

# Liquid crystalline polymers as additives to enhance the device properties of low molecular mass liquid crystals

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Magnetic and electric fields have been used to determine the splay ( $k_{11}$ ) and bend ( $k_{33}$ ) elastic constants in a series of polymer/monomer liquid crystal solutions using the well known Freedericksz transition technique. Measurements have been carried out as a function of concentration and temperature. The polymer used was a smectogenic polysiloxane side chain liquid crystal with both cyanobiphenyl and benzoate ester side groups. The monomeric solvent was the nematogen 4-n-pentyl-4'-cyanobiphenyl. All of the solutions studied were nematogenic up to a concentration of 40% w/w. It has been shown that  $k_{11}$ ,  $k_{33}$  and  $k_{33}/k_{11}$  all decrease with increasing polymer concentration and that at high enough concentrations  $k_{33}/k_{11}$  tends to become independent of temperature. The implications of these results are discussed in terms of the performance of the most common liquid crystal display, i.e. the twisted nematic device.

(Keywords: polymer liquid crystals; electro-optic devices)

## INTRODUCTION

Liquid crystal materials have generated considerable interest over the last decade or so because of their use in low cost, low power, high contrast and fairly high level of information displays<sup>1,2</sup>. Of these displays, the twisted nematic has gained the widest acceptance, particularly because of its high visibility under ambient lighting conditions and potential for high information content<sup>3</sup>. In such a device, the information content is increased by using a matrix addressing technique for each cell or picture element<sup>4</sup>. The level of multiplexing (and, therefore, information content) depends essentially on the optical and dielectric properties of the material and its elastic constants. These parameters, along with the relevant deformation viscosity coefficient, will govern the response of the nematic director to an applied voltage and will be discussed further below.

Recently, side chain polymer liquid crystals have been discovered<sup>5</sup> that also exhibit electro-optic effects similar to the low molar mass (or monomeric) materials<sup>6</sup> currently used in the liquid crystal display industry. Generally, however, the polymers have a high viscosity and, for nematic polymers with short flexible spacers, have higher elastic constants than the chemically equivalent low molar mass nematogen<sup>7</sup>. These properties would appear to limit their usefulness in such devices. This is due to their very slow response times unless extremely high temperatures are used<sup>5-7</sup>. Over the last year or so, new polysiloxane polymers have been produced containing highly dipolar cyanobiphenyl liquid crystal side groups<sup>8</sup>. The key features of these side-chain polymers are (a) their high dielectric anisotropy, coming from the mesogenic pendant side groups, and (b) their bulk

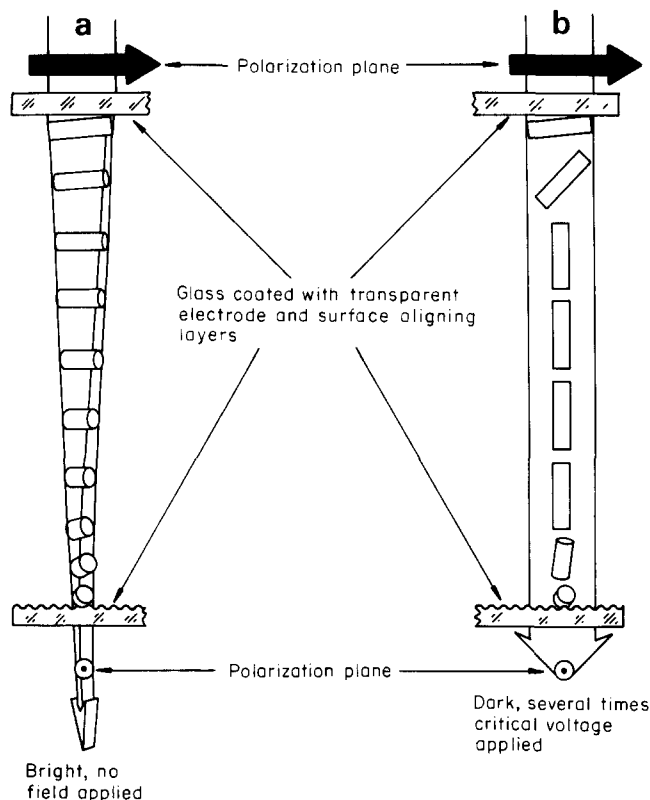
elasticity, due to the flexibility of the polymer main chain. In the pure state, the main use of these polymers appears to be for storage displays. However, recently we have started studying the electro-optic properties of these polymers in solution in low molar mass nematic liquid crystals. Although phase diagram studies have been carried out on non-cyano terminated side chain polysiloxane polymers dissolved in low molar mass liquid crystals<sup>10</sup>, no such data appears to have been published on the cyano terminated compounds. In the current paper we report preliminary data on the phase diagram, elastic constants ( $k_{11}$  and  $k_{33}$ ) and dielectric properties of such polymer/monomer mixtures up to *circa* 40% w/w polymer concentration. By comparison with the pure monomeric liquid crystal solvent we will show, for the first time, how changes in these properties leads to an enhancement in most of the properties essential to a multiplexed twisted nematic device.

