A study of the static and dynamic properties of side-chain liquid crystalline polymers in low molar mass mesogens

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The static and dynamic properties of solutions of a side chain polysiloxane liquid crystal polymer have been studied in a cyanobiphenyl nematic host as a function of concentration and temperature. Refractive index measurements were carried out on aligned samples and the data used to determine the macroscopic order parameter, S, using Haller's method. Photon correlation spectroscopy has been used to measure (k_{22}/γ_1) for the pure nematic solvent and the solutions. From these measurements it appears that the static properties vary slowly and linearly with increasing polymer concentration whilst the dynamic or viscoelastic properties change markedly. This change has been attributed to γ_1, the twist viscosity, and the results have been discussed in terms of the function of the siloxane polymer backbone.

(Keywords: liquid crystalline polymers; mixtures; refractive indices; order parameters; dynamic light scattering)

INTRODUCTION

There has been much interest recently in the properties of solutions formed by polymers and low molar mass liquid crystal solvents[1-10]. Despite the difficulties in interpretation, this recent work has tried, at least phenomenologically, to establish how the properties of the polymer might be influenced by the anisotropic solvent and *vice versa*. For example, George *et al.*[7] have used nematic solvents as a starting point in the production of high strength synthetic yarns, whilst we have used polymers as solutes in nematic solvents in order to modify their bulk electro-optic properties[8-10].

The dissolution of a given polymer in a particular mesomorphic solvent is not, however, readily achieved. For example, Dubault *et al.*[3,4] observed a maximum concentration of 2% (w/w) for polystyrene ($M_w \leqslant 10\,000$) when dissolved in the nematics PAA or EBBA (i.e. *p*-azoxy anisole or ethoxy benzilidene butylaniline). Above this molecular weight the polystyrene was totally insoluble. A different approach[1] was to dissolve polymer liquid crystals with pendant side chain moieties in the nematic solvent. Generally, if the side chain moiety and the solvent had similar core structures then the polymers dissolved fairly readily. However, as shown by Casagrande *et al.*[2] complete miscibility was not always observed. We believe that the primary reason for the lack of miscibility between the two systems is the lack of strong dipole terminations on their polymer side chains. In such systems the polymer–polymer interactions are stronger than those for the polymer–solvent and so phase separation takes place. We have taken the simplistic view that if the side chain moiety and the mesogenic solvent contain strongly dipolar groups (e.g. cyano substituents) then the polymer–solvent interaction will dominate.

Using a polysiloxane backbone polymer with cyanobiphenyl and benzoate ester side groups we have observed, by optical microscopy[11], complete miscibility in a cyanobiphenyl nematic liquid crystal solvent. In this paper we report data on the static and dynamic properties of these solutions for concentrations up to 20% w/w of polymer. At high concentrations the solutions become highly viscous and have a greater use in storage devices[12] rather than in the electro-optic applications envisaged for the current dilute solutions.

EXPERIMENTAL

The monomeric nematic liquid crystal solvent was 4-cyano-4'-pentylbiphenyl (5CB) kindly donated by BDH Ltd (Poole, Dorset). It had a clearing temperature of 35.2°C and was used without further purification. The polymer solute was a polysiloxane of 50 SiO units and an equal proportion of cyanobiphenyl and benzoate ester side groups, *Figure 1*. The polymer ($M_w = 19\,000$) was specially prepared for us by Professor Gray and colleagues of Hull University[13]. The pure polymer has a glass to smectic phase transition at 4°C and a broad smectic to isotropic phase transition between 85°C and 100°C[12,13]. The solutions were prepared by shaking at room temperature for 12 h and exhibited good homogeneous textures and optical properties[9]. The phase diagrams[10] show that, despite the initial smectogenic nature of the polymer, the solutions are nematic up to at least 40% w/w. For the maximum concentration studied herein, i.e. 19.5% w/w, there was no evidence of any smectogenic phase behaviour and the nematic to isotropic transition temperature (T_{NI}) was only increased by 1.0°C from 35.2°C for pure 5CB to 36.2°C for the solution. Concentrations are quoted as weight of polymer to total solution weight.

