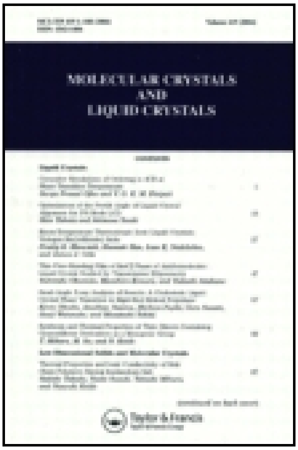

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Dynamic Light Scattering Study of Polymer-Stabilized Liquid Crystal Monodomain

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Dynamic light scattering (DLS) analysis is performed on a polymer-stabilized liquid crystal (PSLC) monodomain in the presence of an AC electric field. The twist elasticity and viscosity of the PSLC are determined. Compared with the nematic solvent (5CB), both the elasticity and the viscosity of the PSLC show substantial increases, reflecting the anchoring effect of the polymeric gel network. Time-resolved DLS measurements during the cure reaction yield information on the kinetics of network formation.

Keywords: Viscoelasticity, Liquid crystal polymer networks.

1. INTRODUCTION

It is well known that dynamic light scattering (DLS) from spontaneous thermally-driven distortions of the nematic order can be used to study the viscoelastic properties of liquid crystal materials.[1] Specifically, when light is scattered from a nematic monodomain, the scattering intensity is inversely proportional to the elastic constants which characterize the energy required to produce the nematic distortions. The relaxation rate of the autocorrelation function of the scattering intensity is determined by the inverse relaxation time of the director orientation fluctuation which is proportional to ratios of the elastic constants to the corresponding viscosity coefficients. By choosing appropriate combinations of nematic director orientation, polarizations of the incident and scattered light, and, the scattering angle, one can detect the pure splay, twist, and bend distortion modes.[2] For example, if the director is oriented parallel to the incoming light, the polarization of the incoming light is perpendicular to the scattering plane (formed by the wave vectors of incoming and scattered light), and the polarization of the detected light is in the scattering plane, one can detect the pure twist mode at small scattering angles.[2] The individual values of the twist elastic constant and viscosity coefficient can be obtained by application of an external field to the monodomain. Thus, for a homeotropic liquid crystal monodomain in an AC electric field, with the scattering geometry as described above, the relaxation rate of the twist deformation mode is[3]:

$$\Gamma_{\text{twist}} = K_{22}q_{\perp}^2/\gamma_1 + \varepsilon_0\Delta\varepsilon E^2/\gamma_1 \tag{1}$$

where K_{22} and γ_1 are, respectively, the twist elastic constant and viscosity, $q_\perp$ is the scattering vector, ε_0 is the dielectric constant in vacuum, $\Delta\varepsilon$ is the anisotropy of the dielectric permittivity of the nematic, and E is the field strength. Therefore, when the twist relaxation rate is plotted as a linear function of the field parameter $\varepsilon_0\Delta\varepsilon E^2$, the slope gives the inverse twist viscosity and the intercept at zero field yields the twist elastic constant K_{22}.

In recent years, liquid crystal polymer dispersions have been studied intensively for their potential applications in display devices. Recently, a new type of material has been developed, referred to as a polymer stabilized liquid crystal (PSLC), in which a reactive monomer is photopolymerized *in situ* to form an anisotropic network in a suitably aligned low molar mass liquid crystal. The function of the polymer network, which is present at levels of only a few percent w/v in this type of dispersion, is to anchor certain director configurations in either the field-ON or the field-OFF condition.[4]

The formation of a polymer network in a nematic solvent is expected to distort the director orientation profiles, and also may modify the elastic constants and viscosities. Such effects are important since they may influence threshold voltages or switching times of display devices based on PSLC materials. The influence of a polymer network on director orientation and dynamics can be probed by measuring the viscoelastic properties using the DLS technique. In a previous study, Jakli *et al*[5] measured the twist viscosities of PSLC dispersions cured in the isotropic state. On subsequent cooling into the nematic state, it was shown that the presence of the polymer network results in an increase in the twist viscosity. However, the reproducibility of the data was relatively poor, presumably because the preparation method yielded polydomain materials. In this communication , we present preliminary DLS studies of PSLC materials in three areas:

a. We compare DLS relaxation spectra for PSLC samples polymerized in the isotropic state, in the homeotropic state without the application of an electric field and in the homeotropic state with the application of electric field. We show that the latter preparation method leads to a more unoform PSLC specimen.
b. We evaluate the changes in the twist elastic constant and viscosity of a PSLC monodomain induced by the presence of the polymer network.
c. The kinetics of the network formation is followed by monitoring the time-dependence of the DLS relaxation rate following UV radiation.

