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Light Scattering Studies of the Viscoelastic Ratios of Mixtures of Side Chain Liquid Crystalline Polymers in Low Molar Mass Mesogens†

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Using dynamic light scattering, we have studied the behaviour of (k_{22}/γ_1) as a function of polymer concentration for a number of solutions of a side chain polymer liquid crystal dissolved in a monomeric liquid crystal host. The polymer had a polysiloxane backbone and cyanobiphenyl and benzoate ester side groups. The monomeric solvent was pentyl cyanobiphenyl. Values of the refractive indices n_e and n_o have been determined, and we have also studied the influence of cell thickness on (k_{22}/γ_1). The apparatus, its use and essential experimental precautions for the correct interpretation of dynamic light scattering, are all discussed in detail.

INTRODUCTION

Side chain polymer liquid crystals have excited considerable interest over the last few years because of their potential use in novel electro-optic devices. As evident from the recent work of Finkelmann et al[1] and Ringsdorf and Zentel,[2] the operating parameters for such nematic polymers appear to be worse than those observed for structurally equivalent monomers. Generally the elastic constants, although of

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the same order of magnitude, are higher for polymers than monomers (which leads to an increase in threshold voltage) and the response times are slower (2–10 times) even at high operating temperatures. It would appear, therefore, that the main use of such thermotropic polymers is in slow response time or storage devices. Using the existence of a glass transition (at temperature Tg), Finkelmann[3] has considered below Tg storage in some detail. We have recently studied storage above Tg in the smectic phase[4] exhibited by similar side chain polysiloxane polymer liquid crystals but with cyanobiphenyl and benzoate ester side groups.[5] The optical properties of these storage devices[6] are significantly better than those of equivalent monomeric systems.[7] As part of our research programme on these new liquid crystals, we have been examining the influence of low concentrations of polymers on the properties of monomer-polymer liquid crystal mixtures. Recently there has been some discussion in the literature as to the necessity of using identical polymer side chain moieties to those of the monomeric host[8] in order to obtain stable mixtures. If this condition is not met then phase separation of the monomers and polymers occurs. A different approach[9] has been to dissolve non-mesogenic polymer liquid crystals to modify the visco-elastic properties. However, in this case severe solubility problems were experienced and only very low concentrations of polymer could be solvated. In this paper we show how these limitations may be overcome. We report data on the twist elastic constant/viscosity ratio (k_{22}/γ_1) and refractive indices for several polysiloxane side chain liquid crystal mixtures with a pentyl cyanobiphenyl (5CB) monomeric host.

In order to measure (k_{22}/γ_1), we have developed[10] a new dynamic light scattering apparatus with several advantageous features for liquid crystal studies. We believe that such an experiment may now be used routinely for visco-elastic constant studies and we have, therefore, presented a review of the apparatus and its performance.

THEORY

The strong scattering of light in a nematic liquid crystal results from thermal fluctuations of the director. Such dynamic distortions of the nematic structure can be characterised in terms of three elastic and six viscotic constants, and the Orsay group[11] have derived expressions relating these constants to both the intensity and the power spectrum of the scattered light.

The Orsay theory predicts that an incident laser beam will receive

a Lorentzian broadening due to scattering from two overdamped modes within the nematic medium. The first mode is due to a combination of splay and bend distortions (Mode 1) and the second mode to a combination of twist and bend distortions (Mode 2). For a light scattering photon correlation experiment, in the absence of an applied field, the Lorentzian linewidths (Γ_α) for these two modes ($\alpha = 1, 2$) are given respectively by:

$$\Gamma_1 = \frac{k_{11}q_\perp^2 + k_{33}q_\parallel^2}{\gamma_1 - \beta} \tag{1}$$

$$\Gamma_2 = \frac{k_{22}q_\perp^2 + k_{33}q_\parallel^2}{\gamma_1 - \delta} \tag{2}$$

where

$$\beta = \frac{2(q_\perp^2\alpha_3 + q_\parallel^2\alpha_2)^2}{q_\perp^4(\alpha_2 + 2\alpha_3 + \alpha_4 + \alpha_5) + 2q_\perp^2q_\parallel^2(\alpha_1 + \alpha_3 + \alpha_4 + \alpha_5) + q_\parallel^4(-\alpha_2 + \alpha_4 + \alpha_5)}$$

and

$$\delta = \frac{2\alpha_2^2q_\parallel^2}{q_\perp^2\alpha_4 + q_\parallel^2(\alpha_4 + \alpha_5 - \alpha_2)}$$

In these expressions k_{ii} ($i = 1, 2, 3$) are the Frank elastic constants, α_j ($j = 1$–6) are the Leslie viscosity coefficients, γ_1 is the twist viscosity (equal to α_3–α_2) and q is the scattering vector (where the subscripts $\parallel$ and $\perp$ denote parallel and perpendicular to the nematic director). These expressions have been shown to be applicable to light scattering experiments from monomeric liquid crystal systems.[12] It has also been shown recently[13] that, if the liquid crystals are aligned homeotropically with the director in the direction of propagation of the incident light, if the incident light is polarised perpendicularly to the scattering plane and if the depolarised scattered component is detected (i.e. parallel to the scattering plane), then:

$$\Gamma_2 = \frac{k_{22}}{\gamma_1} q_\perp^2 \tag{3}$$

where

$$q_{\perp}^2 = \left[\frac{2\pi}{\lambda_0}\right]^2 n_m^2 \sin^2\theta$$

In these expressions λ_0 is the incident laser wavelength, n_m the refractive index of the index matching fluid (see below), θ is the measured scattering angle, and it has been assumed that $(q_{\parallel}/q_{\perp})^2 \ll 1$.