## THEORY

A schematic twisted nematic cell is illustrated in *Figure 1*. Surface alignment agents or fine grooves on the electrode surface promote a planar (or homogeneous) alignment of the liquid crystal molecules at the electrode surface. The alignment direction of the two surfaces are then arranged at right angles and this forces a helical structure on the orientation of the molecules between the electrodes. In the absence of an applied field, this helical structure guides the polarization plane of the incident light and rotates it through 90°, *Figure 1(a)*. With the polarization directions arranged as shown, the liquid crystal cell assembly therefore transmits light. If a voltage is then applied across the electrodes, a threshold voltage,  $V_1$ , is observed at which the liquid crystal starts to deform<sup>11</sup>, i.e.

$$V_1 = \pi \sqrt{\frac{k_{11} + \frac{1}{4}(k_{33} - 2k_{22})}{\epsilon_0 \Delta \epsilon}} \quad (1)$$

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**Figure 1** Schematic operation of a twisted nematic cell for (a) no electric field and (b) electric field across the two electrodes. The dark arrows and the circles indicate the directions of polarization of the input polarizer and output analyser respectively. The electrodes typically would be indium tin-oxide coated transparent glass slides and the cell thickness would be 10–20  $\mu\text{m}$

where  $k_{11}$ ,  $k_{22}$  and  $k_{33}$  are the splay, twist and bend elastic constants respectively and  $\Delta\epsilon$  is the dielectric anisotropy of the material ( $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ , the subscripts refer to values parallel and perpendicular to the director axis respectively). Increasing the applied voltage still further leads to a reorientation of the liquid crystal molecules and a loss of the light guiding property, *Figure 1(b)*. In this case the polarization plane of the incident light is no longer rotated and the cell assembly does not transmit light because of the crossed polarization planes of the incident light and the lower analyser. This is the normal optical arrangement for a twisted nematic device.

Experimentally, it is more convenient for the cell off state to correspond to a zero light level. This is achieved by rotating the analyser through  $90^\circ$ . Therefore, once the threshold voltage has been attained, the cell starts to transmit light and a gradual increase in  $V$  results in a gradual increase of the transmission of light through the cell. It is convenient<sup>13</sup> to define two voltages  $V_{50\%}$  and  $V_{10\%}$  at which the light transmission is 50% and 10% of its final level, respectively. This allows a slope,  $S$ , to be defined where

$$S = \frac{V_{50\%} - V_{10\%}}{V_{10\%}}$$

This is directly related to the maximum number of lines,  $N_{\text{max}}$ , which may be matrix addressed using a twisted nematic cell<sup>13</sup>, by the following:

$$N_{\text{max}} = \left[ \frac{(S+1)^2 + 1}{(S+1)^2 - 1} \right]^2 \quad (2)$$

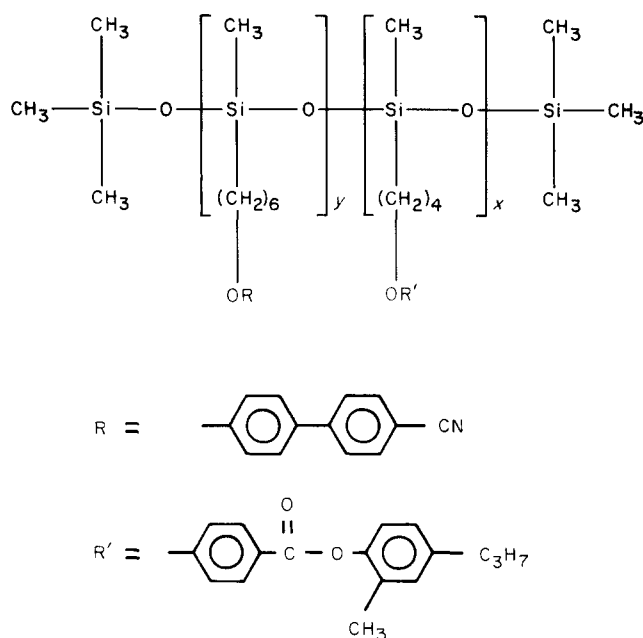
Schadt and Gerber<sup>14</sup> have presented analytical expressions for both  $S$  and  $V_{50\%}$  which relate the material parameters to the performance of twisted nematic displays. As pointed out by these authors, the elaborate numerical calculations of Berreman<sup>15</sup> are required to calculate exactly the performance of such displays but, due to the complex non-analytical calculations involved, such an approach is difficult. Instead using one of Berreman's computer programmes, Schadt and Gerber have deduced analytical expressions for both  $S$  and  $V_{50\%}$ , denoted  $S^+$  and  $V_{50\%}^+$  respectively, which have been shown experimentally to be in excellent agreement with the material parameters for a wide range of low molar mass liquid crystal mixtures<sup>14</sup>. One feature of these mixtures is the similarity of their chemical structures, especially for the cyanobiphenyl and benzoate ester mixtures, with those of the materials studied herein. Therefore, for a realistic appraisal of the polymer/monomer mixtures in comparison with low molar mass materials, we have used the same approach. Following Schadt and Gerber the expression for  $S^+$  is given by:

$$S^+ = 0.1330 + 0.0226 \left[ \frac{k_{33}}{k_{11}} - 1 \right] + 0.443 \left[ \ln \frac{\Delta n d}{2\lambda} \right]^2 \quad (3)$$

where  $\lambda$  is the wavelength of light incident normally on the display,  $\Delta n$  is the birefringence of the material and  $d$  the cell thickness.