2. EXPERIMENTAL

The reactive monomer, 4,4′-bisacryloylbiphenyl (BAB), at a concentration of 2.8% w/w was added to the nematic, pentylcyanobiphenyl (5CB) with 0.46% w/w benzomethyl ether as photoinitiator. The BAB sample used was determined to be 99% pure as evaluated by HPLC analysis, 5CB (98% pure) was obtained from BDH Ltd. and used as received. The sample cell was constructed from two ITO coated glass slides separated by a 12.5 μm mylar spacer. The inner surface of the sample cell was treated with 0.35% w/v lecithin in ethanol to produce a homeotropic alignment of the nematic mixtures. The mixtures were heated to the isotropic temperature and introduced into the sample cell by capillary action. The filled cell was sealed with a five-minute epoxy (Devcon). The low molar mass nematic liquid crystal solvent 5CB used in this study was purchased from BDH Ltd and used as received. A Carl Zeiss optical polarizing microscope equipped with a Mettler FP82 hot stage and a Mettler FP 800 central processor was used to evaluate the miscibility and determine the nematic to isotropic transition temperature T_{N-I} of the sample. The T_{N-I} of 5CB was measured as 35.0 °C. The T_{N-I} for the fully-reacted PSLC were found to be slightly lower than that of 5CB ($T_{N-I} = 34.8$ °C), and a narrow biphasic region at the T_{N-I} was observed. A photon correlation spectrometer equipped with a 15 mW He/Ne laser and a Brookhaven Instruments BI 2030 AT 256-channel digital correlator was used in the dynamic light scattering measurements. Methodological procedures have been described in our previous papers, but we note here that the distribution of relaxation times characteristic of the director orientational functions was calculated by multi-exponential fits to the DLS decays. A scattering angle of 18 ° in the laboratory frame was chosen. Since the polymer concentration in the mixture is in the dilute regime, the refractive indices of the PSLC sample were considered to be identical to those of pure 5CB, and the resulting error is expected to be comparable to the experimental error.[6] The dielectric anisotropy $\Delta\varepsilon$ of the PSLC was also considered to be identical to that of pure 5CB. The sample temperature was controlled at 5.0 °C below the T_{N-I} of the refrigerated circulating bath accurate to better than 0.1 °C. The dielectric anisotropy $\Delta\varepsilon$ of 5CB was determined by measuring the capacitance of the sample cell while an increasing bias voltage is applied. The details of the measurement procedure are described elsewhere[7]. The AC electric field applied to the homeotropic sample was provided by a Hewlett-Packard audio-frequency signal generator model 200 CDR at 3000Hz. A mecury spot lamp of 100 watts and radiation of wavelength $\lambda = 360$ nm was used as the UV source for initiating the polymerization. The lamp was placed 0.60 meter from the homeotropic sample cell. Three sample cells containing polymer networks were prepared: the first was polymerized in the isotropic state; the second was polymerized in the nematic state but without application of any aligning field; the third one was polymerized in the nematic state in the presence of an AC electric field (sinusoidal wave with $f = 3000$ Hz, $V_{rms} = 15$ volts) applied across the sample cell.

