and, therefore, allow these material parameters to be varied systematically. We have presented data for pure 5CB, as well as for the solutions, and the agreement between our data and that presented elsewhere for 5CB confirm that the experimental method adopted was reliable. This has been described in detail. Fourthly, we have established that the polymer has only a very slight effect on the nematic to isotropic phase transition and induces a small biphasic region. The polymer, however, decreases the crystallisation temperature and leads to a broad temperature range nematic phase. There was no evidence for injected smectic phases despite the smectogenic nature of the pure polymer. Finally, we have shown that the polymer appears to decrease the amount of antiparallel ordering in the polymer solutions.

Clearly from the above summary, the side chain polymer has a significant influence on the properties of the monomeric host. This suggests an important potential application for such polymer liquid crystal, i.e. in the production of new nematogenic mixtures for display devices. It will now be interesting to examine polymers with (i) a different backbone flexibility, i.e. acrylates and methacrylates, (ii) different spacer lengths for the side chain moieties, (iii) different degrees of side chain substitution and (iv) side groups of different dipole moment and sign, i.e. $\Delta\epsilon < 0$. We are currently examining these systems and the data will be reported at a later date along with that for k_{22}, the twist elastic constant, and γ_1, the viscosity coefficient. Finally, we have recently studied the performance of the solutions studied herein in twisted nematic devices and this is being reported elsewhere.[21]

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References

1. H. Finkelmann and G. Rehage, *Adv. in Poly. Sci.*, **60/61**, 99 (1984).
2. V. P. Shibaev and N. A. Platé, **ibid**, **60/61**, 173, (1984).
3. H. Finkelmann, V Kiechle and G. Rehage, *Mol. Cryst. Liq. Cryst.*, **94**, 343 (1983).
4. H. Ringsdorf and R. Zentel, *Makromol. Chem.*, **180**, 803 (1979).
5. H. Finkelmann, *Phil. Trans. Roy. Soc.*, **309**, 105 (1983).
6. H. J. Coles and R. Simon, Brit. Patent App. (1983).
7. M. S. Sefton, A. R. Bowdler and H. J. Coles, *Mol. Cryst. Liq. Cryst.*, (in press).
8. G. W. Gray, K. J. Harrison and J. A. Nash, *Electronic Letts.*, **9**, 130 (1973).
9. A. Ashford, J. Constant, J. Kirton and E. P. Raynes, *Electronic Letts.*, **9**, 118 (1973).
10. P. A. Gemmell, G. W. Gray and D. A. Lacey, *Mol. Cryst. Liq. Cryst.*, **122**, 205, (1985).
11. H. J. Coles and R. Simon, *in Recent Advances in Liquid Crystalline Polymers* (Ed L. L. Chapoy), (Elsevier, London 1984), **22**, pp323.

12. P. G. de Gennes, *The Physics of Liquid Crystals*, (Clarendon Press, Oxford, 1974), pp85.
13. H. Gruler, T. J. Scheffer and G. Meier, *Z. Naturforsch*, **27A**, 966 (1972).
14. Hp. Schad, G. Baur and G. Meier, *J. Chem. Phys.*, **71**, 3174 (1979).
15. M. G. Clark, E. P. Raynes, R. A. Smith and R. J. A. Tough, *J. Phys. D: App. Phys.*, **13**, 2151 (1980).
16. J. D. Bunning, T. E. Faber and P. L. Sherrell, *J. de Physique*, **42**, 1175 (1981).
17. P. P. Karat and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, **36**, 51 (1976) and **40**, 239 (1977).
18. M. J. Bradshaw, E. P. Raynes, J. D. Bunning and T. E. Faber, *J. de Physique*, Paris, (in press).
19. M. J. Bradshaw and E. P. Raynes, *Mol. Cryst. Liq. Cryst. Letts.*, **72**, 73 (1981).
20. A. J. Leadbetter, R. M. Richardson and C. N. Colling, *J. de Physique* C1, **36**, 37 (1975).
21. H. J. Coles and A. I. Hopwood, *Mol. Cryst. Liq. Cryst. Letts.*, (in press).