Following an analogous procedure, the following expression for  $V_{50\%}^+$  was obtained:

$$V_{50\%}^+ = V_t \left[ 2.044 - \frac{1.044}{1 + k_{33}/k_{11}} \right] \times \left\{ 1 + 0.123 \left[ \left( \frac{\Delta\epsilon}{\epsilon_{\perp}} \right)^{0.6} - 1 \right] \right\} \times \left\{ 1 + 0.132 \ln \frac{\Delta n d}{2\lambda} \right\} \quad (4)$$



**Figure 2** Structure of PG 296, where  $x = y = 25$

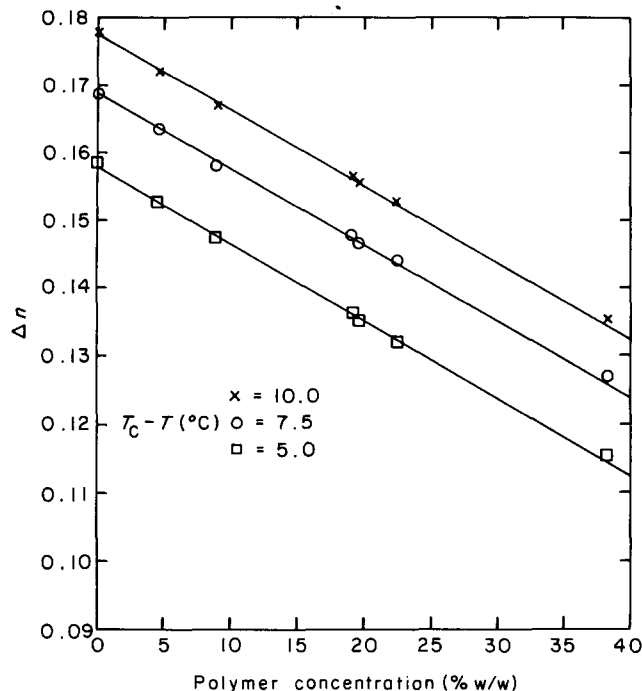


Figure 3 Variation of the solution birefringence  $\Delta n$  with polymer concentration (% w/w) for three reduced temperatures

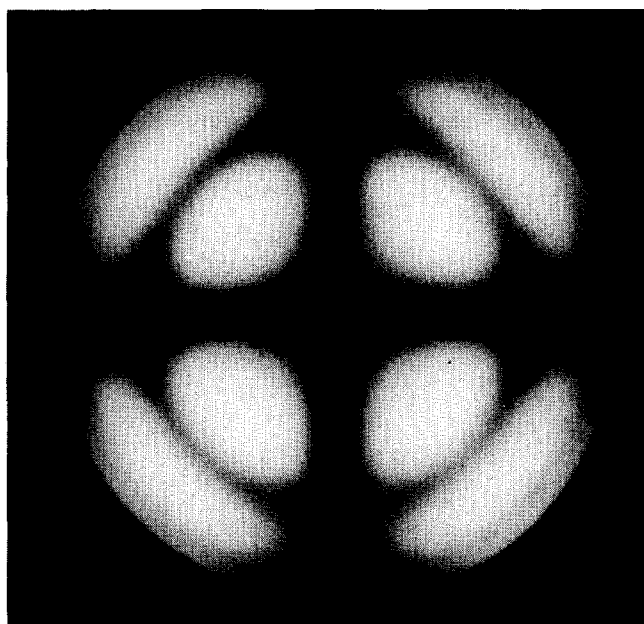


Figure 4 Conoscopic figure for a 38.3% w/w solution obtained using a polarizing microscope and Bertrand lens. The cross and the clarity of the fringes indicate good homeotropic alignment of the mesogenic groups. Insertion of a  $\lambda/4$  plate showed that the system was optically positive and uniaxial

From equation (3) it is evident that  $S^+$  may be minimized and hence  $N_{max}$  maximized, by reducing  $k_{33}/k_{11}$  and arranging that  $\Delta nd/2\lambda = 1$ . In the case of  $V_{50\%}^+$ , the situation is slightly more complex. Although a reduction of  $k_{33}/k_{11}$ ,  $\Delta\epsilon/\epsilon_{\perp}$  and  $\Delta nd/2\lambda$  will slightly reduce  $V_{50\%}^+$ , the parameter is strongly dependent on  $V_1$  (equation (1)). If the usual assumption of  $k_{33} \approx 2k_{22}$  is made, then  $V_1$  and  $V_{50\%}^+$  will depend directly on  $(k_{11}/\Delta\epsilon)^{1/2}$ . In the current paper we will be concerned with how the  $k_{11}$ ,  $k_{33}$ ,  $k_{33}/k_{11}$ ,  $\Delta\epsilon$ ,  $\Delta\epsilon/\epsilon_{\perp}$ ,  $\Delta n$  (and therefore  $S^+$  and  $V_{50\%}^+$ ) values of a low

molar mass nematic liquid crystal are altered by the addition of various amounts of a side chain polymer liquid crystal.

## EXPERIMENTAL

### Sample preparation

The nematic monomeric liquid crystal used in these studies was pentyl cyanobiphenyl (5CB) provided by BDH Ltd (Poole, Dorset, UK). It has been used without further purification; the nematic–isotropic transition temperature,  $T_c$ , being within  $0.05^\circ\text{C}$  of that accepted for 5CB (i.e.  $T_c = 35.2^\circ\text{C}$ ). The polymeric liquid crystal used as a solute was synthesized for us by Professor Gray and colleagues at Hull University<sup>8</sup>. The chemical structure of this polysiloxane side chain liquid crystal is given in Figure 2 and, for consistency with other published work<sup>9</sup>,