3. RESULT AND DISCUSSION

Prior to carrying out the photo-induced polymerization, the field-dependent relaxation rates of the twist mode for the monomer/5CB mixture was measured, and the results were found to be numerically identical to those measured for pure 5CB in our previous studies.[3] When the monomer-initiator-5CB mixture was polymerized in the isotropic state, upon decreasing the sample temperature to the nematic state, we found that a polydomain appeared instead of the original monodomain as evidenced by observation under a cross-polarizing optical microscope. We note that, as reported by Jakli *et al*[5], these three films are strongly light scattering in the nematic state and become transparent when an electric field is applied. However, under the cross-polarizing microscope, polydomain texture is still evident in this transparent state. As shown in Figure 1, the relaxation spectrum of the director orientational fluctuations, measured

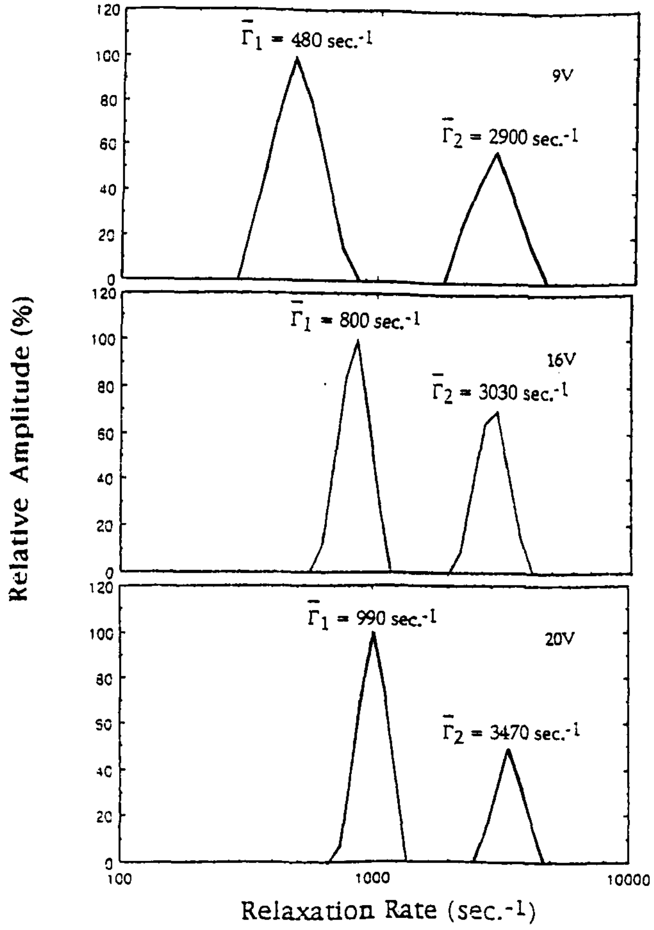

FIGURE 1 The presence of a bimodal relaxation spectrum in DLS from a PSLC sample polymerized in its isotropic state indicates that the network structure disturbs the director orientation.

using the dynamic light scattering technique, shows a bimodal distribution corresponding approximately to a double exponential decay process. The slow component and the fast component have, respectively, lower and higher relaxation rates than that of the monomer/5CB mixture before the polymerization which is about 1370 s^{-1}. With increase of the applied field, both peaks move to higher relaxation rates and the overall distribution becomes narrower, indicating that the aligning effect of the electric field reduces the inhomogeneity of the director orientation distribution.

Similar to the sample polymerized in the isotropic state, a polydomain structure was observed microscopically in a homeotropic PSLC sample which was polymerized in a nematic state but with the electric field off. Under the cross-polarizing microscope, this texture was evident both in the presence and absence of an applied electric field. Figure 2 shows the relaxation spectrum of this PSLC sample at different applied voltages. Evidently, the distribution is again bimodal. It is clear that, for this sample of

15 μm thickness polymerized in the nematic state without an external field, the surface anchoring force is not strong enough to align the network and maintain a uniform monodomain. An interesting difference, when compared with the PSLC polymerized in the isotropic state, is that the fast component of the double exponential decay modes is similar to that of the unreacted monomer/5CB mixture. The reason for this distinction remains unclear. Nevertheless, both Figure 1 and Figure 2 indicate that the polymer network, formed either in the isotropic state or in the nematic state without application of an aligning electric field, disturbs the director orientation. Thus in addition to the twist deformation mode, some contributions from the other two deformation modes, i.e. the splay and the bend, may be detected.