For both the static and dynamic measurements, samples were aligned perpendicularly (homeotropically)
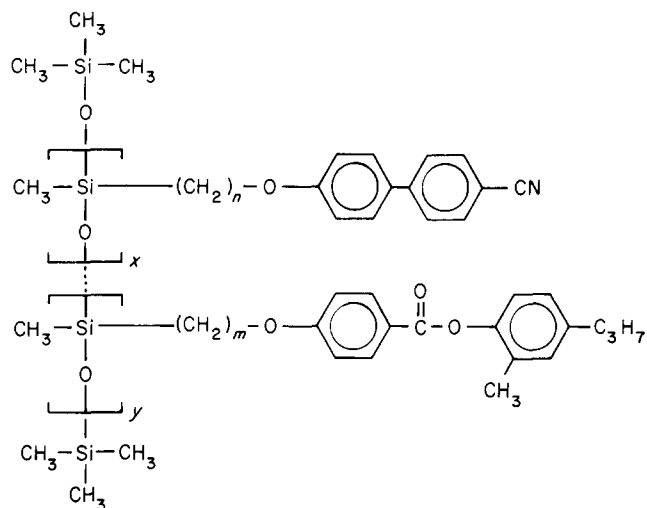
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Figure 1 Schematic of copolymer liquid crystal, PG296, where $x = y = 25$, $n = 6$ and $m = 4$

to the glass surfaces using lecithin (BDH, Egg Grade II) as the surface aligning agent. For solution concentrations up to 40% w/w good homeotropic alignment was observed, by optical conoscopy[10], with no evidence of a decrease in surface alignment efficiency with increasing polymer concentration.

The experimental arrangements for measuring the refractive indices and dynamic properties of the materials have been discussed recently[8]. Refractive index data were obtained using a modified Bellingham and Stanley 60/HR Abbé refractometer and homeotropically aligned thin samples. The refractometer was temperature stabilized to ±0.05°C using a circulating water bath and it was estimated that the refractive index data were accurate to ±0.0002. The dynamic properties were determined using a specially constructed photon correlation spectrometer. The precautions necessary and the performance of the apparatus, when applied to liquid crystals, have been considered[8] and a detailed constructional description has been given[14]. The important experimental features of apparatus were (i) a stable coherent light source (±0.3%), (ii) a double stage sample chamber, index matched and temperature stable to ±0.05°C, capable of being heated to 250°C, (iii) a heterodyne detection system capable of use at scattering angles between −20° and 140° and (iv) a photon counting correlator interfaced, on line, to a PDP 11/34 minicomputer. This computer, which uses BBC B microcomputers as terminals, allowed rapid data analysis to be carried out using new and improved fitting routines[15].

RESULTS AND DISCUSSION

Static properties

Refractive index data. At optical frequencies nematic liquid crystals exhibit a strong birefringence, Δn (where $\Delta n = n_e - n_o$), that reflects the degree of order in the system. For monomeric liquid crystals, aligned uniaxially, typical values of $\Delta n = 0.15$ are observed. In the current work we examine the effect of increasing polymer concentration on the refractive index data and order in the system (see 'Order parameters' section below).

With the systems aligned homeotropically, the values of n_e and n_o were recorded for pure 5CB and several solutions as a function of temperature, *Figures 2 and 3*. From these

