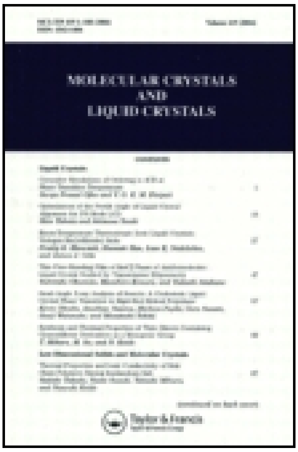

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Viscosity Coefficients and Elastic Constants of Nematic Solutions of a Side-Chain Polymer

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Viscosity Coefficients and Elastic Constants of Nematic Solutions of a Side-Chain Polymer

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Nematic solutions of a side-chain mesomorphic polymer in a commercially available eutectic mixture (E7) were characterised by electric field dynamic light scattering (EDLS). Results are presented for twist and splay viscosity coefficients and elastic constants along with dielectric constants and refractive indices. For the polymer solutions, the measured twist viscosity was greater than the splay viscosity, and the elastic constants reduced relative to E7 in a manner consistent with slight disruption of the nematic order by the polymer backbone.

Keywords: light scattering, nematic, polymer liquid crystal, viscosity, elastic constant

INTRODUCTION

The electro-optic properties of side-chain polymers have attracted much interest in recent years.[1–5] It is found that the voltages required to induce electro-optic effects in such materials are typically within an order of magnitude of those for low molar mass systems. However, the response times are usually many orders of magnitude greater. From this we can infer that low molar mass and side-chain polymer nematogens greatly differ in viscosity coefficients, whereas elastic constants may be of the same order of magnitude. In order to examine this behaviour further we have carried out a study of solutions of a side-chain liquid crystal polymer in a nematic eutectic mixture.

The side-chain polymer used in this work was generously provided by Professor G. W. Gray and Drs. D. Lacey and P. A. Gemmell of the University of Hull. It is known as PG296[3,6] and the chemical structure is shown in Figure 1. PG296 has a fifty unit siloxane backbone, randomly substituted in equal proportions with cyanobiphenyl and benzoate ester side groups. It is smectic at room temperature and becomes isotropic between 85°C and approximately 100°C.

There has been considerable interest in the physical properties of side-chain

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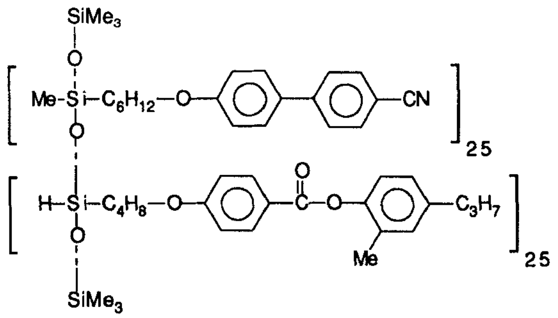

FIGURE 1 Chemical structure of the random side-chain polysiloxane copolymer PG296. Me represents a methyl group.

polymer-monomer mixtures (see for example References 7–14). Solution studies of PG296 in pentyl cyanobiphenyl (5CB) have previously been carried out using electric field dynamic light scattering (EDLS) and Fréedericksz transition techniques.[12–14] The extensive interest in the PG296/5CB system arises from the wide range of polymer concentrations which form thermodynamically stable nematic solutions. A concentration of 80% w/w PG296 in 5CB has been observed to be nematic.[15] The similarity between the cyanobiphenyl side groups and 5CB is thought to be an important factor in the extensive miscibility. These previous studies have shown that the splay and twist viscosity coefficients and elastic constants may be modified in a controlled and advantageous manner for device applications.[14]

The nematic eutectic mixture E7 was developed by BDH Ltd and DRA (Malvern) to retain the desirable physical properties of cyanobiphenyl liquid crystals over a wide temperature range suitable for electro-optic applications.[16] Since the components of E7 are similar to the cyanobiphenyl side group of PG296, it was expected that PG296 would form nematic solutions with E7. Of considerable advantage over solutions in 5CB are the higher clearing points, facilitating alignment and the study of higher polymer concentrations. The present study was therefore carried out to examine the behaviour of the refractive indices and dielectric and elastic constants, as well as the viscosity coefficients as functions of polymer concentration and temperature.

EXPERIMENTAL

Solutions of 5%, 13% and 48% by weight of PG296 in E7 were prepared. Analytical grade acetone was used to dissolve the polymer and the low molar mass material to give an isotropic solution, and the acetone was evaporated off at 60°C under dry nitrogen.

The quasi-elastic light scattering apparatus was built in this laboratory[17] and its calibration and use for liquid crystals is described in detail elsewhere.[14] An extremely important feature of the spectrometer is its heterodyne detection capability which allows the effects of stray light to be eliminated. The study of polarized scattered light from thin liquid crystal films is otherwise plagued by the almost unavoidable presence of stray scattered light which in turn distorts the measured spectral linewidths (see below). Thin film light scattering cells were made from indium-tin oxide coated glass using 50 micron thickness fibre optic spacers. Lecithin was used to obtain good uniform homeotropic orientation of the nematic films, as observed by conoscopic polarising microscopy.