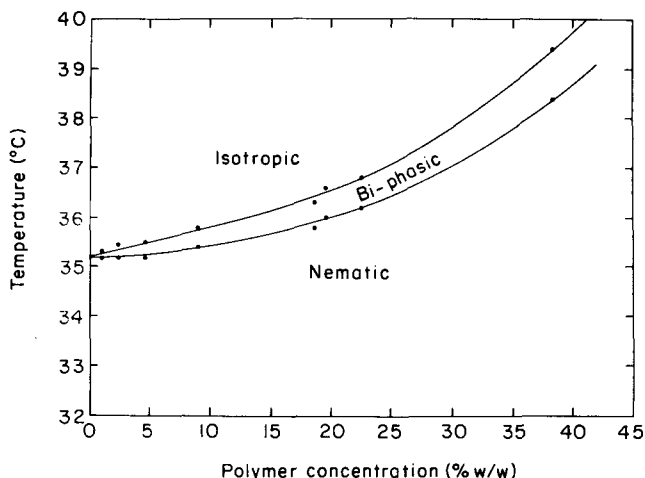


Figure 5 Phase diagram of the nematic to isotropic transition as a function of polymer concentration. The transition temperatures were determined using optical microscopy and a Mettler FP8000 hot stage system

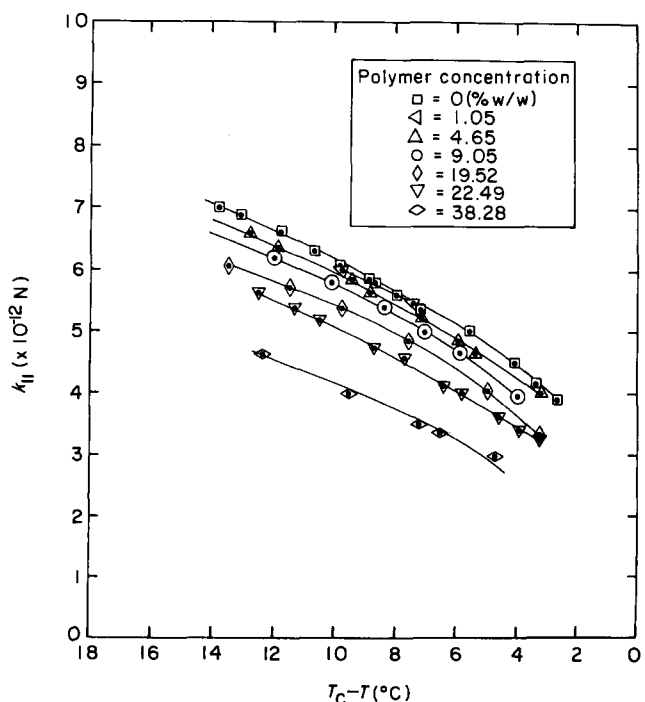
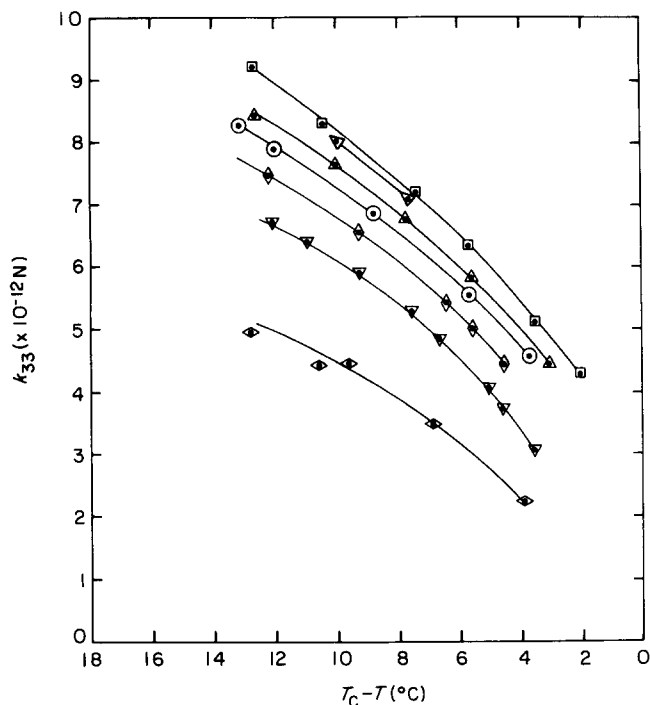


Figure 6 Splay elastic constant  $k_{11}$  as a function of reduced temperature  $T_c - T$  for various polymer concentrations. The inset provides a key for the symbols used in Figures 6, 7 and 8



**Figure 7** Bend elastic constant  $k_{33}$  as a function of reduced temperatures  $T_c - T$  for various polymer concentrations. The key is given in Figure 6

is denoted PG 296. The transition temperatures, from differential scanning calorimetry<sup>8</sup>, for this polymer with 50 siloxane units are:

glass to smectic phase,  $T_g = 4.0^\circ\text{C}$ ,

smectic to isotropic phase,  $T_{si} = 85.9^\circ\text{C}$ .

For the solution measurements, using 5CB as the polymer solvent, the concentrations are expressed gravimetrically in terms of weight of the solution, i.e. weight/weight (w/w). Polymer concentrations were used up to  $38.3 \times 10^{-2}$  w/w and dissolution was achieved by shaking at room temperature for several days. We have recently shown that  $\Delta n$ , the solution birefringence, varies linearly with polymer concentration<sup>16</sup> and in the current work we remeasured and rechecked the  $\Delta n$  data to confirm the concentration and homogeneity of the solutions, Figure 3.  $\Delta n$  values were determined using a temperature controlled Abbé refractometer.