Figures it is evident that the polymer has only a very small effect on n_o even for the 19.5% w/w solution but does have a larger influence on n_e. Further, n_e has a much greater temperature dependence than n_o, although the data for the pure 5CB and the solutions all behave in a similar and regular way. We have studied, in greater detail, the influence of polymer concentration on n_e and n_o at various fixed temperatures, *Figure 4*. From these data it is evident that both n_e and n_o are linearly dependent on concentration. Such a linear dependence on concentration has also been observed[9,10] in $\Delta\varepsilon$ (the low frequency dielectric anisotropy), k_{11} and k_{33} (the splay and bend elastic constants, respectively). This linear behaviour in the physical properties of the solutions can only be interpreted as evidence of the quality of mixing between the polymer and monomer liquid crystals and, therefore, the high degree of mutual order between the side chain moieties and the monomeric solvent. From these data we may extrapolate to 100% polymer concentration to obtain implied values of n_e and n_o for the pure polymer. For example, at $T = 26.0°C$, $n_e = 1.625$ and $n_o = 1.547$ at $\lambda_o = 589$ nm for the polymer. For the pure side chain polymer systems studied by Finkelmann *et al.*[16] (where the mesogenic side group was a benzoic acid phenyl ester), $n_e = 1.571$ and $n_o = 1.501$ at the same reduced temperature.

Order parameters. If nematic liquid crystal molecules may be considered as long rigid rods (with respect to their diameter) then the order in the nematic phase can be simply visualized[17]. The phase is considered as consisting of molecules exhibiting an ensemble average orientational order about an axis direction (called the director, $\hat{n}$) but with no long range positional order of their centres of mass. For this model the degree of order can then be most simply described[17] by the Maier–Saupe order parameter, S, given by:

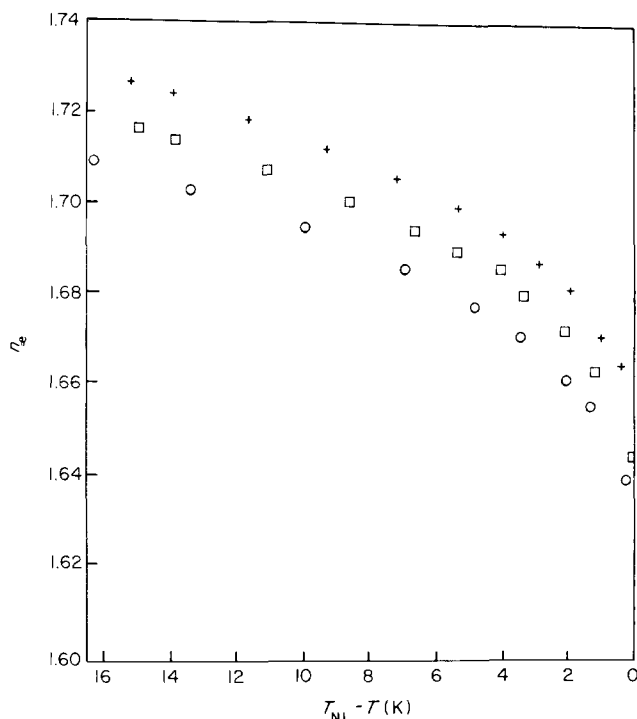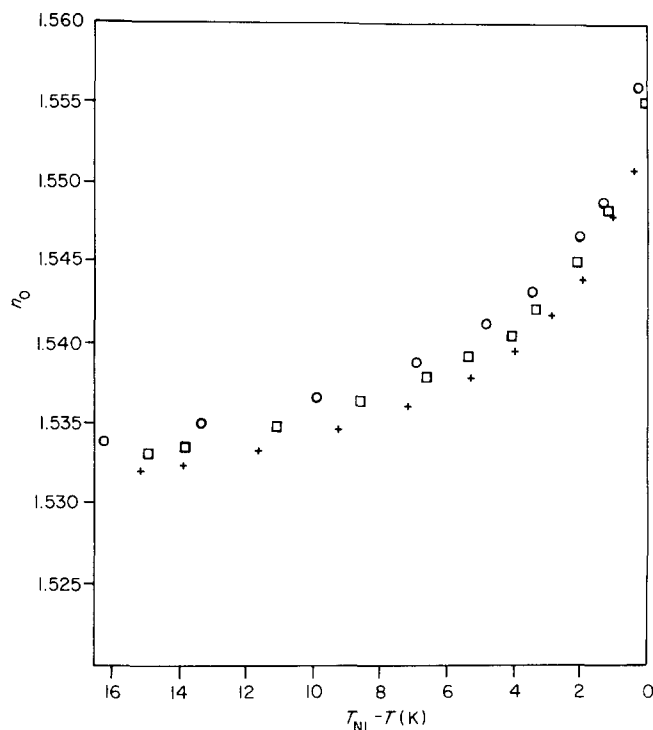$$S = \tfrac{1}{2}\langle 3\cos^2\theta - 1 \rangle \tag{1}$$