For a homeotropic PSLC sample ($d = 16.4\,\mu$m, $V = 15$ volts), polymerized in its nematic state in the presence of an AC electric field, a uniform homeotropic monodomain was obtained as assessed by optical examination in the cross-polarizing microscope. In addition, the spectrum of the relaxation process of the director orientational fluctuation showed a unimodal exponential distribution, suggesting that the pure twist deformation mode was detected. The spectra of the relaxation rates at three different

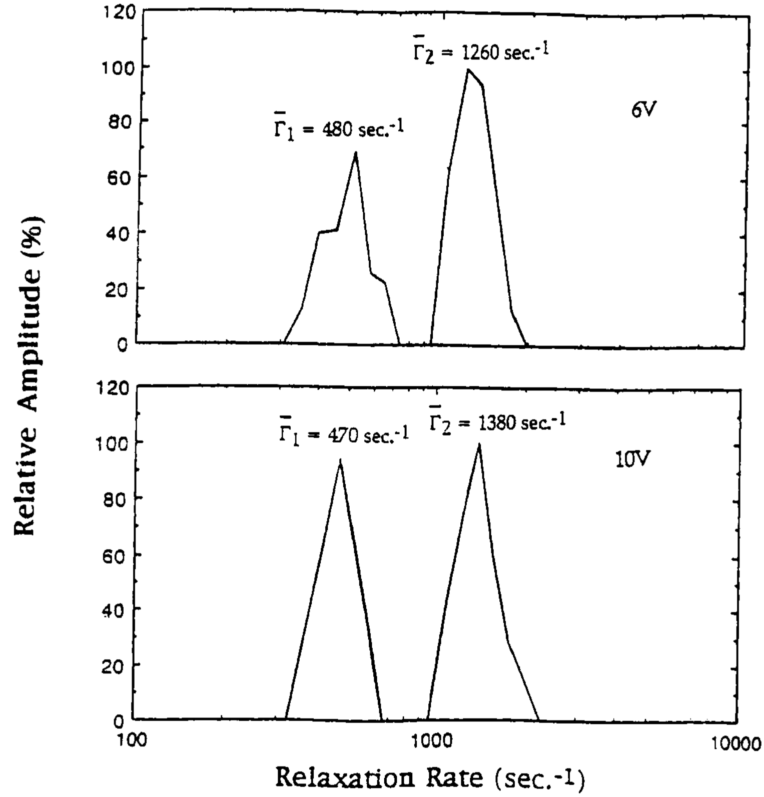

FIGURE 2 A PSLC sample polymerized from an initially homeotropic monodomain with electric field off shows bimodal relaxation spectrum. This result shows that the surface anchoring force for a sample with 15 μm thickness is not strong enough to overcome the stiffness of the network structure, and the director orientation profile is no longer homogeneous.

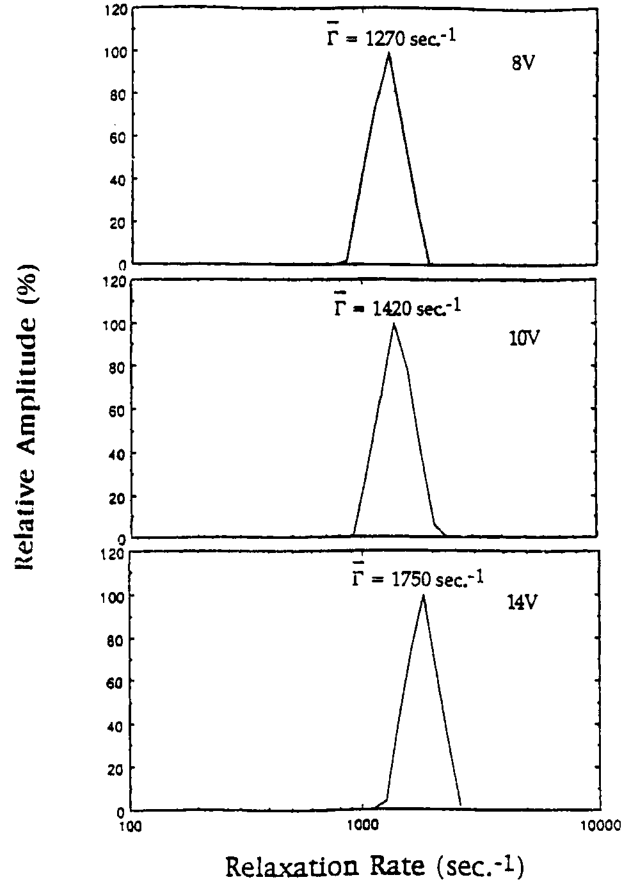

FIGURE 3 The PSLC sample studied in this figure was polymerized in its homeotropic state in the presence of an electric field parallel to the director ($d = 16.4\,\mu$m, $V = 15$ volts). The DLS spectrum shows a unimodal exponential decay process, indicating a uniform director orientation profile. The twist relaxation rate increases with the field strength.