EXPERIMENTAL

The polymer liquid crystal (PG296) used in these studies comprised a polysiloxane backbone of fifty SiO units and equal ratios of cyanobiphenyl and benzoate ester side chain moieties, Figure 1. The sample was kindly prepared for us by Professor Gray and colleagues at the University of Hull.[5] The monomeric host was 4-cyano-4′ pentyl - biphenyl (5CB) and was provided by BDH Chemicals Ltd. Both materials were used without further purification. Homogeneous mixtures were achieved, over the concentration range reported, by shaking at room temperature for twelve hours. The uniformity of the optical textures and the linearity of the birefringence (Δn) were taken as evidence of the homogeneity of the solutions. All concentrations are expressed as weight ratios, i.e. weight of polymer divided by total mixture weight (w/w).

The refractive indices n_e and n_o of both 5CB and the solutions with PG296 were measured using a Bellingham and Stanley 60/HR Abbé refractometer. The samples were aligned homeotropically using lecithin coated glass plates and all solutions showed excellent alignment even at the higher polymer concentrations. The samples were illuminated transversely, using a sodium lamp (λ_0 = 589.6nm), a mercury lamp (λ_0 = 546.1nm) or a He-Ne laser (λ_0 = 632.8nm). Variation of the direction of the polarisation plane ($\parallel$ and $\perp$) allowed n_o and n_e to be measured. The refractometer was temperature controlled using a pumped water circulation system stable to ± 0.05°C and temperatures were measured using a platinum resistance thermometer accurate to $\pm 0.1\%$. The lecithin (BDH–Egg Grade II) was applied as a 0.5% solution in chloroform to the surface and then allowed to dry. This procedure was also used to align the solutions for the light scattering measurements. The sample spacing of the light scattering cells was achieved using kapton film and they were sealed using an epoxy resin. The nematic-isotropic transition temperatures (T_{NI}) were

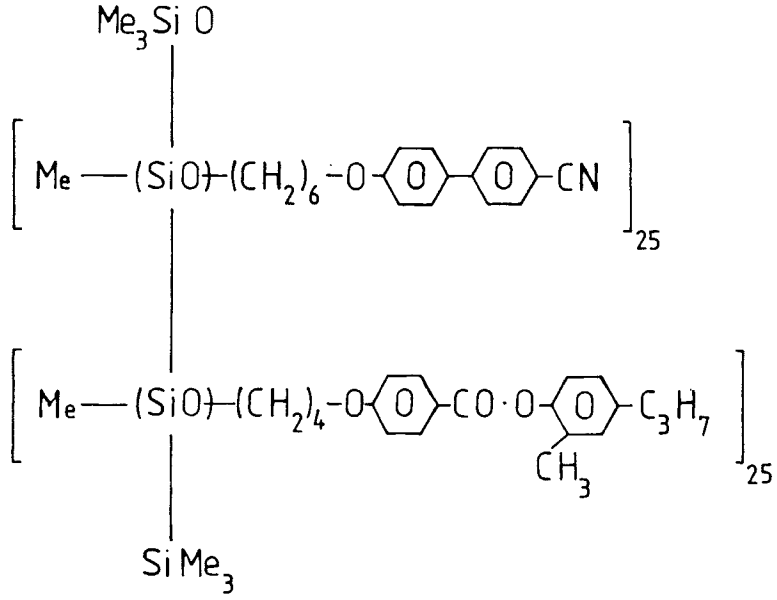

FIGURE 1 Chemical structure of PG296. For this polymer Tg = 4.0°C and T_{SI} = 85.9°C.

monitored throughout the experiments to ensure no sample degradation had taken place.

Using an interferometric technique with the filled cell *in situ* in the scattering apparatus, the thickness of each individual sample could be determined prior to light scattering measurements. For this technique, the sample is rotated by a known angle with respect to the incident laser beam. Light reflected from the first glass-liquid crystal interface will have a different path length to that which traverses the liquid crystal film and is reflected at the second interface, and hence the two beams will interfere. If the sample is then rotated to a second known angle, interference fringes will be seen to cross the reflected beam, the number of which is related to the thickness of the sample. As the limiting accuracy of this method is in measurement of the reflection angles, and these can be measured to within 5′ of arc using a vernier scale, the absolute accuracy of this method is $\pm 0.25\%$.