Figure 2 Variation of n_e with $T_{NI} - T$ for 5CB (+), $T_{NI} = 35.2°C$; 9.0% w/w PG296 in 5CB (□), $T_{NI} = 35.6°C$; 19.5% w/w PG296 in 5CB (○), $T_{NI} = 36.2°C$, at $\lambda = 589$ nm

Figure 3 Variation of n_o with $T_{NI} - T$ for 5CB (+), $T_{NI} = 35.2°C$; 9.0% w/w PG296 in 5CB (□), $T_{NI} = 35.6°C$; 19.5% w/w PG296 in 5CB (○), $T_{NI} = 36.2°C$, at $\lambda = 589$ nm

where θ is the angle between the long axis of an individual molecule and the director $\hat{n}$ and the brackets denote an ensemble average. In this formalism maximum order is obtained for $S = 1$ and total disorder (i.e. the isotropic phase) corresponds to $S = 0$.

A technique much used to determine the macroscopic order parameter S, is to scale the refractive index data using Haller's approach[18]. In this technique it is assumed following Vuks, that the local field is isotropic even in an anisotropic medium. This leads to the following relation:

$$S\frac{\Delta\alpha}{\bar{\alpha}} = \frac{n_e^2 - n_o^2}{\bar{n}^2 - 1} \qquad (2)$$

where $\bar{n}^2 = (n_e^2 + 2n_o^2)/3$, $\Delta\alpha = \alpha_\parallel - \alpha_\perp$, $\bar{\alpha} = (\alpha_\parallel + 2\alpha_\perp)/3$ and $\alpha_\parallel$ and $\alpha_\perp$ are the molecular polarizabilities parallel and perpendicular to the long axis of the molecule respectively. If, following Haller, one assumes $S = (1 - T/T^+)^B$, where $T^+ > T_{NI}$ then the following expression is obtained:

$$\log_{10}\left[\frac{n_e^2 - n_o^2}{\bar{n}^2 - 1}\right] = \log_{10}\left[\frac{\Delta\alpha}{\bar{\alpha}}\right] + B\log_{10}\left[1 + \frac{T}{T^+}\right] \qquad (3)$$

Hence a plot of $\log_{10}[(n_e^2 - n_o^2)/(\bar{n}^2 - 1)]$ against $\log_{10}$ $[1 - T/T^+]$ is a straight line where T^+ is chosen as an empirical parameter to be varied to obtain a linear plot of the data. For both pure 5CB and the 19.5% w/w solution (of PG296 in 5CB), we have given the data in the form of the so called Haller plot (i.e. equation (3)), see *Figure 5*. The data has been presented for $\lambda_0 = 589$ nm and clearly there is good agreement with the theoretical equation, for $T^+ = 36.0°C$ for pure 5CB and $T^+ = 36.9°C$ for the 19.5% w/w solution. We feel that this justifies the continued use of the Haller technique to determine order parameters for

the polymer solutions considered herein. It is worth noting at this point that the technique scales an average macroscopic property and hence the order parameter obtained is the average for the whole system. A recent approach by Tough and Bradshaw[19] questioned the validity of the Haller method. These authors produced a fitting procedure that appeared to agree better with experimental results in the temperature range from $T = T_{KN}$ to $T = 0.97T_{NI}$. However, for a material such as 5CB use of this procedure would exlude three quarters of the nematic range and its use was not considered further.