In order to measure  $\Delta n$  and the elastic constants, it is necessary to be able to produce good surface alignment of either the homeotropic type (i.e. with the liquid crystal molecules aligned perpendicularly to the substrate) or of the planar type (i.e. with the liquid crystal molecules aligned unidirectionally in the plane of the substrate). Good homeotropic alignment was achieved by treating the surface with lecithin for all of the polymer solutions studied herein. This is evidenced by the high quality of the conoscopic figures, observed using a microscope with crossed polars and a Bertrand lens. A typical conoscopic figure for the highest concentration solution is shown in Figure 4. This figure confirms that, despite the high polymer concentration used, this alignment technique, which was originally developed for low molecular mass liquid crystals, is equally successful for the polymer solutions. Disclination free planar alignment was achieved over areas of a few  $\text{mm}^2$  with a rubbed poly(vinyl

alcohol) (PVA) layer on the electrode surface. The alignment method was found to be suitable for all of the solutions studied. Interestingly, it was observed that the higher concentration solutions exhibited fewer non-uniformities in alignment when observed microscopically through crossed polars than the low concentration solutions. Although the rubbed PVA introduces a very small surface tilt angle, the effect appears negligible in the current work since a comparison, for the 0% and 22.5% w/w solutions, with an SiO prepared surface indicated a maximum difference of only 3% in  $k_{11}$  (see below). In comparing the data for pure 5CB with the literature, we find this variation to be within the range of values presented. We have, therefore, ignored this small effect in the data below since we are primarily interested in trends with increasing polymer concentration.

#### Experimental techniques

The Frank elastic constants of nematic liquid crystals can be readily measured using the Freedericksz transition technique<sup>17</sup>. For the elastic constants,  $k_{11}$  and  $k_{33}$ , a suitable geometry may be chosen such that the threshold magnetic field  $H_c$ , or applied voltage,  $V_c$ , at which a uniformly aligned nematic layer just starts to deform, contains only one elastic constant. Our apparatus and the sample geometry chosen have been described in detail elsewhere<sup>18</sup>.

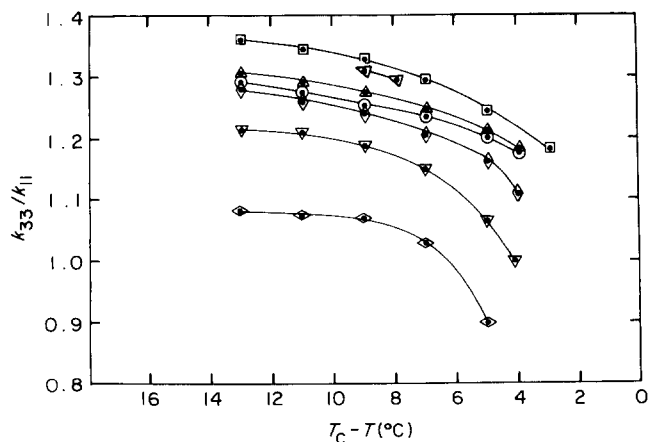
The splay constant,  $k_{11}$ , was determined from the threshold voltage,  $V_c$ , needed to deform a planar nematic layer with the voltage applied orthogonally to the nematic director. Under these conditions,  $V_c$  is given by:

$$V_c = \pi \sqrt{\frac{k_{11}}{\epsilon_0 \Delta \epsilon}} \quad (5)$$

where  $\epsilon_0$  and  $\Delta \epsilon$  are as previously defined. The bend elastic constant,  $k_{33}$ , was determined from the threshold magnetic field needed to deform a homeotropic nematic layer with the nematic director in the viewing direction and the magnetic field applied transversely across the sample. With such a geometry,  $H_c$  is given by:

$$H_c = \frac{\pi}{d} \sqrt{\frac{k_{33}}{\Delta \chi}} \quad (6)$$

where  $d$  is the thickness of the nematic layer and  $\Delta \chi$  is the diamagnetic anisotropy. The equivalence of using either



**Figure 8** Bend/splay elastic constant ratios  $k_{33}/k_{11}$  as a function of reduced temperature  $T_c - T$  at various polymer concentrations. See Figure 6 for the concentration key

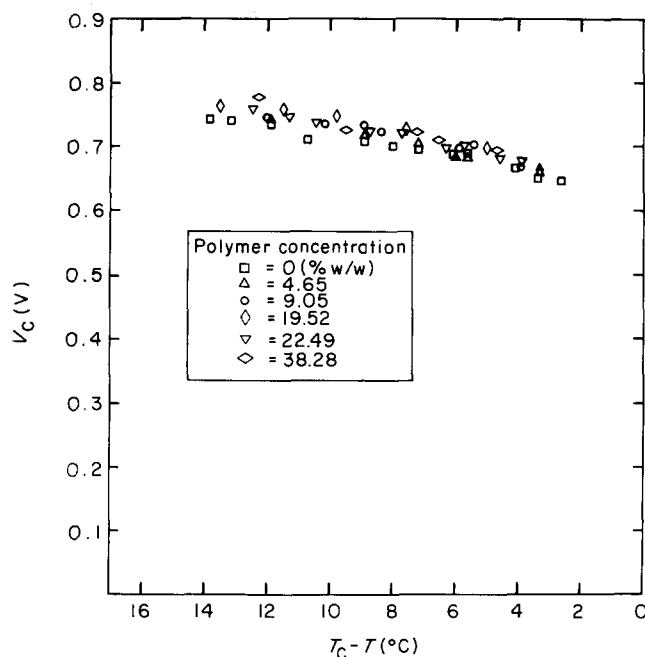


Figure 9 Fredericksz transition threshold voltage  $V_c$  for various polymer liquid crystal solutions as a function of the reduced temperature  $T_c - T$ . The inset gives a key to the polymer concentrations

magnetic or electric perturbing fields in this way has been demonstrated by Gruler *et al.*<sup>19</sup>.