The use of homeotropic alignment allows study of either Mode 1 (splay-bend mode) or Mode 2 (twist-bend mode) of director fluctuations by detecting either polarised or depolarised scattered light, respectively.[18] The perpendicular component of the scattering vector arises from the twist or splay deformations. Hence these fundamental distortions can be studied in effective isolation at scattering angles less than 15 degrees, where the perpendicular component predominates.[14] Measurement of the director relaxation time in thermal equilibrium, from the autocorrelation function of the scattered light, gives an elastic constant to viscosity ratio. Applying an electric field parallel to the director, for a nematogen of positive dielectric anisotropy ($\Delta\varepsilon > 0$), dampens the fluctuations and allows a viscosity term to be found.[12,19–21] For example for twist deformations, the linewidth (Γ in Hz) of the scattered light is given by Reference 18.

$$\Gamma = (k_{22}/\gamma_1)q_\perp^2 + \varepsilon_0\Delta\varepsilon E^2/\gamma_1.$$

Here, $q_\perp$ is the perpendicular component of the scattering vector, k_{22}/γ_1 is the twist elastic constant to viscosity coefficient ratio, and E is the applied electric field. Thus, measurement of Γ as a function of E^2 allows both k_{22} and γ_1 to be determined. There is an analogous expression for splay deformations[20] that allows k_{11} and η_{SPLAY} to be determined.[20,21]

In principle, electric field dynamic light scattering (EDLS) is an extremely valuable method for extracting the splay, twist and bend elastic constants and corresponding viscosity terms for a nematogen. Martinand and Durand were the first to apply this technique,[19] detecting light scattered from bend distortions in a homogeneously aligned cell of MBBA. These fluctuations were then damped out using an electric field applied across the cell, allowing the bend viscosity and elastic constant to be determined. As MBBA has a negative dielectric constant, there are no Fréedericksz distortions in this configuration, which is an important consideration.

For materials with a positive dielectric anisotropy, the twist and splay viscosities are conveniently measured using electric fields applied across a homeotropically aligned cell in the geometry described above. This experiment was first performed by Waters at DRA Malvern.[20] The twist elastic constant and viscosity were readily determined, and good agreement with the existing literature was obtained. However, anomalous effects dependent on the frequency of the applied electric field were seen when Mode 1 (splay-bend) distortions were studied. A theory was then developed by Leslie[20] which suggested that conductivity and flexoelectric effects, if present, would only affect the measured Mode 1 decay rates. Hence the anomalous results were attributed to such effects.

Several further experiments using this geometry were carried out at Manchester University by Sefton and Coles.[12,21,22] Two extremely important results were obtained. Firstly, it was discovered that the use of heterodyne detection was essential if reliable results from the splay-bend mode were to be found. In this case, the scattered light is polarised in the same plane as the incident light, so that stray light scattered from e.g. interfaces can easily cause partial heterodyning of the signal if homodyne detection is attempted as in the Waters experiment. This is discussed in more detail in the relevant papers. Secondly, accurate values of splay elastic constants and viscosities were only found if applied fields of greater than 1.5 kHz were used. We will return to this point later.

Hence values for twist and splay elastic constants and viscosities can be determined to good accuracy, i.e. ±3% as discussed elsewhere.[21] A sinusoidal AC voltage of known frequency is applied across the cell to provide an electric field E equal to the rms applied voltage divided by the cell thickness. Values for the appropriate dielectric constants are needed and their determination is discussed below. The cell thickness was measured using a laser interferometric technique.[22]

Dielectric constants ($\varepsilon_{\parallel}$, $\varepsilon_{\perp}$) were measured using a magneto-capacitance method. A homeotropic thin film aligned in a 3 terminal guard ring cell gave the parallel component, $\varepsilon_{\parallel}$. Reorientation of the film by a magnetic field orthogonal to the director allowed determination of the perpendicular component, $\varepsilon_{\perp}$, by extrapolating the field dependent capacitance measurements to infinite field.[21] The dielectric measurement apparatus, based on a Wayne-Kerr 6425 Multi Bridge, was under computer control, and the ramping speed of the magnetic field was considerably reduced for the study of the polymer solutions.[24]

Refractive indices ($n_{\parallel}$, $n_{\perp}$) of the nematic solutions were determined at a wavelength of 633 nm using an *Abbé* refractometer and a helium-neon laser as a light source. The glass faces of the refractometer were treated with lecithin, so that the homeotropic alignment was obtained and the two refractive index components determined using light of the appropriate polarisation.[22]

RESULTS AND DISCUSSION

Polarising microscopy of the solutions showed that the polymer formed uniform nematic phases. Clearing points were measured using a Mettler hot stage and were found to be 60.0°C, 58.8°C, 58.0°C and 55.5°C, respectively, for the 0, 5, 13 and 48 per cent by weight polymer nematic solutions. The solutions were ideally suited for the characterisation of nematic parameters. Excellent alignment was obtained on lecithin coated glass on cooling from the isotropic phase. Addition of polymer PG296 to E7 slightly lowers the clearing temperature (i.e. by 4.5°C at 48% w/w), whereas when 5CB was used as the host, the clearing temperature increased by the same amount (at 38% w/w of polymer in 5CB).[13]