We have studied pure 5CB and several solutions of PG296 in 5CB up to 19.5% w/w. Representative values of S for the highest concentration and an intermediate (at 9% w/w) as a function of temperature are given in *Figure 6*. Data obtained for the same solutions from refractive index measurements at different wavelengths agreed within $\pm 1\%$. The data for pure 5CB also agreed, to within 5%, with that obtained by Horn[20] using the Haller fit to refractive index data. As the current calculations are based upon refractive index measurements which are four times more accurate than that previously used, we do not consider the difference significant. The interesting feature of the data of *Figure 6* is the gradual decrease of S, both with temperature for the pure 5CB, and with increasing concentration for the PG296/5CB solutions. For example, at $T/T_{NI} = 0.96$ which corresponds to a room temperature of approximately 24°C, the order parameter for the 19.5% w/w solution decreases by 10% in comparison with pure 5CB. Despite this reduction the temperature dependence of the order parameter is similar for the pure compound and the solutions. We believe that these data clearly reflect the quality of ordering in the mesogenic side groups of the polymer. It seems likely that the small reduction in S is due to steric hindrance of the flexible spacer preventing the individual polymer side groups from aligning totally with the monomeric solvent. It would, therefore, be interesting to use both shorter and
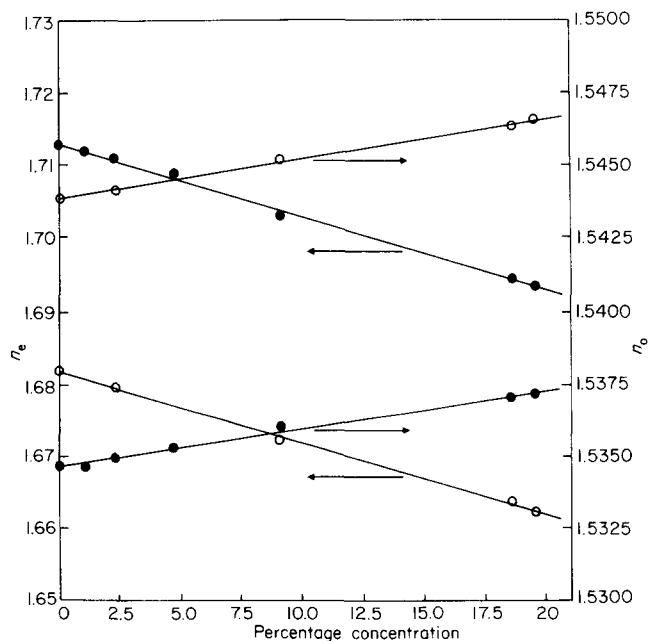

Figure 4 Variation of n_e and of n_o with percentage concentration (w/w) of polymer PG296 in 5CB at two reduced temperatures. $T_{NI} - T = 2°C$ (○), $T_{NI} - T = 9.3°C$ (●), $\lambda = 589$ nm
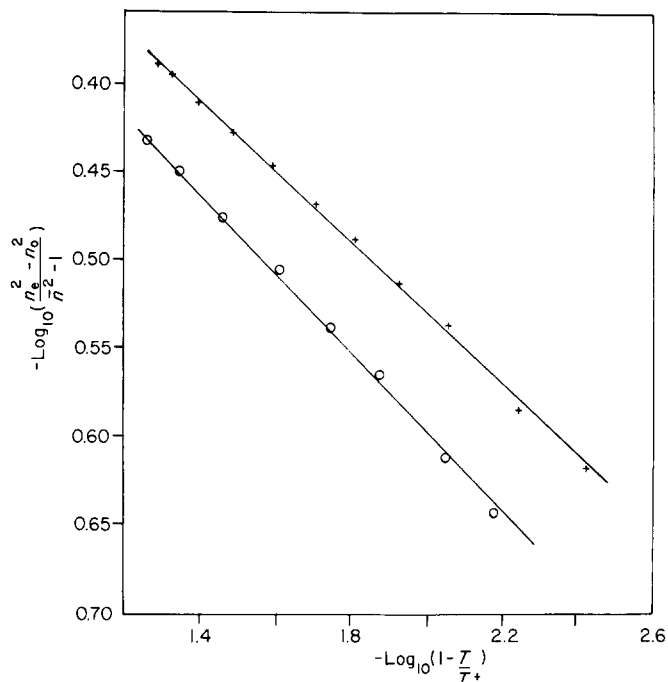
Figure 5 Sample Haller plot for pure 5CB (+), $T^+ = 36.0^\circ$C, and for a 19.5% w/w solution of polymer PG296 in 5CB (O), $T^+ = 36.9^\circ$C. Refractive indices at $\lambda = 589$ nm

longer spacer groups to look for subtle changes in S between equivalent polymer solutions.