The photon correlation light scattering apparatus is shown schematically in Figure 2. The apparatus[10] was constructed to operate in either the homodyne or the heterodyne detection modes over a continuous range of angles from $-30°$ to $+150°$. The temperature range available is from 0° to 250°C and the computational facilities allow direct on line data analysis.

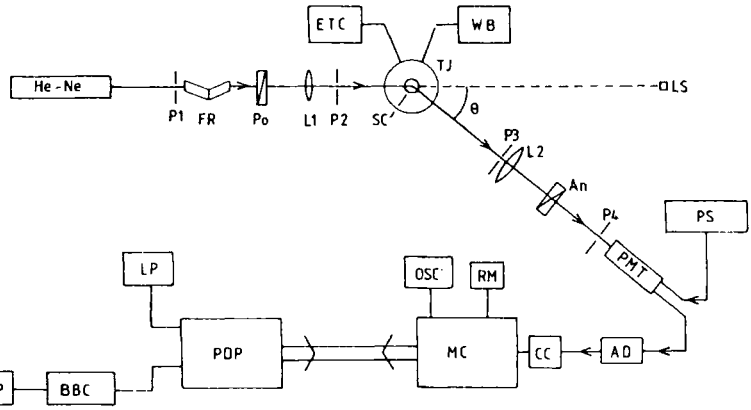

FIGURE 2 Schematic of the Photon Correlation Spectrometer. Key to schematic symbols: He-Ne, helium-neon laser: P1 and P2, variable apertures: FR, Fresnel rhomb: Po, polariser: L1, input lens: SC, sample cell: TJ, temperature jacket: ETC, electronic temperature controller: WB, water bath: LS, light stop: P3 and P4, variable pinholes: L2, collection lens: An, analyser: PMT, photomultiplier tube: PS, power supply: AD, amplifier-discriminator: CC, clipping counter: MC, Malvern digital correlator: RM, rate meter: OSC, oscilloscope: PDP, PDP 11/34 A minicomputer: LP, line printer terminal: BBC, BBC micro-computer: EP, Epson printer.

The light source used was a 10mW Hughes Aircraft Corporation He-Ne gas laser. This source exhibits excellent intensity ($\pm 0.3\%$) and polarisation stability. A Fresnel rhomb (FR) was used in the input optics to rotate the polarisation plane of the input light as required. The polarisation of the beam was refined using a Glan-laser polariser (Electro-optic Developments GT2) and pinholes P1 and P2 used to remove stray surface reflections. Lens L1 focussed the incident light into the temperature stabilised scattering cell. The temperature control was achieved using a water circulating system which provided a long term stability (days) of ± 0.05°C at the sample scattering volume. This was monitored using a platinum resistance thermometer as before. The sample cell was immersed in an index matching fluid (dibutylphthalate) to prevent flare spots and to provide good thermal coupling to the heater jacket. This index matching fluid was chosen because of its high stability and temperature range, (-30°C to 340°C). Use of the electrical heating element and two stage feature of the cell allows temperatures up to 250°C to be achieved at the sample. The scattered light was collected with the lens L2 and the polarisation components resolved with a second Glan-laser polariser (An). The size of the pinhole P3 determined the acceptance angle of the collection optics and hence also the uncertainty in the detected value of $q_{\perp}^2$ (e.g. for a 200μm diameter pinhole and $\theta = 5°$ the

uncertainty was ±1%). The pinhole P4 (100μm dia) determined the observed size of the scattering volume. The scattered light was then detected using a Hamamatsu R649 photon counting photomultiplier tube. The distance from the scattering volume to the detector was approximately 40cm. The photo tube's output was conditioned by a Le Croy MV L100 amplifier-discriminator before being analysed with a Malvern K 7023 digital correlator. The correlator was interfaced directly to a DEC PDP 11/34A minicomputer and on-line data analysis was carried out. Two exponential fitting programs were used in the data analysis. The first being a forced single exponential fit based on the well known Marquadt algorithm. The second was a powerful multiple exponential fitting routine recently developed in this laboratory.[14] The detailed construction and performance of the spectrometer will be given elsewhere and in this paper we have concentrated on those features essential to light scattering studies of nematic liquid crystals.

RESULTS AND DISCUSSION

The variation of n_e and n_o for pure 5CB and a 20% w/w PG296 solution are given as a function of temperature in Figure 3. From this figure it can be seen that the polymer slightly reduces n_e whilst n_o is virtually constant. We have, therefore, examined the effective decrease in Δn ($\Delta n = n_e - n_o$) for a number of solutions at different temperatures, Figure 4. All solutions up to 20% w/w were nematic and with the higher concentrations a small biphasic region was observed over a 1°C temperature range. We have taken T_{NI} as at the midpoint of this region as this also marks the end of behaviour commensurate with Freedericksz transitions in these materials.[15] Figure 4 shows that at a fixed temperature the decrease in Δn varies linearly and, therefore, predictably with polymer concentration. This indicates that the solutions are homogeneous and that the nematic order is uniform. We have also observed[15] a similar trend in $\Delta\epsilon$. At lower temperatures Δn increases indicating the higher order in the system. We are currently examining this behaviour in greater detail.