The values of the dielectric constants for the polymer solution at 1 kHz are shown in Figure 2. This value of frequency was chosen so that no possible electrohydrodynamic instabilities were induced in the nematic solutions by the applied field. The parallel component is predominantly dipolar in origin and its reduction, as the polymer concentration increases, can be partly attributed to the volume exclusion effect of the siloxane backbone and benzoate ester side-chains. The latter side-

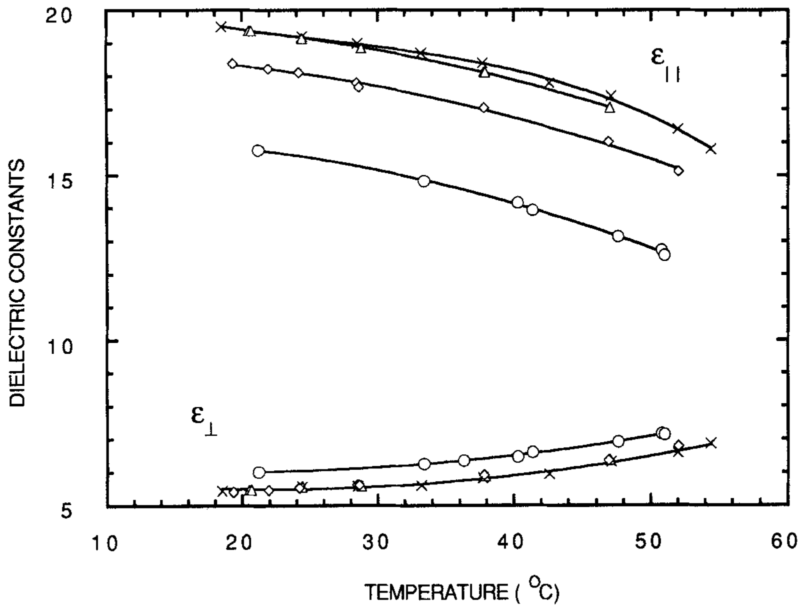

FIGURE 2 Dielectric constants of E7(×), 5% polymer solution (Δ), 13% polymer (◇) and 48% polymer (○). The larger values are the parallel components. Measurements were carried out at a frequency of 1 kHz.

chains would be expected to have a lower Δε value than cynanobiphenyl moieties due to the ester groups. Consequently for high concentrations of polymer, $\varepsilon_{\parallel}$ decreases as $\varepsilon_{\perp}$ increases. The polymer backbone also slightly disrupts the nematic order, which will decrase Δε, as discussed below.

The refractive index measurements are shown in Figure 3. The parallel (extraordinary) component is principally affected, reducing with increased polymer concentration. The decrease in Δ*n* is also partially attributed to a volume exclusion effect, as the large extraordinary component arises primarily from extensively electron delocalized molecular moieties such as the cyanobiphenyl group. Again the side-chains would be expected to have a lower value of Δ*n* due to the ester groups. Thus, as the concentration of polymer increases, $n_{\parallel}$ decreases and $n_{\perp}$ increases, as shown in Figure 3.

The twist and splay elastic constant to viscosity ratios are presented in Figures 4 and 5, respectively. These were obtained using a scattering angle of 14 degrees. The auto-correlation functions of the scattered light were fitted using both single and multi-exponential fitting programs, and the data were found to be single exponentials. Light scattering from the 'fast mode' of director fluctuation is unlikely to become observable, as its relative contribution is inversely proportional to viscosity terms.[18] The same values for viscoelastic ratios were obtained using a scattering angle of 10 degrees. However, reducing the scattering angle below this value increases the effect of low frequency mechanical noise on the autocorrelation function at high polymer concentrations. Also, cell boundary effects are known to give rise to an anomalously high viscoelastic ratio at small scattering angles (when using

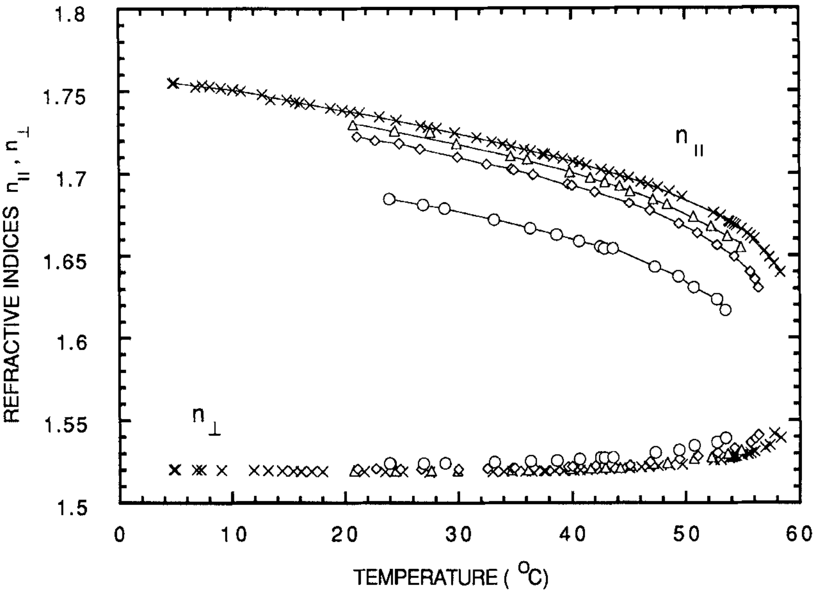

FIGURE 3 Refractive indices of E7 and the polymer solutions. Symbols are as for Figure 2. The larger values are the extraordinary refractive indices, and data are given for a measuring wavelength of 632.8 nm.