applied voltages are shown in Figure 3. Clearly, upon increase of the field strength, the mean relaxation rate of the distribution shifts to higher values, in agreement with Equation 1. These results indicate, that, with an aligning electric field, the monodomain character of the monomer/5CB mixture is maintained after the network is formed. It is expected that the network in this circumstance should be highly anisotropic, with its rigid segments aligned along the direction of nematic director. In Figure 4, the measured relaxation rates of the twist mode are plotted against the field parameter $\Delta\varepsilon\varepsilon_0 V^2/d^2$ for pure 5CB and 2.8% PSLC, together with the results of linear least-squares fits to Equation 1. The slopes of these lines are the inverse of the twist viscosities, γ_1, and from the intercepts on the y-axis, the twist elastic constants, K_{22}, can be determined. The values of K_{22} and γ_1 obtained in each case, via least-squares fit of Equation 1 to the measured relaxation rates are also shown in Figure 4. Evidently, the

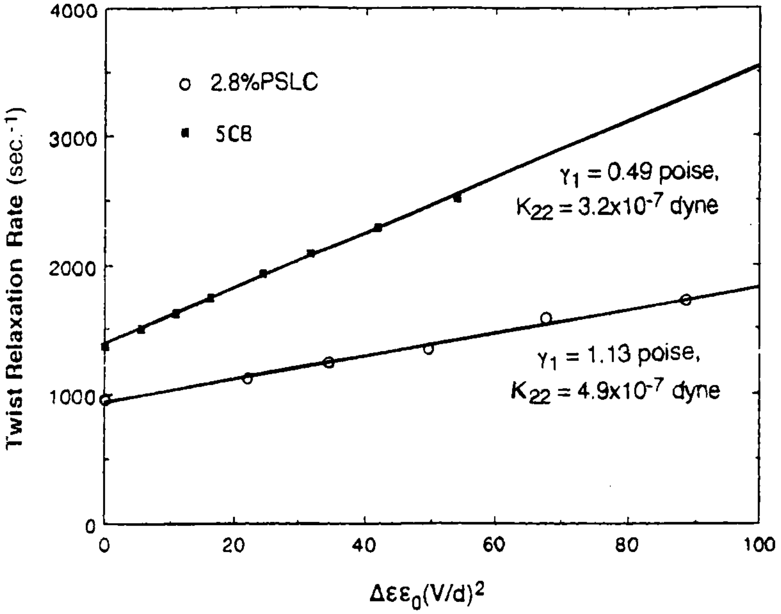

FIGURE 4 Dependence of twist relaxation ratio on electric field for 5CB containing 4,4'-bisacyloylbiphenyl before and after polymerization. The presence of the PSLC network causes large increases in the elastic constant and viscosity coefficient for the twist deformation mode. This result shows that we can probe the effect of polymer network structure on the viscoelastic properties of PSLCs using DLS.

formation of the network increases both the viscosity and the elasticity associated with the twist mode. The twist viscosity is increased by 130% and the twist elasticity increased by 53%.

It is interesting to compare these results with those obtained in our earlier studies of miscible mixtures of two liquid crystal polymers (LCP) with 5CB[3]. Qualitatively, we note that the change in elastic constant in PSLC is substantially larger than those in LCP/LMMN mixtures, whereas the change in viscosity is comparable. To examine this more quantitatively, we define the intrinsic twist elastic constant increment

$$[K_{22}] = \frac{K_{22} - K_{22}^0}{cK_{22}^0}. \tag{2a}$$

Likewise, to compare the twist viscosity increments, we define the intrinsic twist viscosity as,