Due to the paucity of data on polymeric/monomeric liquid crystal solutions, it is difficult to compare the above results with other systems. As shown in refs. 7 and 10, the polymer/monomer systems are of current technological interest and the effect of the polymer on the order parameter is highly relevant to display devices. The only other relevant solution study would seem to be that of Dubault *et al.*[4]. These authors, using n.m.r. techniques, have investigated the influence of polystyrene ($M_w = 2100$) on the order parameter in a 1.5% w/w solution of EBBA (ethoxy benzilidene butyl aniline). They were unable to detect any difference in S for the same reduced temperature (T/T_{NI}) between pure EBBA and the polystyrene/EBBA mixture. Considering the low concentration, limited by considerable solubility problems, and the low polymer molecular weight, this result is perhaps not surprising.

Finkelmann *et al.*[16] have presented data on the order parameter for pure side chain polysiloxane liquid crystalline polymers. A comparison of the order parameter in this polymer with a chemically similar monomeric liquid crystal showed that S decreased by about 10% for the polymer. This could be due to the influence of the polymer backbone but the comparison is difficult since the order parameter for different members of the same homologous species may vary readily by 10% or more at the same reduced temperatures[21,22]. Changing the polymeric liquid crystal molecular weight (i.e. the number of SiO units in the backbone) could equally have an effect on S. Given that none of the systems previously studied have the same side chain liquid crystal moieties and the lack of other relevant solution data, it is extremely difficult to draw comparisons with our current work. However, it is clear that the order parameter in our systems is altered in a reliable and repeatable manner over

a wide concentration range and that this has important technological implications.

Dynamic properties

Nematic liquid crystals often have a white, milky appearance in the bulk due to their high light scattering power. In 1969 the Orsay group[23] described this scattering as being due to two overdamped director fluctuation modes within the medium. Following their analysis, both the intensity and the power spectrum of the scattered light may be related to (i) the viscotic and elastic constants of the medium, (ii) the scattering vector q and (iii) the polarization directions of the incident and scattered light. The Orsay analysis has been shown to characterize successfully the viscoelastic properties of monomeric nematic liquid crystals[24,25].

The Orsay expressions are in principle extremely complex involving three elastic and six viscotic constants. However, careful selection of the experimental arrangement and sample alignment allows considerable simplification of these expressions and the subsequent data analysis. For the optical arrangement used herein, that is with vertically polarized incident light, horizontally polarized scattered light and the nematic director in the direction of the incident laser beam, it has been shown[26] that the linewidth Γ_2 of the scattered light is related solely to the twist mode (see *Figure 7* for a pictorial representation of the twist mode). At scattering angles less than $\sim 15^\circ$ the linewidth is given by:

$$\Gamma_2 = \frac{k_{22}}{\gamma_1} q_\perp^2 = \frac{k_{22}}{\gamma_1} n^2(\theta) \sin^2 \theta, \tag{4}$$

where:

$$n^2(\theta) = \frac{n_e^2 n_o^2}{(n_o^2 \sin^2 \theta + n_e^2 \cos^2 \theta)},$$