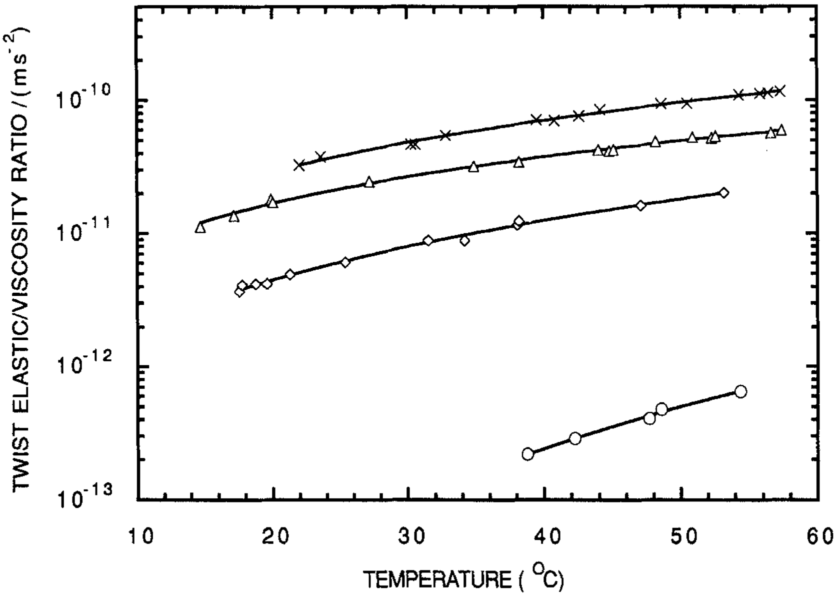

FIGURE 4 Twist elastic constant to viscosity ratio, k_{22}/γ_1 for E7 and the polymer solutions as a function of temperature. Symbols are as for Figure 2.

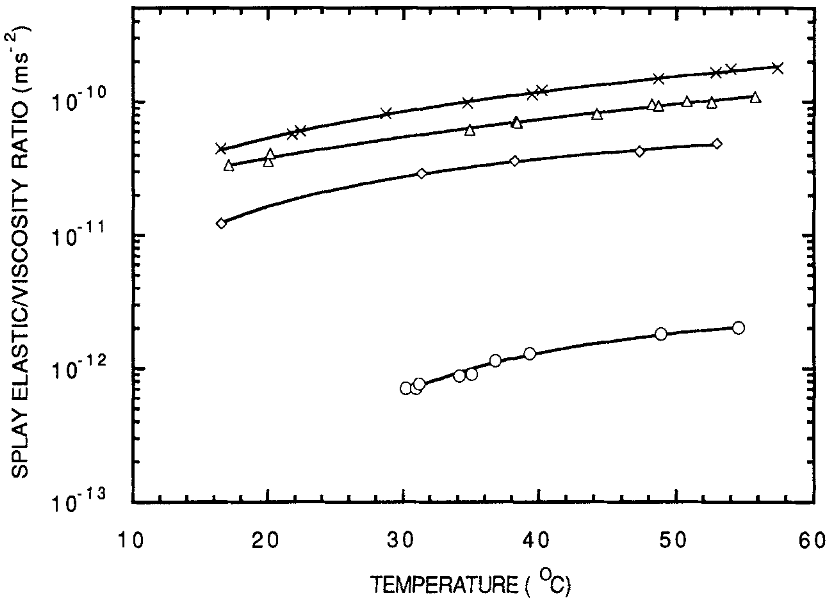

FIGURE 5 Splay elastic constant to viscosity ratio k_{11}/η_{SPLAY} for E7 and the polymer solutions as a function of temperature. Symbols are as for Figure 2.

much reduced cell thicknesses)[14] due to director damping effects and such data are not considered further.

The absolute values of the twist and splay viscosity coefficients and elastic constants were determined using EDLS. The twist and splay data were determined using applied sinewaves of 1 kHz and 5 kHz, respectively. The reasons for using slightly different frequencies will be discussed below. The twist (γ_1) and splay (η_{SPLAY}) viscosities are shown for the neat E7 material and the three solutions (5%, 13% and 48% w/w) in Figure 6. It is clear that for the neat material, γ_1 equals η_{SPLAY} over the temperature range of the nematic phase studied. This has been observed for other low molar mass nematic materials where there are no low temperature smectic phases present.[21,25] As the polymer is added to E7, the twist viscosity increases proportionally more, with increasing concentration, than does the splay viscosity. The difference between the twist and splay viscosities may be in the usual notation related to the ratio of the square of the third Leslie coefficient (α_3^2) to the second Miesowicz viscosity term (η_b), i.e., $\gamma_1 - \eta_{SPLAY} = \alpha_3^2/\eta_b$. Since the Miesowicz viscosities are all positive, these data imply that the third Leslie coefficient is of appreciable magnitude and positive for the polymer solutions. This difference may be clearly seen in Figure 7 where the twist and splay viscosities have been given for the same reduced temperature ($T_c - T = 20$°C), as a function of concentration. Both the twist and splay viscosities have an approximately exponential dependence on polymer concentration, although the range available to us does not enable the different concentration regimes identified by Mattoussi *et al.*,[9] using the dynamic Fréedericksz transition technique on a structurally similar system, to be seen in the present work. However, it is interesting to note that