$$[\gamma_1] = \frac{\gamma_1 - \gamma_1^0}{c\gamma_1^0}, \tag{2b}$$

where c is the polymer concentration and K_{22}^0 and γ_1^0 are the twist elastic constant and viscosity of pure 5CB. These quantities are thus, respectively, measures of the fractional incremental change in elastic and viscosity coefficient per unit mass concentration (g/g) of added monomer. The twist intrinsic viscosity for PSLC obtained here is 47 g/g, much higher than values determined for a methyacrylate side-chain LCP mixture (14 g/g)[3] and a polyvinylether side-chain LCP mixture (5.9 g/g)[3], but much smaller than that of mixtures of a high molecular weight main-chain LCP, TPB-x (550 g/g). The corresponding change in the intrinsic elastic constant increment is, for the PSLC, 19 g/g, as compared with values of approximately zero for the LCP mixtures.[3] Thus, in contrast to the situation in nematic LCP mixtures where the presence of the LCP produces very little change in the twist elastic constant, the formation of the polymer network in 5CB produces a large increase in K_{22}, indicating that the twist deformation becomes energetically more difficult.

To investigate the ability of dynamic light scattering to probe the kinetics of the formation of the network, a homeotropic monodomain containing monomer/5CB mixture was exposed to UV radiation for 10 min and the twist relaxation rate was subsequently determined as a function of the elapsed time. The results of this experiment are shown in Figure 5, where the twist relaxation rates are plotted as a function of the reaction time which includes the first 10 min of UV radiation. As shown in Figure 5, a constant twist relaxation rate is achieved about 20 min after 10 min UV radiation. Within experimental error, the time evolution of the twist decay rate is exponential with a rate constant of 0.1 min^{-1}. These results are consistent with kinetic data derived from dielectric relaxation measurements during cure[8].

On a final heuristic note, we discuss the origin of the increase in the twist elastic constant. It seems possible that this effect indicates a coupling between the nematic

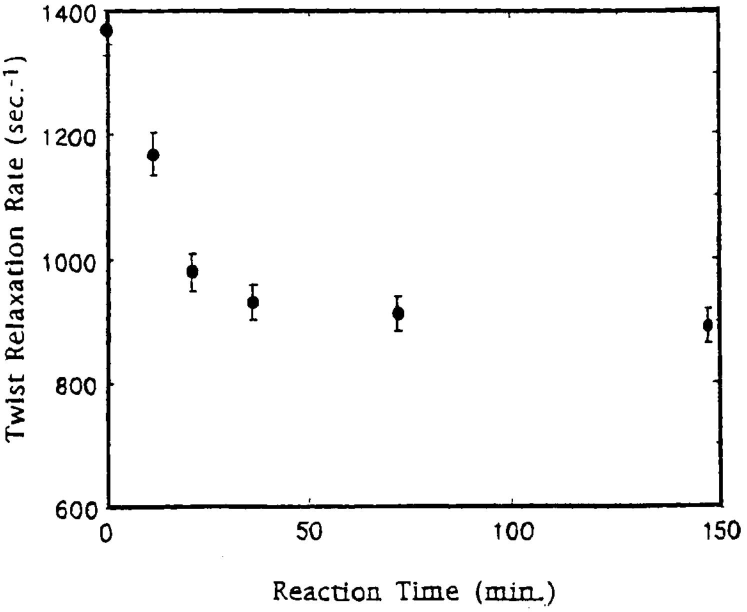

FIGURE 5 Time evolution of twist relaxation rate during cure reaction of PSLC network. DLS can be used to probe the kinetics of formation of the polymer network. A constant twist relaxation rate is obtained about 20 min after a 10 min UV radiation.