The values of  $\epsilon_{||}$  and  $\epsilon_{\perp}$  were determined in collaboration with Drs E. P. Raynes and M. J. Bradshaw of RSRE, Malvern, UK using a capacitance bridge technique developed at RSRE<sup>20</sup>. The values of  $\Delta\chi \times d^2$  were determined using the method of Schad *et al.*<sup>21</sup>. Because the elastic constants vary with temperature, all measurements were carried out in a special constant temperature enclosure stable to  $\pm 0.01^\circ\text{C}$  over 1 h.

## RESULTS AND DISCUSSION

The effect of increasing amounts of the polymer PG 296 on the transition temperatures of the solutions is shown in Figure 5. Two features emerge from this data. Firstly, despite the high polymer concentration, the nematic to isotropic transition temperatures are only marginally increased from the value of  $35.2^\circ\text{C}$  for pure 5CB even though the polymer itself has a smectic to isotropic phase transition at  $\sim 86^\circ\text{C}$ . Secondly, a stable narrow biphasic region is observed which extends over  $1^\circ\text{C}$  for the most concentrated solution. In this region the nematic and isotropic phases coexist in equilibrium. Homeotropically aligned cells containing these solutions respond to an applied field in a manner commensurate with the Fredericksz distortion until a temperature in the middle of the biphasic region is attained. In the results that follow,  $T_c$  is taken as at this mid point. Further, it is worth noting that, despite the smectic nature of the polymer liquid crystal, the solutions were observed to be nematic over their entire mesomorphic range.

The effect of increasing polymer concentration on the elastic constants  $k_{11}$  and  $k_{33}$  can be seen in Figures 6 and 7 respectively. It is noteworthy that, whilst the critical temperature,  $T_c$  (approximating to the clearing temperature in pure monomeric liquid crystals), only changes marginally, both  $k_{11}$  and  $k_{33}$  decrease markedly. For

example, for the 38.3% w/w solution, as compared to pure 5CB at  $T_c - T = 10^\circ\text{C}$ ,  $k_{11}$  decreases from  $6.2 \times 10^{-12}$  N to  $4.2 \times 10^{-12}$  N while  $k_{33}$  decreases from  $8.2 \times 10^{-12}$  N to  $4.4 \times 10^{-12}$  N. Thus, it would appear that the addition of polymer liquid crystals to monomeric materials is a convenient way of significantly modifying the absolute values of the elastic constants. The advantages of the polymer/monomer mixtures are further illustrated by the ratio  $k_{33}/k_{11}$  (see Figure 8). This Figure shows two key features of the mixtures. Firstly, the ratio  $k_{33}/k_{11}$  at  $T_c - T = 10^\circ\text{C}$  is decreased from  $\sim 1.34$  to 1.07 in comparison with pure 5CB. This reflects the greater decrease in  $k_{33}$  with respect to  $k_{11}$  with increasing polymer concentration, and this is exactly the trend required to improve device multiplexing. In fact, following the analysis presented above, the number of lines theoretically addressable for the 38.3% w/w solution would be 59 in comparison with 46 lines for pure 5CB at  $T_c - T = 5^\circ\text{C}$ , at zero viewing angle, a cell thickness of  $10\ \mu\text{m}$  and  $\lambda = 633\ \text{nm}$ . For a practical device, one should also consider how the contrast ratio varies with viewing angle since this will reduce the number of lines which may be acceptably multiplexed. However, since for any device an improvement at zero angle (or normal incidence) will also tend to lead to an improvement at higher viewing angles<sup>12</sup>, we have, for comparison between materials under identical experimental conditions, only considered the zero angle case herein. The second feature of the higher concentration solutions is the trend towards temperature independent  $k_{33}/k_{11}$  ratios for  $T_c - T \geq 8^\circ\text{C}$ . For practical devices it is useful if  $N_{\text{max}}$  and  $V_l$  are temperature independent. For the case of  $N_{\text{max}}$ , the addition of the polymer would seem to help in this respect. The variation of  $V_l$  is only marginally dependent on  $k_{33}/k_{11}$ . If the approximation is made that  $k_{33} \approx 2k_{22}$ , then  $V_l$  (equation (1)) =  $V_c$  (equation (5)). As shown in Figure 9,  $V_c$  is apparently independent of concentration and only slightly dependent on temperature. Therefore, it would appear that changes in  $k_{11}$  are compensated by changes in  $\Delta\epsilon$  and  $V_l$  remains almost constant on addition of the polymer (i.e.  $V_c$  only increases by 10% at  $T_c - T = 14^\circ\text{C}$  as compared with  $T_c - T = 4^\circ\text{C}$ ).

We have also examined the  $k_{11}$ ,  $k_{33}$  and  $k_{33}/k_{11}$  data to look for systematic trends as a function of polymer concentration. These parameters have been plotted as a

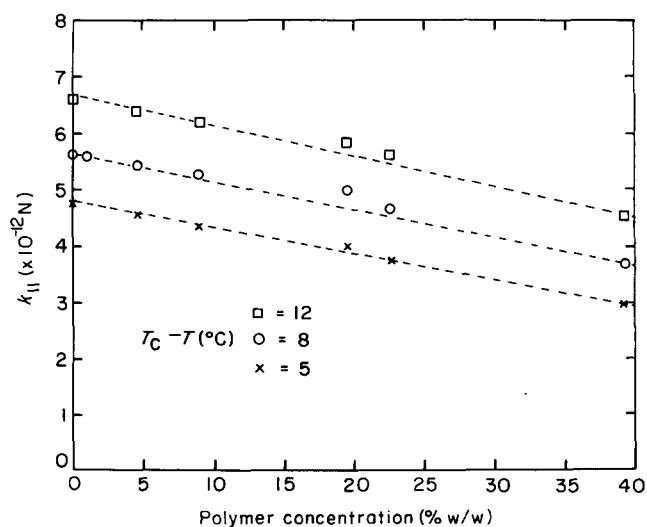


Figure 10 Splay elastic constant  $k_{11}$  as a function of polymer concentration at various reduced temperatures,  $T_c - T$