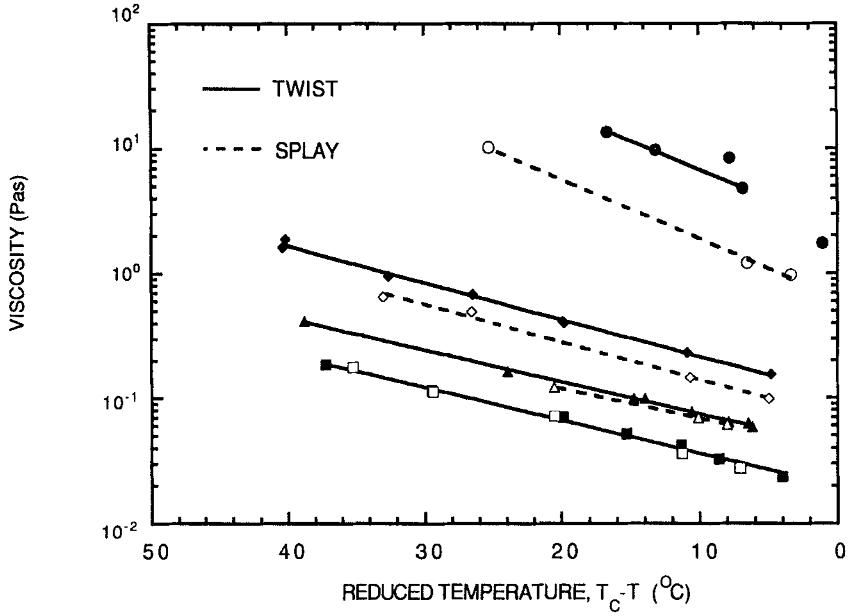

FIGURE 6 The twist and splay viscosities as determined from EDLS as a function of reduced temperature ($T_c - T$). The curves join twist viscosity data (filled symbols) for E7 (■), 5% polymer (▲), 13% polymer (◆) and 48% polymer (●).The corresponding unfilled symbols joined by dashed lines are for splay viscosity data.

α_3^2/η_b also becomes appreciably large for low molecular mass nematics on cooling towards a S_A phase.[26] Since twist deformations are forbidden in the S_A phase, whilst splay deformations are finite at the transition, this divergence in α_3^2/η_b (or $\gamma_1 - \eta_{\text{SPLAY}}$) strongly suggests pretransitional effects due to the imminent S_A phase. For the polymer solutions, the data also show a similar divergence, but as a function of concentration. The pure polymer PG296 is smectogenic, and although the solutions studied were nematic and stable over many months, this property does appear to be influencing more markedly the twist rather than the splay viscosities.

The splay and twist elastic constants, as determined from EDLS, are given as a function of temperature for E7 and the three PG296/E7 solutions, in Figure 8. From this Figure it is clear that both elastic constants decrease at high polymer concentrations.

The values of k_{11} for E7 agree to with 3% with the values determined by Raynes *et al.*[16] from the threshold field for an electric field induced splay Fréedericksz transition. These values were considered to be accurate to within approximately 1%. The excellent agreement between light scattering and Fréedericksz transition data is very rewarding. The values of k_{22} given by Raynes *et al.*[16] were determined from the threshold electric field for distortion of a twisted nematic cell and have an accuracy of only 10%. Our values for k_{22} tend to be slightly lower than these, but are within the combined experimental errors.

Given the viscosity data, Figures 6 and 7, it is obvious that changes in the $k_{11}/\eta_{\text{SPLAY}}$ and k_{22}/γ_1 (c.f. Figures 4 and 5) are dominated by changes in the viscosity