Previous measurements using dynamic light scattering techniques to study liquid crystals[12,13] have tended to use homodyne or self beat spectroscopy. In such techniques[16] only the light scattered from the material is detected and the frequency broadened signal beats with itself at the detector. However, if the scattered, broadened laser light is coherently mixed with non-broadened light at the detector, then

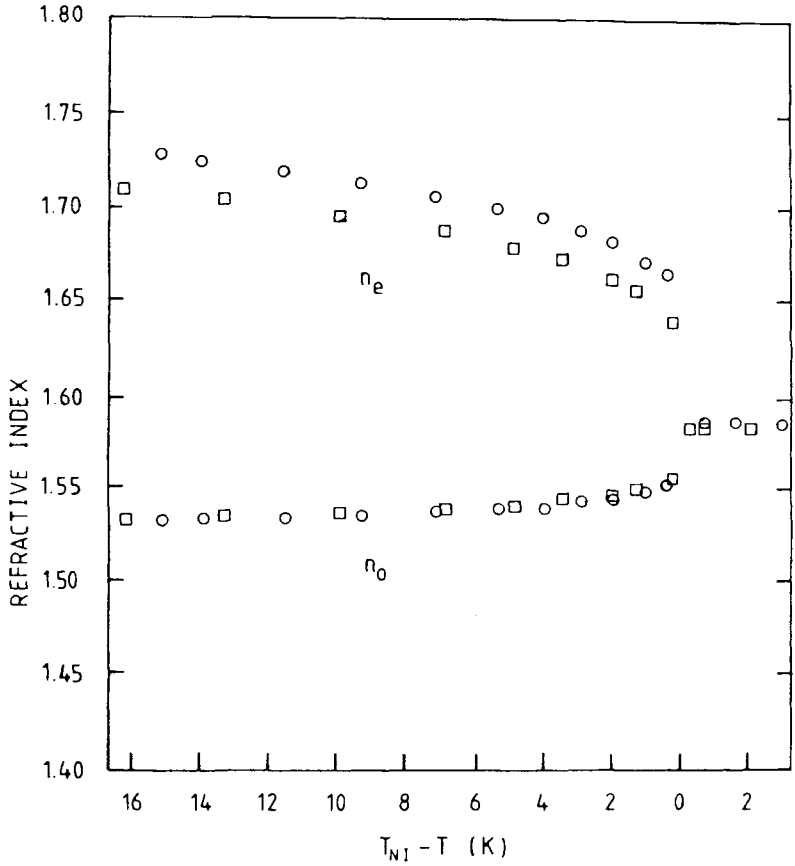

FIGURE 3 Refractive indices as a function of $T_{NI} - T$, for pure 5CB (○) and 19.5% w/w solution, (□) T_{NI} = 35.2°C and 36.2°C respectively. The subscripts *e* and *o* denote the extraordinary and ordinary rays, respectively, of the homeotropic (or uniaxial) alignment.

heterodyne detection takes place. The measured linewidth for heterodyne detection is different to that for the homodyne case.[16] The source of the non-broadened or reference signal may be either a static scatterer in the scattering volume or laser light guided to the detector without passing through the sample. It is the latter approach[10] that we have used in the current experimental arrangement. If the intensity ratio of the reference to scattered signal is of the order of or greater than 20:1, then pure heterodyne detection takes place and the measured linewidth is half that obtained in pure homodyne detection. We have varied the ratio of intensities of the reference to scattered signals,