θ is the scattering angle, $q_\perp$ the scattering vector
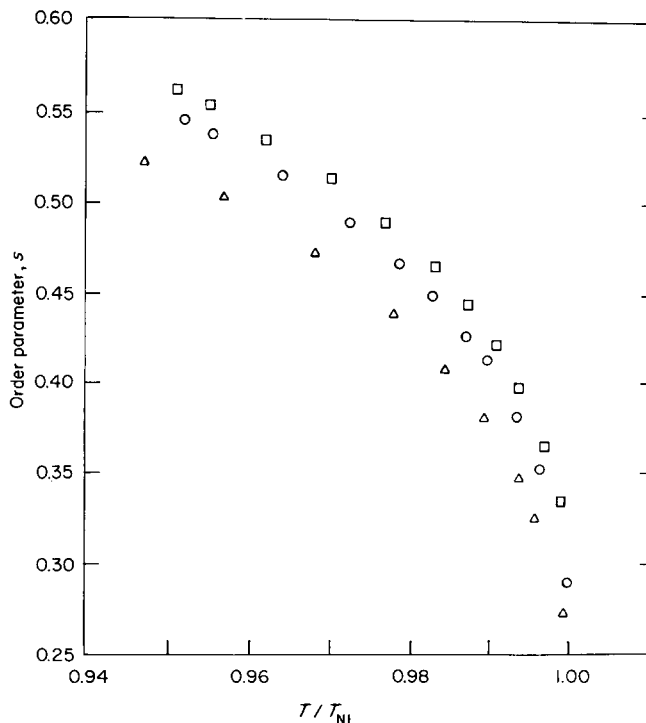

Figure 6 Variation of order parameter, S, with temperature for pure 5CB ($\square$), 9.0% w/w PG296 in 5CB (O) and 19.5% w/w PG296 in 5CB ($\triangle$)
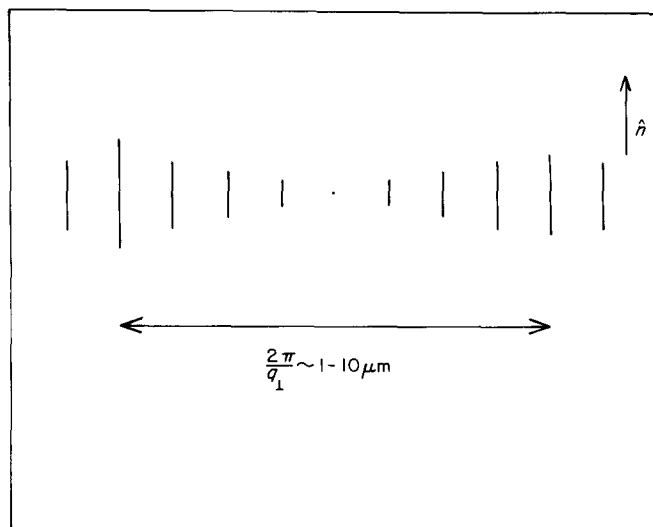
Figure 7 Pictorial representation of the twist mode in the nematic phase of liquid crystals

perpendicular to the director, k_{22} the twist elastic constant and γ_1 the twist viscosity. At scattering angles greater than 15°, the bend mode distorts the linear dependence of Γ_2 on $q_\perp^2$ and equation (4) is no longer valid[8].

We have used photon correlation spectroscopy to determine k_{22}/γ_1 for pure 5CB and several of the PG296/5CB solutions from the linewidth Γ_2. At low scattering angles ($\theta \leqslant 15°$), Γ_2 was found[8] to be linearly dependent on $\sin^2\theta$ in keeping with the Orsay theory. This observation also confirms that the solutions scatter light as a homogeneous medium rather than as independent solute and solvent molecules following different scattering laws. Further, the correlation functions exhibited good single exponential decay constants which is additional confirmation of this observation. The k_{22}/γ_1 data have been given for the solution as a function of temperature in *Figure 8*. From this Figure it is clear that (k_{22}/γ_1) decreases markedly with increasing polymer concentration. For example, for the 6% w/w solution, (k_{22}/γ_1) falls by a factor of two in comparison with 5CB. However, the rate of change of $\ln(k_{22}/\gamma_1)$ with temperature appears, over this concentration range, to be independent of solution composition. From recent data on k_{11} and k_{33}[9,10] we would expect the change in k_{22} to be $\sim 5\%$ for a 6% w/w solution and, therefore, the factor of two change must come primarily from the twist viscosity γ_1. This would be in good agreement with the data of Casagrande *et al.*[5] on a different system.