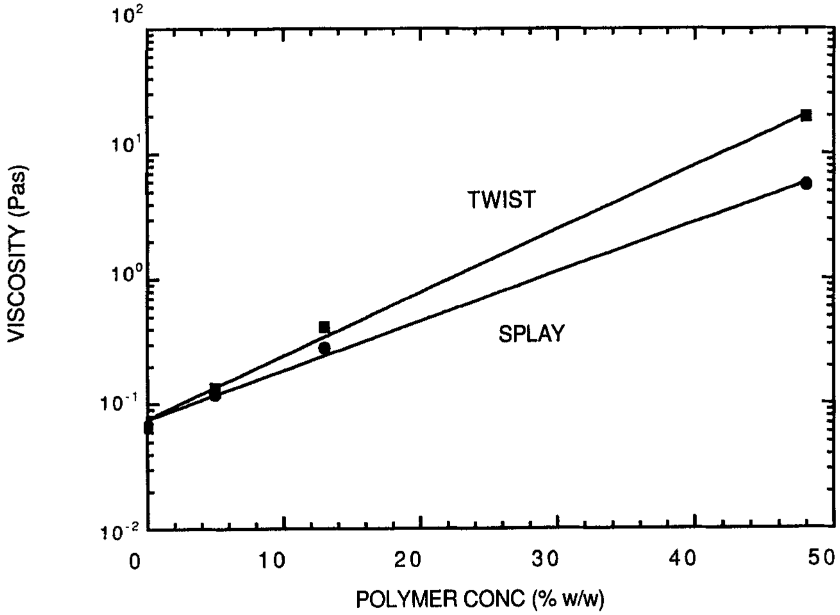

FIGURE 7 Concentration dependence of twist (■) and splay (●) viscosities at the reduced temperature $T_c - T = 20°C$.

coefficients. Nonetheless, it is interesting to consider the likely origins of the change in the elastic constants. From the refractive index data, and using the Haller technique,[27] we have calculated the orientational order parameter, S, for E7 and the polymer solutions.[24] From these data we have determined the ratio k_{22}/S^2 as a function of concentration and temperature, Figure 9. From the original theory[28] k_{22} should be proportional to S^2, i.e., k_{22}/S^2 is a constant in the limit that $k_{11} = k_{33}$. Apart from very close to the clearing temperature, these data appear to be approximately independent of temperature and concentration at a value of approximately 15 pN. Although the accuracy, over a wide temperature range, of the Haller technique has been questioned recently,[29,30] its use in the comparative studies between the solutions would seem acceptable. From the data, it is a reasonable conclusion that the reduction of the elastic constants is due to the disruption of the nematic order by the polymer backbone. This is also consistent with the slight decrease in the clearing temperature with increasing polymer concentration. The limited data for k_{11} has not allowed a similar comparison to be carried out, although k_{11} is similarly reduced with decreasing S.

Thus, the most dramatic physical effect of dissolving a side-chain polymer into a low molar mass host is to increase the twist or splay viscosity coefficients. Unfortunately, a theoretical understanding of the mechanism of the viscosity increase is quite difficult. Brochard's theory[31] predicts a linear increase in viscosity with increasing polymer concentration for solutions of a flexible polymer in a nematic solvent. The physical origins of this viscosity increase lie with the resistance of the polymer chain to distortion, and the frictional forces which resist motion of the chain relative to the solvent. This theory does not fully describe a solution of a

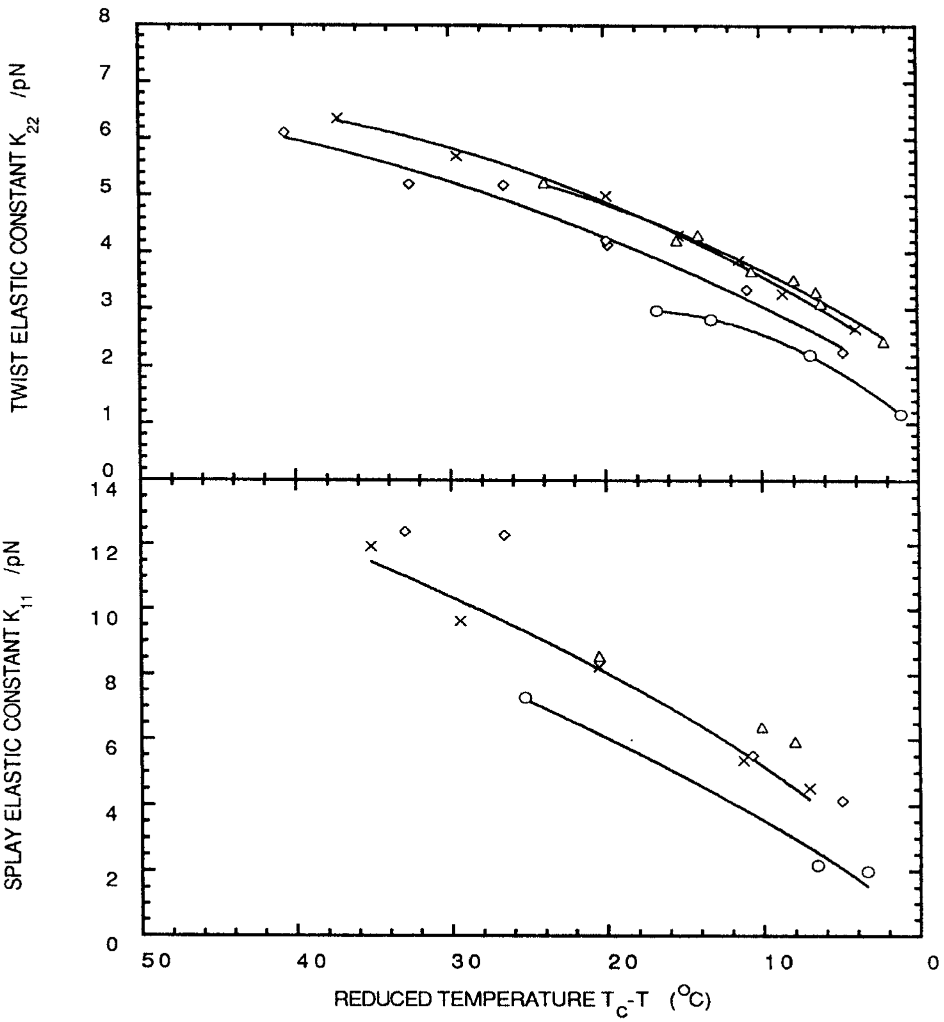

FIGURE 8 Splay (k_{11}) and twist (k_{22}) elastic constants for E7 and for the polymer solutions as a function of reduced temperature. Symbols are as for Figure 2.