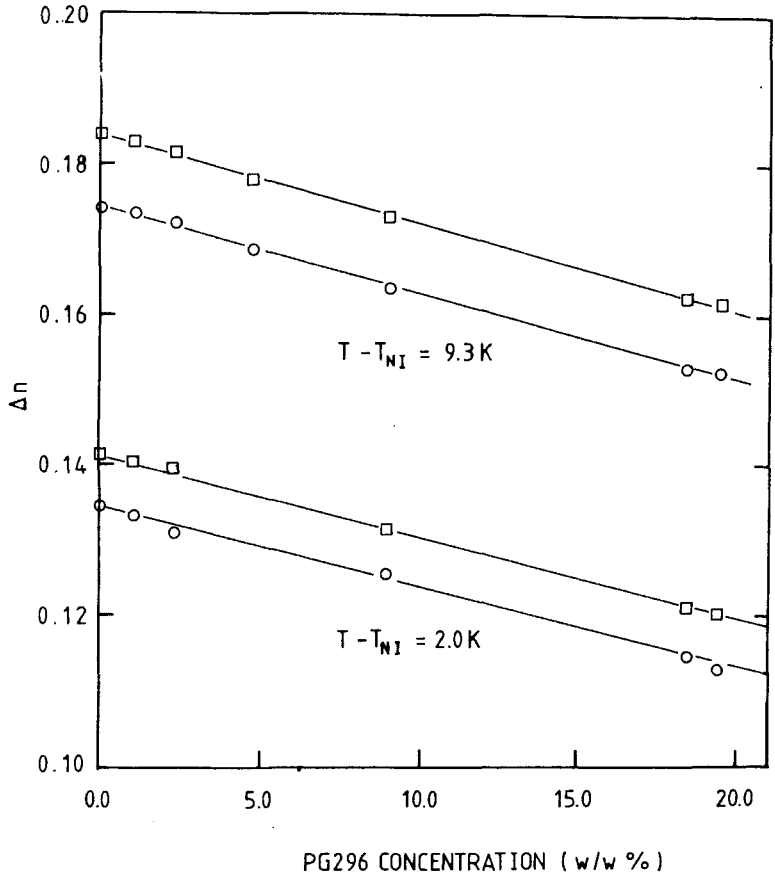

FIGURE 4 Birefringence, Δn, as a function of the concentration of PG296 in 5CB. for λ_o = 546nm (□) and λ_o = 633nm (○).

Figure 5. This shows clearly that, above a ratio of 20:1, the heterodyne linewidth is exactly half that of the pure homodyne case. However, near the pure homodyne condition, trace amounts of reference signal will lead to a large decrease in the detected linewidth. As it may be very difficult to avoid some flare or static surface scatterers in a thin nematic cell, such non-broadened signal could lead to serious errors in the measured linewidth and, therefore, k_{22}/γ_1. If homodyne detection is used and trace amounts of static scattering are present, then the measured k_{22}/γ_1 values will always be erroneously small. In the extrapolation procedures used in the data analysis, Γ_2 is measured as a function of q at low θ. We have, therefore, measured the homodyne/heterodyne ratio over all scattering angles used herein (θ = 4.5° to

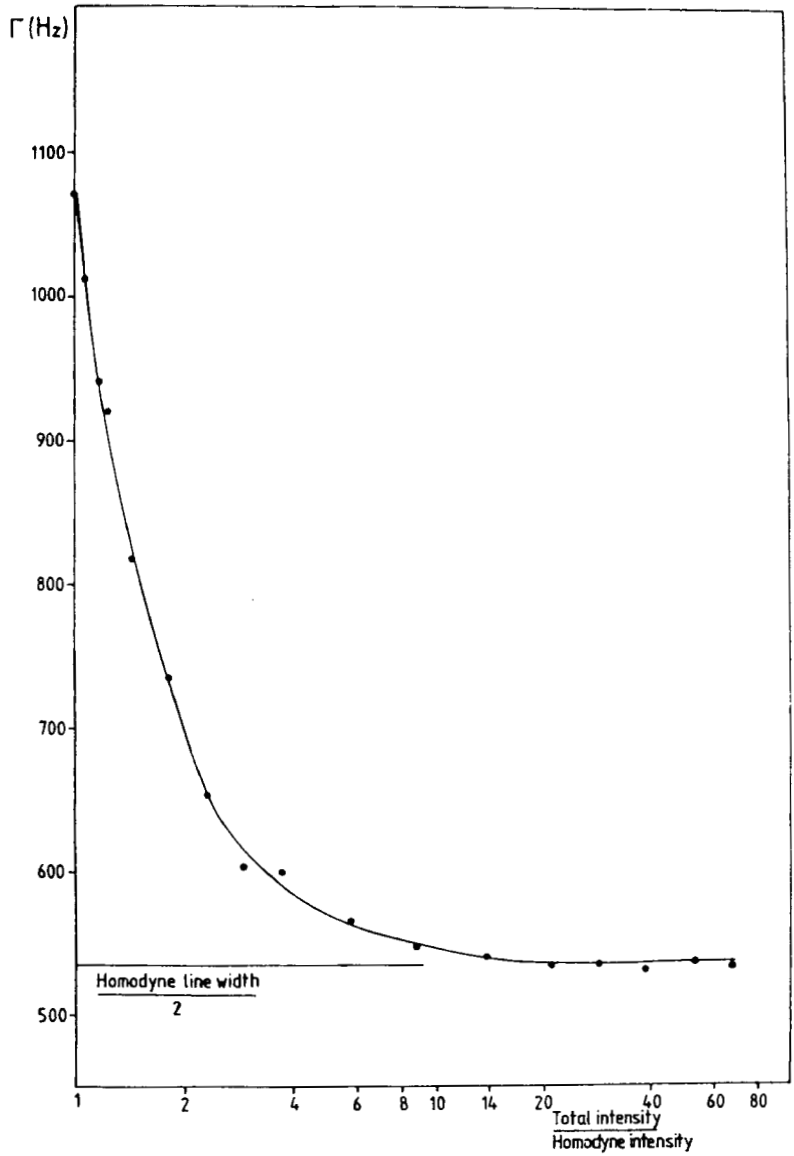

FIGURE 5 Variation of mean correlation linewidth with the ratio of the total intensity to the homodyne beam intensity. Pure 5CB, 21°C, $\theta = 14°$.