elasticity and the molecular elasticity of the polymer network. Such a phenomenon was recently proposed by Halperin and Williams[9], in a theoretical analysis of a doubly-anchored brush of a main-chain liquid crystal polymer, immersed in a nematic solvent, and subjected to a Freedericksz transition. The molecular origin lies in the fact that the chain configuration of a main-chain LCP is influenced by the coupling with the molecular field due to the nematic order. As a result, the chain is stretched along the director, i.e. the chain dimension $R_{\parallel} > R_{\perp}$. It follows that there is a coupling between distortions of the nematic matrix and the tethered LCP chain configuration, and hence between the nematic and polymeric elasticity. Here we are dealing with a different situation, viz. that of a phase-separated polymer network immersed in a nematic solvent. However, there are certain analogies. Since the network was formed in the presence of an aligning electric field, or an orienting surface, its morphology is anisotropic, with the network strands oriented along the director. Thus, we expect the network elasticity to be anisotropic, with a component of the form[10] $\mu_{\parallel} = kTH/\zeta^2_{\parallel o}\Sigma$ along the director, and a component $\mu_{\perp} = kTH/\xi^2_{\perp o}\Sigma$ perpendicular to the director. Here $\zeta_{\parallel o}$ and $\zeta_{\perp o}$ are the average spacings between cross-links parallel and perpendicular to the director, respectively. H is sample thickness, and Σ is area per cross-link. In addition, the electro-optic properties and Freedericksz transition measurements of these systems indicate a coupling between the nematic and network elasticity[10]. Assuming this is so, and following the arguments of Halperin and Williams[9], one reaches the same conclusion i.e. that the energy required to bring about a director distortion is the sum of the contributions necessary to overcome the nematic and network elasticities. We infer that the effective twist relaxation rate (in the absence of an applied electric field) is:

$$\Gamma_{\text{twist}} = (K_{22}q_{\perp}^2 + 4\pi^2\mu_{\parallel})/\gamma_1. \tag{3}$$

This assumes that the additional force required to produce a twist distortion of wavelength $\Delta = 2\pi/q_{\perp}$ is $\sim \mu_{\parallel}\Delta^2$. Applying Equation 3 to the experimental data in Figure 4, we estimate that the network modulus is $\mu_{\parallel} \approx 9$ dynes/cm^2. This appears to be a reasonable value for a weak polymer network.

4. CONCLUSIONS

The formation of a network, when polymerized either in the isotropic or in a nematic monodomain without application of an external electric field, produces highly scattering PSLC materials whose polydomain texture remains in the transparent state as evidenced by microscopic examination and the observation of a bimodal DLS relaxation spectrum. Application of an electric field during the polymerization reaction maintains a uniform director orientation in a homeotropic monodomain. DLS from this specimen yields a narrow unimodal relaxation spectrum, and we have demonstrated that the twist elastic constant and viscosity of the PSLC sample can be determined at network concentrations comparable with those utilized in PSLC devices. Our preliminary results show that the formation of the polymer network structure increases both the twist elastic constant and viscosity. We propose that the apparent increase in the elastic constant arises from the coupling between the nematic elasticity and that of the polymer network, and deduce that is is possible to estimate the network elastic modulus from the DLS relaxation rate. We have further shown that DLS can be used to monitor the cure kinetics of the PSLC gel network. In future work, we will explore the effect of monomer concentration and structure on the viscoelastic properties of PSLC samples and their relationship to the device characteristics.

Acknowledgements

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References

1. P. G. de Gennes, *The Physics of Liquid Crystals*, Oxford University Press, Oxford, Cha. 3, 5 (1974).
2. D. Gu, A. M. Jamieson, C. Rosenblatt, D. Tomazos and V. Percec, *Macromolecules*, **24**, 2385 (1991).
3. D. Gu, A. M. Jamieson, M. Lee, M. Kawasumi and V. Percec, *Liq. Cryst.*, **12**, 961 (1992).
4. D.-K. Yang, L.-C. Chien and J. W. Doane, *Appl. Phys. Lett.*, **60**, 3102 (1992).
5. A. Jakli, D. R. Kim and L.-C. Chien, *J. Appl. Phys.*, **72**, 3161 (1992).
6. D. Gu, A. M. Jamieson, M. Lee, M. Kawasumi and V. Percec, *Macromolecules*, **25**, 2151 (1992).
7. D. Gu, S. R. Smith, A. M. Jamieson, M. Lee and V. Percec, *J. Phys. II (France)*, **3**, 937 (1993).
8. Z. Z. Zhong, S. W. Smith, D. E. Schuele and W. L. Gordon, *J. Appl. Phys.*, submitted (1994).
9. A. Halperin and D. R. M. Williams, *Phys. Rev.*, **49**, R986 (1994).
10. S. Mora and A. M. Jamieson, *manuscript in preparation* (1995).