The rapid increase in γ_1 is clearly in marked contrast to the very slow changes observed in the static properties. We, therefore, believe that this increase in γ_1 is due to the polymer backbone restricting the large scale motion of the individual nematic molecules.

CONCLUSIONS

The influence of the polysiloxane side chain liquid crystal polymer on the nematic liquid crystal solvent can be considered in two distinct ways.

Firstly, with the help of the flexible backbone and spacer the side chain moieties are able to align freely in the

nematic medium and indeed form an integral part of that medium. Thus, the static properties of the solutions vary only slightly from those of the pure nematic host. Refractive index and order parameter data have been presented that support this statement. Indeed, other measurements[9,10] of $\Delta\varepsilon$, k_{11} and k_{33} over the same concentration range show a similar behaviour. In all of these measurements the parameters decrease slowly and linearly with increasing polymer concentration. It would appear from this that the side chain moieties shield the polymer backbone from having a large effect on the static properties.

The second important consideration is in the way the existence of the polymer backbone affects the dynamic properties. For example, the twist viscosity γ_1 approximately doubled for a 6% w/w solution. This suggests that the polymer backbone is limiting a bulk motion of the nematic director. In this context it is worth recalling the work of Casagrande *et al.*[5] who found that higher molecular weight polymer liquid crystals had the smallest effect on γ_1 in comparable solutions. This observation would be consistent with an increased 'effective' molecular flexibility for the higher molecular weight, due to the increased number of links, when such a system can no longer support a rigid molecular conformation. This is consistent with our belief that changes in the backbone and side chain spacer lengths should be studied to examine their effect on the static and dynamic properties. We are currently carrying out such measurements and the results of these will be reported at a later date. We are also using an electric field method to separate k_{22} and γ_1 and differential scanning calorimetry to determine exactly how S varies at the first order nematic to isotropic phase transition.
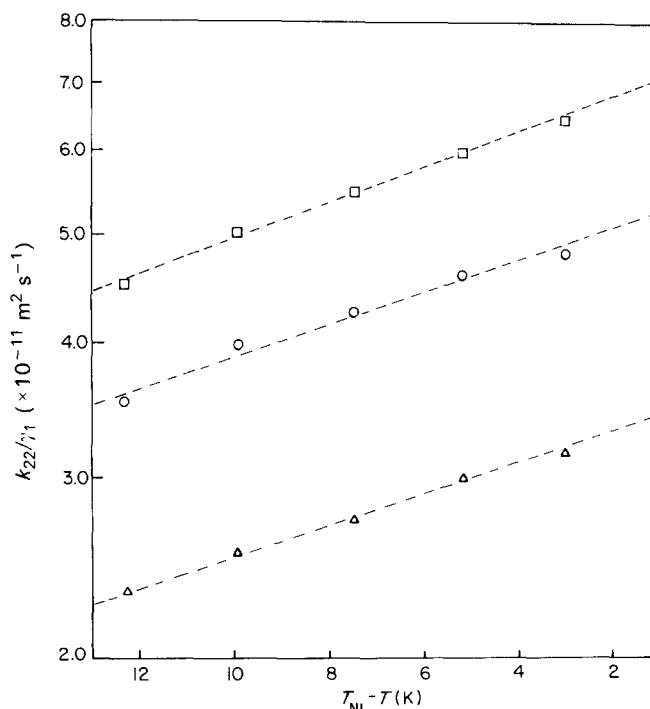

Figure 8 Variation of viscoelastic ratio, (k_{22}/γ_1), with temperature, for pure 5CB (□), $T_{NI} = 35.2°C$; 2% w/w PG296 in 5CB (○), $T_{NI} = 35.2°C$, and 6.5% w/w PG296 in 5CB (△), $T_{NI} = 35.4°C$

ACKNOWLEDGEMENTS

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