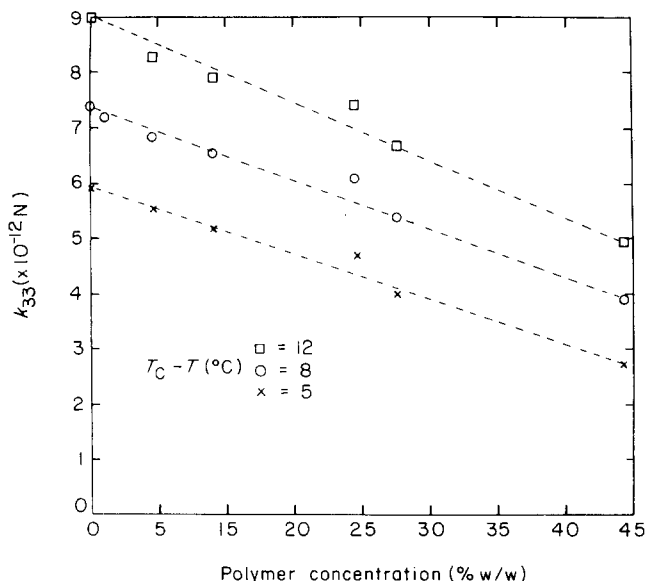


Figure 11 Bend elastic constant  $k_{33}$  as a function of polymer concentration at various reduced temperatures,  $T_c - T$

function of concentration for various fixed temperatures in Figures 10, 11 and 12. From these Figures it would appear that the elastic constants are approximately linearly dependent on concentration at least up to 40% w/w. This suggests that the elastic constants and their ratios may be chosen at will merely by altering the concentration of polymer in the solution. This, when coupled with the trend towards temperature independence of  $k_{33}/k_{11}$  below  $T_c - T \geq 8^\circ\text{C}$ , shows that polymers could have an important part to play in engineering multiplexable mixtures for display devices.

This feature of the polymers is further exemplified by consideration of the two other parameters, i.e.  $\Delta n$  and  $\Delta\epsilon/\epsilon_\perp$ , which influence the threshold voltage. From Figure 3 it is evident that  $\Delta n$  decrease with increasing polymer concentration in a well controlled way. As seen from equations (2) and (3), this is a desirable feature for increasing the number of lines  $N_{\text{max}}$  that may be multiplexed using a twisted nematic device. Further, a reduction in  $\Delta n$  also leads to a slight reduction in  $V_{50\%}^+$  (equation (4)). Following the analysis presented above, the predicted value of  $V_{50\%}^+$ ,  $V_{50\%}^+$  is 1.01V for the 38.3% w/w solution in comparison with 1.17V for pure 5CB at  $T_c - T = 5^\circ\text{C}$ , a cell thickness of  $10\ \mu\text{m}$  and  $\lambda = 633\ \text{nm}$ . We have studied the reduction of  $\Delta\epsilon/\epsilon_\perp$  with increasing polymer concentration over a more restricted concentration range (see Figure 13). As this data shows, the rate of change of  $\Delta\epsilon/\epsilon_\perp$  with concentration is approximately independent of temperature. At  $T_c - T = 4^\circ\text{C}$  for a 20% w/w solution,  $\Delta\epsilon/\epsilon_\perp$  decreases by approximately 25% with respect to pure 5CB and at  $T_c - T = 12^\circ\text{C}$  the decrease is approximately 20%. Following the linear dependence of both  $\Delta n$  and  $\Delta\epsilon$  on concentration, it would be reasonable to expect  $\Delta\epsilon/\epsilon_\perp$  to decrease by the same amount again if the polymer concentration was increased to 40% w/w, i.e. for  $T_c - T = 4^\circ\text{C}$   $\Delta\epsilon/\epsilon_\perp = 0.77$  and for  $T_c - T = 12^\circ\text{C}$   $\Delta\epsilon/\epsilon_\perp = 1.23$ . These changes in  $\Delta\epsilon/\epsilon_\perp$ , predicted for the 40% w/w solution from those already observed up to  $\sim 20\%$  w/w, together with the lack of significant change in  $V_t$ , should then produce the desired decrease in the  $V_{50\%}^+$  values.

## CONCLUSIONS

We have studied the effect of increasing concentrations of a solute side chain liquid crystal polymer dissolved in a monomeric solvent on the parameters that control the operation of a twisted nematic device. By choosing systems with similar dielectric constants, it has been shown that the Freedericksz transition threshold voltage  $V_c (\approx V_0)$ , for the splay deformation, is independent of concentration and only marginally dependent on temperature. However, the parameters  $k_{11}$ ,  $k_{33}$ ,  $k_{33}/k_{11}$ ,  $\Delta n$  and  $\Delta\epsilon/\epsilon_\perp$ , that control the degree of multiplexing of such a device, all decrease with increasing polymer concentration. These decreases are all highly desirable and lead, for a 38.3% w/w solution, to an increase from 46 to 59 in the number of lines theoretically addressable in the device for zero viewing angle. Further, from the changes in  $k_{33}/k_{11}$ ,  $\Delta n$  and  $\Delta\epsilon/\epsilon_\perp$  should also lead to a slight decrease in  $V_{50\%}^+$ . If we assume  $k_{33} \approx 2k_{22}$ , then  $V_{50\%}^+$  decreases at  $T_{N1} - T = 5^\circ\text{C}$  by 14%. We have not been able to confirm this absolutely as  $k_{22}$  was not measured in the present experiment. We are currently studying this problem and the data will be presented at a later date.