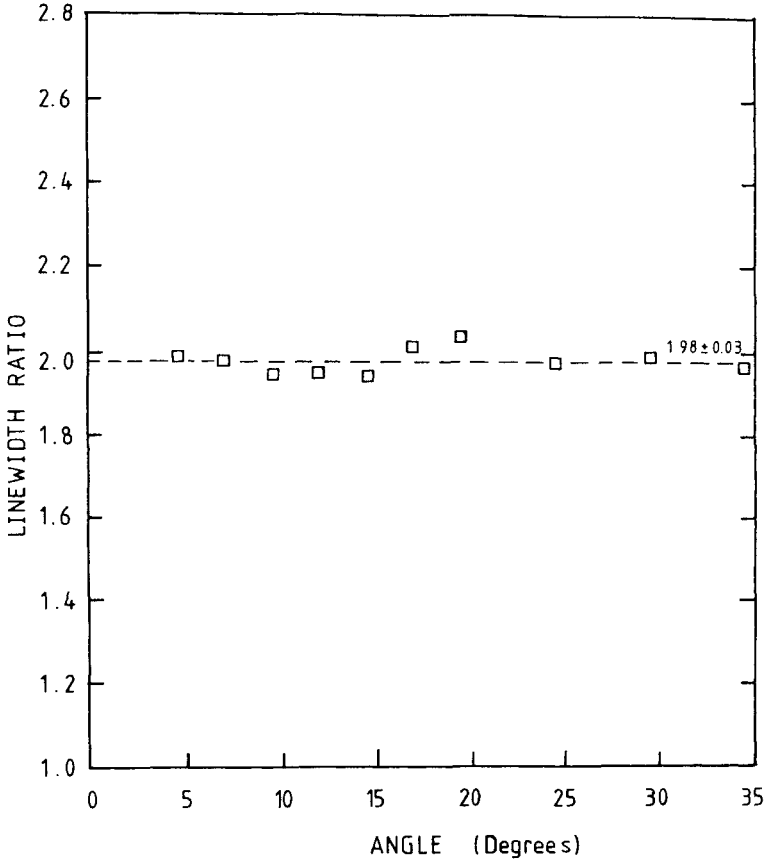

FIGURE 6 Ratio of the homodyne to heterodyne correlation linewidths as a function of the scattering angle.

35°), Figure 6. Within the experimental error of the homodyne measurements the ratio is always 2. This confirms that our apparatus and preparation techniques were appropriate and no stray light was generated in the system. Because the signal to noise ratio for heterodyned signals are always much higher than those in the homodyne case, we have used heterodyne detection throughout our work. Further, should stray non-broadened light ever be scattered in our system, the linewidths, unlike the homodyne case, will always be correct.

As mentioned above, from the Δn versus concentration data, all concentrations up to 20% w/w gave good homogeneous solutions. We have confirmed this at the microscopic level using hot-stage microscopy.[15] In the current paper we have carried out measurements of the viscoelastic ratio, (k_{22}/γ_1), for pure 5CB and two polymer

solutions in order to assess the technique and problems arising in such measurements. As shown in the Orsay theory (Eq. 3) under suitable polarisation conditions, the linewidth Γ_2, arising from twist distortions, should show a linear dependance on $\sin^2\theta$ for $(q_{\parallel}/q_{\perp})^2 \ll 1$. However, if this condition is not met, the amplitude of bend mode distortions becomes significant and causes the apparent value of (k_{22}/γ_1) to increase. As shown in Figure 7, this condition is upheld for $\theta \leqslant 20°$ for both pure 5CB and the 6.5% w/w polymer solution. Above this angle the linearity clearly breaks down and $(k_{22}/\gamma_1)_{\text{apparent}}$ shows an increasing upward curvature. It is worth noting that at $\theta = 14°$, the factor $(q_{\parallel}/q_{\perp})^2$ is 1% and this seems to be a good experimental limitation on the range of scattering angles used. The condition that $(q_{\parallel}/q_{\perp})^2 \ll 1$ also puts limitations on the thickness of sample used for experiments. In the homeotropic geometry, $q_{\parallel}$ is associated with bend