side-chain mesomorphic polymer, where the backbone is coupled by flexible spacers to mesogenic elements which are part of the nematic ordering. Unfortunately, investigations of the effects of simple flexible polymer chains such as polystyrene upon the viscous properties of nematogens are hindered by solubility problems. For solutions of a side-chain mesomorphic polymer, the degree of coupling between the backbone and the mesogenic moieties will depend upon the length and flexibility of the linking groups. A full investigation of this dependence would assist the development of a comprehensive theory which may help to explain the logarithmic dependence of γ_1 and η_{SPLAY} on concentration, observed herein and previously.[12]

Finally we return to a brief discussion of the choice of frequency of the a.c. applied field in the EDLS measurements. The viscosity coefficient γ_1 (or η_{SPLAY})

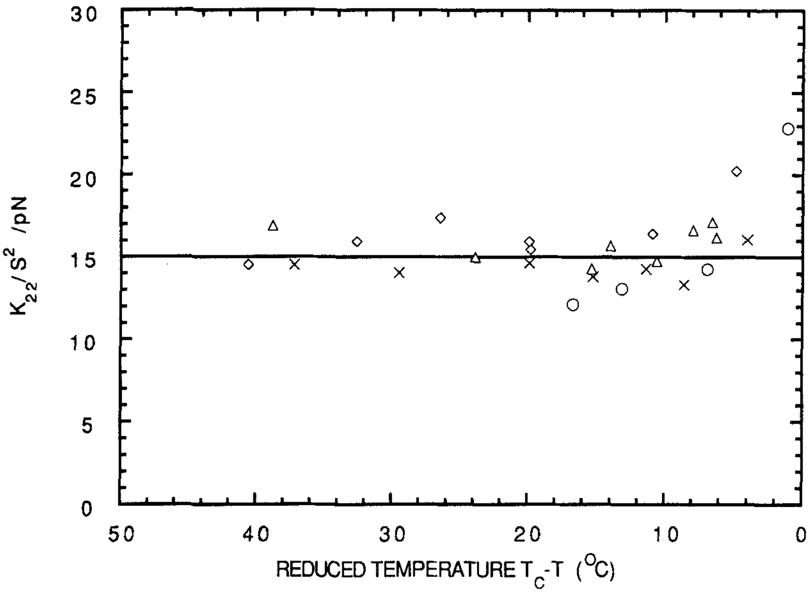

FIGURE 9 Reduced twist elastic constant k_{22}/S^2 as a function of reduced temperature ($T_c - T$) for E7 and the polymer solutions. Symbols are as for Figure 2.

is determined from the gradient of the linewidth Γ versus E^2 plot. This gradient, G, is given by $\varepsilon_0\Delta\varepsilon/\gamma_1$ for the case of Mode 2 fluctuations. A slightly more complex form of gradient is obtained for Mode 1 or splay deformations, but it still contains a term in $\Delta\varepsilon/\eta_{\mathrm{SPLAY}}$. It is therefore important, for correct determination of γ_1 and η_{SPLAY}, that there is no dispersion of $\Delta\varepsilon$ at the measuring frequency. We have measured G as a function of frequency for two of the polymer solutions, Figure 10. For ease of comparison we have normalised G to the value obtained in both Modes above 5 kHz. The Mode 2 (twist) fluctuations give values of G independent of frequency between 50 Hz and 20 kHz. At frequencies lower than ~50 Hz, G decreases anomalously due, presumably, to charge injection effects and electrohydrodynamic instabilities. Mode 2 data behave correctly if measured above 100 Hz for these systems. The Mode 1 (splay) data are more curious. Above ~5 kHz the gradient G is independent of frequency up to at least 20 kHz. Below the lower frequency limit, there is a rapid decrease in G centered at ~600 Hz. Above 100 Hz, Γ was always proportional to E^2. Similar anomalous behaviour in Mode 1 fluctuations has been observed[21] with 5CB below ~1.5 kHz. Theoretically it has been shown that flexoelectricity and conductivity effects can couple to Mode 1 fluctuations exclusively.[20] Flexoelectric effects couple linearly to the field E, so they can be eliminated. If these effects are due to conductivity, then, as in the Mode 2 case, the critical frequency will depend on viscosity as ionic mobility is reduced in more viscous solutions.[32] As can be seen from Figure 10, the critical frequency is virtually independent of the polymer concentration or viscosity. Further the shift in critical frequency, for a given polymer concentration, does not scale with the viscosity (or the constants involved) for the two different Modes. It is not likely therefore that this effect is due to conductivity either. At present, the