We believe that the above preliminary observations will lead to a new application of specialized liquid crystal polymers, i.e. as additives to produce the required dielectric and elastic properties in mixtures suitable for twisted nematic and other electro-optic liquid crystal displays. As is well-known from the literature<sup>12,14,22</sup>, mixtures of monomeric liquid crystals suitable for such applications have been commercially available for a number of years. However, the compositions of such mixtures are not generally available and it is difficult, therefore, to assess critically the material properties leading to improved device performance. In the case of polymer–monomer mixtures we have shown that the simple addition of a polymer liquid crystal to a monomeric material will lead to significantly improved material properties. Since generally the grafting of different sidechain moieties on the polymer is fairly readily achieved<sup>8</sup>, we anticipate a situation where copolymers might be synthesized specifically as additives for low molar mass liquid crystals to produce a specified device performance. It is interesting to mention a further feature of the polymer–monomer mixtures. We have observed a marked supercooling of the mixtures when included in thin cells. In the case of the 9% solution the apparent crystallization temperature was decreased to

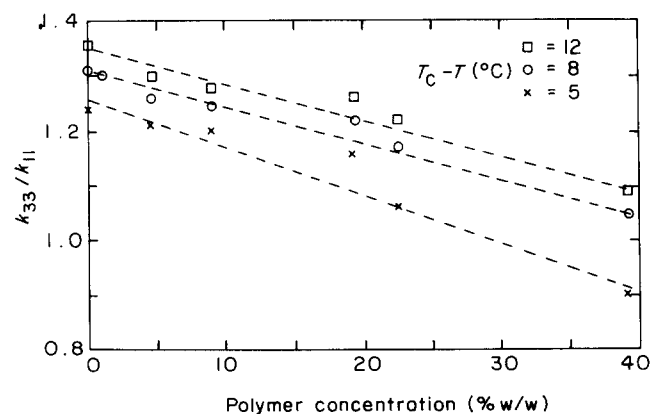


Figure 12 Bend/splay elastic constant ratios  $k_{33}/k_{11}$  as a function of concentration for different reduced temperature,  $T_c - T$

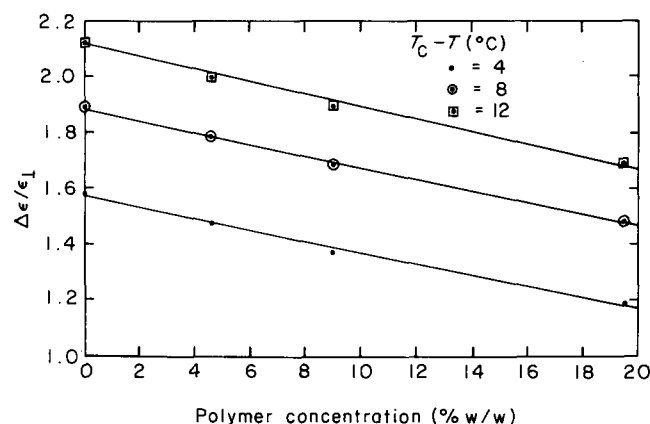


Figure 13 Variation of  $\Delta\epsilon/\epsilon_{\perp}$  with polymer concentration for different reduced temperatures,  $T_c - T$

$\approx 3^{\circ}\text{C}$ . In the bulk<sup>23</sup> the crystallization temperature was reduced from  $22.5^{\circ}\text{C}$  in pure 5CB to  $19.5^{\circ}\text{C}$  in the same mixture. Thus the polymers serve to broaden the nematic range. Further, contrary to monomeric mixtures, using cyanobiphenyl and benzoate ester based liquid crystals<sup>24</sup>, we have observed no injected smectic phases in thin samples down to  $-60^{\circ}\text{C}$ . These studies are still continuing and the results will be presented in greater detail at a later date.

Finally, in this paper we have concentrated on the material parameters important for improved multiplexing capability in the polymer–monomer mixtures. Clearly, because of the high viscosity encountered in pure nematic side chain polymer liquid crystals, one might expect the viscosity of the polymer–monomer mixtures to increase significantly. As shown in the accompanying paper<sup>25</sup>, the increase in the relevant twist viscosity suggests an increase in response time of only a factor of about eight for the 22.5% w/w solution studied herein. We are currently carrying out measurements using these mixtures in twisted nematic cells and for the same mixture with an applied voltage of 5 Vrms switching times of a few hundred milliseconds have been readily achieved. For this mixture supercooled to  $-32^{\circ}\text{C}$ , a switching time of approximately 5 s was observed with an applied voltage of 32 Vrms. Although the twist viscosity shows an increase, these initial measurements suggest that this is not a critical performance factor. Further, it is to be expected that changes in (a) the length of the polymer backbone, (b) the degree of lateral substitution and (c) the spacer length will further alter the dynamic and static properties of these mixtures. Since we believe that it is the polymer backbone flexibility coupled with the mesogenic spacer length that is altering the material parameters in such a marked way, we would suggest that future research using similar highly

dipolar polymers, but with differing molecular flexibility and coupling, will be rewarding.

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