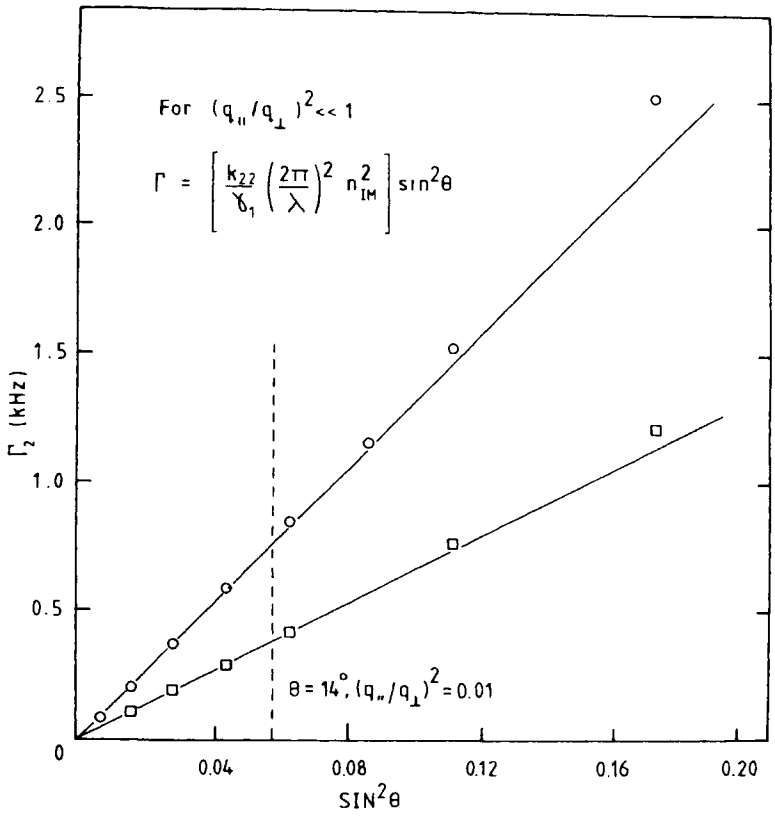

FIGURE 7 Dependence of the heterodyne linewidth, Γ_2, on $\sin^2\theta$ for pure 5CB (○) and for a 6.5% w/w solution of PG296 in 5CB (□). λ_o = 632.8nm, $T_{NI} - T$ = 5.4K.

distortions parallel to the director, i.e. normal to the sample walls. Since the light scattering experiment is associated with long wavelength modes, it is possible that the sample thickness will impose a minimum value for $q_{||}$. At low angles, where $q_{||}$ decreases sharply, it could be expected that such thickness dependent effects might become measurable. This has been observed in the thickness dependence of $(k_{22}/\gamma_1)_{apparent}$ as a function of scattering angle, Figure 8. At an angle of 12°, the $(k_{22}/\gamma_1)_{apparent}$ ratio diverged for a thickness of ~12μm whereas for $\theta \leq 7°$, this divergence occurred for much thicker samples of ~35μm. Above a sample thickness of 40μm, no divergence in the (k_{22}/γ_1) ratio was observed even for scattering angles as low as 4.5°. Therefore, in order to avoid such problems, dynamic scattering should be carried out on samples with a thickness of 40μm

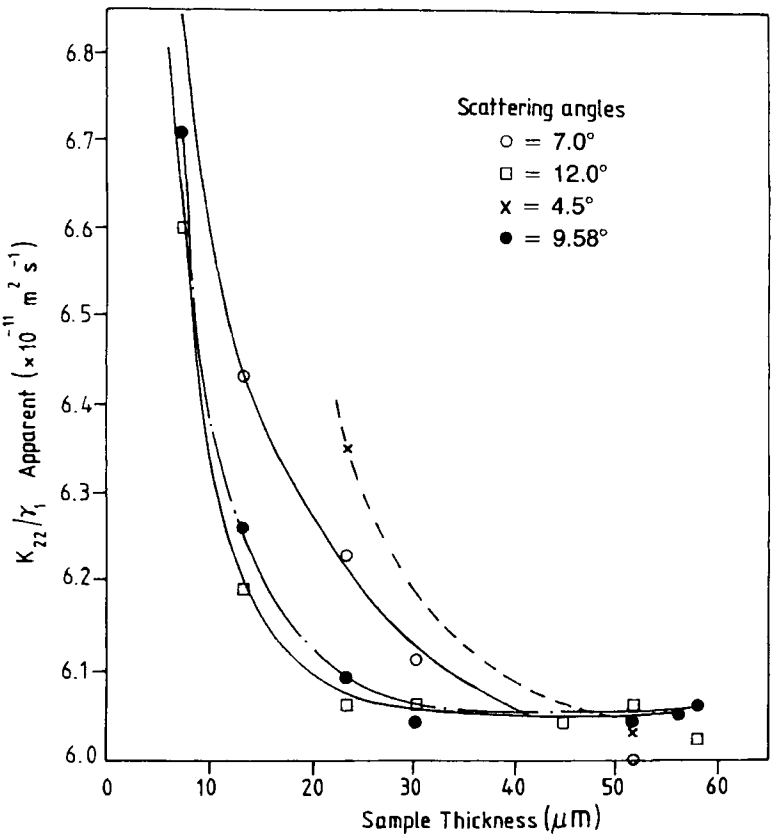

FIGURE 8 Apparent viscoelastic ratio, $(k_{22}/\gamma_1)_{apparent}$, as a function of thickness for different scattering angles, θ. Pure 5CB, $T_{NI} - T$ = 5.4K.

or more and, in this present work, all following results refer to samples of between 40μm and 60μm. Figure 8 also gives an indication of the reproducibility of results from these light scattering measurements. We feel that the sample to sample reproducibility is of the order of ±0.5%. The linear dependence upon $\sin^2\theta$ observed in Figure 7 for both systems demonstrates the strong nematic ordering inherent in both the polymer solution and the pure monomeric liquid crystal.