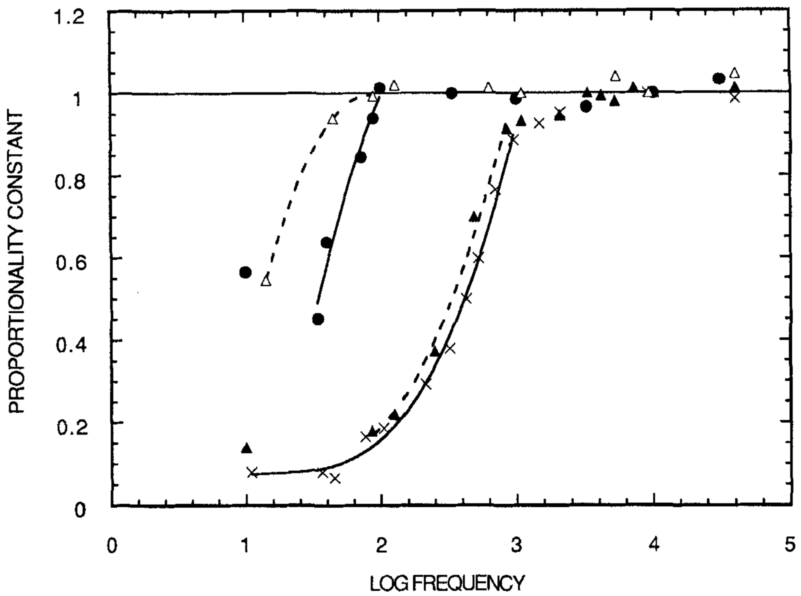

FIGURE 10 Frequency dependence of the EDLS experiments for two polymer concentrations. The ordinate is the proportionality constant between scattered linewidth and applied electric field, normalized at 5 kHz. Mode 2 data: 5% polymer (●) and 13% polymer (Δ). Mode 1 data: 5% polymer (×) and 13% polymer (▲).

origins of the dispersion in Mode 1 fluctuations is unclear and the data do suggest an interesting area for further study. Above the critical frequency range, the Mode 1 fluctuations behave normally and can be used to measure the splay elastic constants and viscosity coefficients.

CONCLUSIONS

In the present work, we have studied the influence of concentration of a side-chain siloxane copolymer, PG296, on the physical properties of a broad temperature range, low molecular mass nematic solvent, E7. Data have been presented for transition temperatures, dielectric constants, optical anisotropy and splay and twist elastic constants and viscosities. For polymer concentrations up to 48% w/w, the nematic to isotropic phase transition temperature is only reduced by 4.5°C. Thus the broad temperature range of the E7 solvent is maintained. Both the dielectric anisotropy ($\Delta\varepsilon$) and the birefringence (Δn) decrease with polymer concentration at a given reduced temperature. This has been attributed to both a decrease in the order parameter, due to the flexible polymer chain, and dilution effects, due to the lower values of $\Delta\varepsilon$ and Δn expected of the polymer. The data for $\Delta\varepsilon$ and Δn have been given as a function of temperature, and they behave as typical nematic materials. The twist (k_{22}) and splay (k_{11}) elastic constants decrease with increasing polymer concentration and this effect appears, essentially, to be due to the decreased order parameter S. The values of k_{11} and k_{22} are of the same order of magnitude for the polymer solutions as the nematic solvent E7. Thus the orders of magnitude change in k_{11}/η_{SPLAY} and k_{22}/γ_1 with increasing concentration can be attributed to the large changes in the twist γ_1 and splay η_{SPLAY} viscosities. We have shown that the difference between γ_1 and η_{SPLAY} may be given by a large increase in the third Leslie coefficient α_3, as the concentration of polymer increases. For neat E7, the values of γ_1 and η_{SPLAY} are identical, so that α_3 goes to zero. Both the twist and splay viscosity coefficients appear to be logarithmically dependent on polymer concentration, as observed with other materials previously.[12] Thus there is a need for theories that explain this logarithmic behaviour and also the divergence of γ_1 and η_{SPLAY} with concentration. It seems likely from our data that short range smectic-like correlations could explain this difference, although no divergence was observed in the elastic constants. At frequencies below ~1.5 kHz, the Mode 1 (splay) fluctuations showed an anomalous decrease with decreasing frequency of the applied field used in the EDLS measurements. The origins of this effect, which appear to be viscosity independent, are not understood. Neither flexoelectric nor conductivity phenomena explain the results. Mode 2 (twist) data behave normally down to ~50 Hz when charge injection effects become important. These phenomena warrant further theoretical and experimental studies.

In summary, EDLS has been used to probe the important viscosity and elastic constants of a liquid crystal polymer dissolved in a low molar mass nematic liquid crystal eutectic mixture. All of the parameters Δn, $\Delta\varepsilon$, k_{ii} and the viscosity coefficients change as a function of temperature and concentration. In future work, based on these stable systems, we will study how (i) spacer coupling length (ii) coupling position to the mesogen (i.e., lateral or transverse) and (iii) degree of substitution (or number of reacted sites on the backbone) also affect these liquid crystal parameters. All of these structural changes would be expected to have a marked and different effect on the splay and twist constants for a given molecular weight of polymer. Finally we will study, for a given polymer, how molecular weight and sample polydispersity also affect each macroscopic parameter.

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