We have measured the temperature dependence for pure 5CB and two polymer solutions of (k_{22}/γ_1), Figure 9. To a good approximation the rate of change of ln (k_{22}/γ_1) with temperature is equal for all three systems. However, for a fixed temperature, the absolute (k_{22}/γ_1) value decreased markedly. For example at $T_{NI}-T = 12°$, $(k_{22}/$

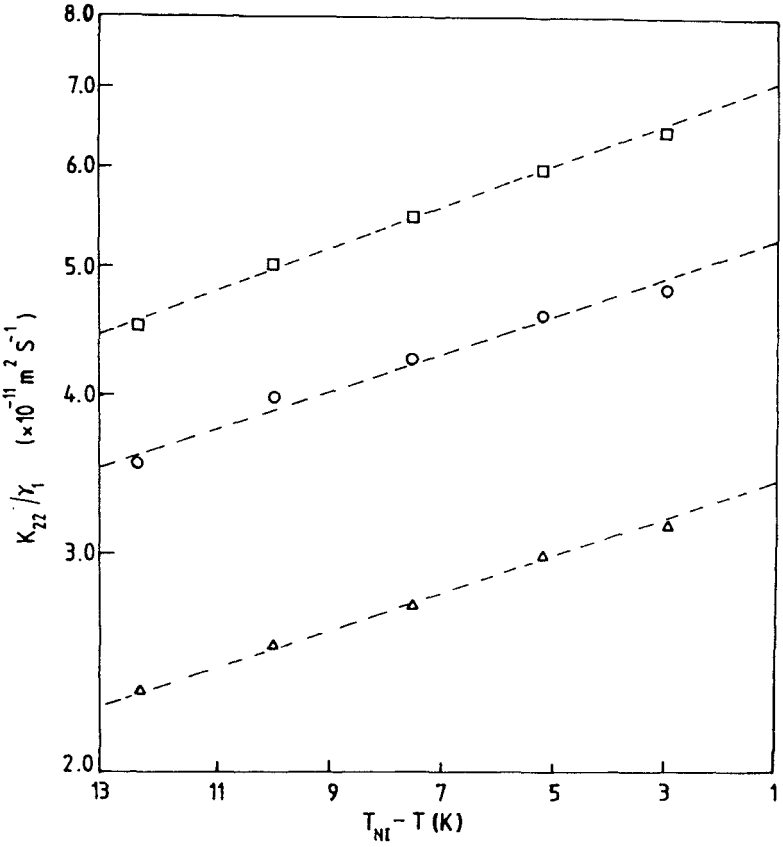

FIGURE 9 Variation of the viscoelastic ratio (k_{22}/γ_1) with $T_{NI}-T$, for pure 5CB (□), 2% w/w PG296 in 5CB (○), and 6.5% w/w PG296 in 5CB (Δ). For these materials, the transition temperatures T_{NI}, are 35.2°C, 35.2°C and 35.4°C, respectively.

γ_1) decreases by a factor of 2 for the 6.5% w/w solution in comparison with pure 5CB. From a comparison with measurements of k_{33} and k_{11} in the same PG296/5CB system (where these constants vary by ~10% under the same conditions) we suggest that the major contributor to the decrease in (k_{22}/γ_1) is the rapid increase of γ_1 with increasing polymer concentration. This suggestion is in accord with measurements on polystyrene/monomeric liquid crystal solutions[9] where 1% of polystyrene induces large changes in γ_1.

CONCLUSIONS

We have shown that both homodyne and heterodyne detection methods may be used, in a carefully set up photon correlation apparatus, to measure the viscoelastic ratio (k_{22}/γ_1) in the nematic phase. It has been shown that trace amounts of non-broadened scattered light lead to serious distortions of the measured linewidths and as a precaution it is better to establish a good heterodyne detection system. Further, it has been shown that at low scattering angles a minimum cell thickness was necessary to eliminate distortions to the (k_{22}/γ_1) data.

Preliminary data has been presented on a pure monomeric solvent (5CB) and several side chain polysiloxane-monomer solutions. It was established that, despite the coexistence of cyanobiphenyl and benzoate ester side chain moieties on the polymer, the solutions were stable up to at least 20% w/w. Refractive index data showed a slow, linear decrease in Δn with increasing concentration, whilst the photon correlation data showed a marked decrease in (k_{22}/γ_1). The decrease in (k_{22}/γ_1) was attributed to a large increase in γ_1. It was also established that all of the monomer/polymer liquid crystal solutions were nematic and stable over a wide temperature range.

We are currently using the method, due to Martinand and Durand,[17] of applying electric fields to the samples to separate the k_{22} and γ_1 data and the results of these studies will be reported at a later date. Finally, in this study we are changing the experimental conditions (i.e. polarisation state and sample alignment) in order to quantify the use of the technique in the determination of the splay and bend modes.

Acknowledgments

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