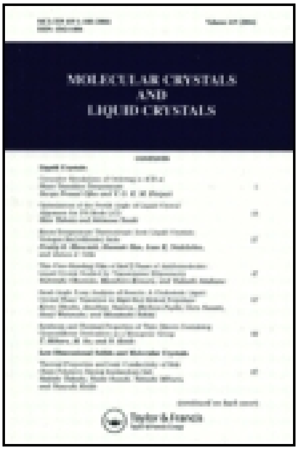

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Dynamic Light Scattering from a Side-Chain Liquid Crystal in a Nematic Solvent

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Nematic monodomains consisting of a side-chain liquid crystal polymer dissolved in a low-molar mass nematogen, pentylcyanobiphenyl, were prepared in planar and homeotropic alignment at polymer concentrations up to 15% w/w. The elastic and viscosity constants associated with the splay, bend and twist distortions of the nematic matrix were determined by analysis of the dynamic light scattering data on these monodomains over a wide range of scattering angles. The addition of the side-chain liquid crystal polymer results in a substantial decrease in the relaxation frequencies for dynamic light scattering. These changes are due to the combined contributions of a decrease in all three elastic constants and larger increases of the three viscosities. The effect is largest for the bend distortion.

Keywords: side-chain liquid crystal, viscoelastic properties

INTRODUCTION

The theoretical and experimental basis for applying the dynamic light scattering experiment to obtain information on the viscoelastic constants of the nematic liquid crystal materials is well established.[1-6] The mean relaxation frequencies of the two director distortion modes can be determined by photon correlation analysis of the scattered light and are given by

$$\Gamma_\upsilon(q) = \frac{(K_{33}q_\parallel^2 + K_{\upsilon\upsilon}q_\perp^2)}{\eta_\upsilon(q)}, \upsilon = 1,2 \tag{1}$$

where $\eta_\upsilon(q)$ are two viscosity functions:

$$\eta_1(q) = \gamma_1 - \frac{(q_\perp^2\alpha_3 - q_\parallel^2\alpha_2)^2}{q_\perp^4\eta_b + q_\perp^2 q_\parallel^2(\alpha_1 + \alpha_3 + \alpha_4 + \alpha_5) + q_\parallel^4\eta_c} \tag{2}$$

and

$$\eta_2(q) = \gamma_1 - \frac{\alpha_2^2 q_\parallel^2}{q_\perp^2\eta_a + q_\parallel^2\eta_c} \tag{3}$$

In Equations (1), (2) and (3), K_{11}, K_{22}, K_{33} are the splay, twist and bend elastic constants, $q_{\parallel}$, $q_{\perp}$ are the parallel and perpendicular components of the scattering vector $\vec{q}$ with respect to the nematic director, the α_i's are the five Leslie viscosity coefficients, γ_1 is the twist viscosity and η_a, η_b, η_c are the Miesowicz viscosities.

Since the scattering intensity depends sensitively on the relative orientations of the scattering vector $\vec{q}$, the nematic director, and the polarizations of the incident laser light and scattered light,[1-6] it is possible to choose different scattering configurations to separate the contributions from the two director deformation modes. We have utilized three scattering configurations: A) a planar sample with the nematic director perpendicular to the scattering plane formed by the incident and scattered wave vectors; B) a planar sample with the nematic director in the scattering plane and perpendicular to the incident wave vector; C) a homeotropic sample with the nematic director parallel to the incident wave-vector, and in the scattering plane. In all three configurations, the incident and scattered polarizations are perpendicular to, and in the scattering plane, respectively. In A, we detect the scattered light from both mode 1 and mode 2, but the scattering intensity of mode 1 is over twenty times larger than that of mode 2 in the scattering angle range of $15° < \theta < 35°$. In B and C, only mode 2 is detected. In each of the three configurations specified above, the angular dependence of the scattering vectors $q_{\parallel}$ and $q_{\perp}$ is different, and this fact provides an opportunity to extract information on the individual viscoelastic constants from analysis of the angle-dependence of the mean relaxation frequencies.[7]

Early light scattering studies focussed on the properties of low molar mass nematics. More recently, investigations of liquid crystal materials containing polymeric nematogens have been reported. Two types of systems have been studied. One class is the lyotropic liquid crystals formed by semi-rigid polymers.[8,9] A second group comprises miscible thermotropic liquid crystal mixtures composed of a low molar mass and a polymeric mesogen.[5,10] Experimental studies on the latter materials have involved reports of bend, splay and twist elastic constants[11] as well as twist viscosities of mixtures of side-chain liquid crystal polymers, with a polysiloxane backbone, in cyanobiphenyl species as solvents. The addition of polymer results in a progressive decrease in all three elastic constants. However, the bend constant K_{33} is reported to be most influenced.[11] The twist viscosity substantially increases as a function of polymer concentration in the mixtures.[12]

In this study we report dynamic light scattering experiments on monodomains formed from pentylcyanobiphenyl (5CB), and from miscible mixtures of 5CB with a side-chain liquid crystal polymer (LCP), poly{6-[4-methoxy-(4′-oxy)-α-methylstilbene] hexyl methacrylate (MSHMA). By combining data on the three scattering geometries listed above, we obtain information on all three elastic and viscosity coefficients. An independent measurement of the bend elastic constant for both 5CB and the polymer mixtures has been obtained via the Freedericksz method.[7]

EXPERIMENTAL METHODS

Pentylcyanobiphenyl (5CB) was obtained from BDH Chemicals and used as received. The nematic-isotropic transition temperature was $T_{NI} = 35.1°C$. The side-chain LCP utilized in our study was synthesized by Professor Virgil Percec and coworkers, and consists of a polymethyl methacrylate backbone to which the pendant mesogenic groups (4′-α-methylstilbene) are attached via a flexible hexamethylene spacer. Three polymer samples of different molecular weights were utilized in our initial studies: MSHMA/36, $M_n = 3600$; MSHMA/45, $M_n = 4500$, and MSHMA/570, $M_n = 57{,}000$, as determined by gel permeation chromatography in tetrahydrofuran using polystyrene standards.[13] For all samples, $M_w/M_n = 1.36$. The polymer exhibits a nematic phase in the temperature range studied with a $T_{N-I} = \sim 94°C$.[13] Monodomain samples, as verified by optical microscopy, were prepared between clean microscopic studies, separated by Mylar spacers. Specimens in the homogeneous orientation were obtained by the classical rubbing technique; specimens in the homeotropic alignment were prepared by treating the glass surfaces with a surfactant, hexadecyltrimethyl-ammonium bromide (HTAB). For the LCP concentration range utilized for our samples, we verified using optical microscopy that the samples were miscible in both the nematic and isotropic phases, with a narrow biphasic region at the transition. The temperature extent of this region was proportional to the LCP concentration. The refractive indices of pentylcyanobiphenyl and the polymer have been determined by other groups.[14,15]

Photon correlation analysis of the light scattered from the nematic monodomains was performed using an instrument (Brookhaven Instruments Corporation, N.Y.) equipped with a 15 mW He/Ne laser, and a BI 2030 AT 256-channel digital correlator. The sample was positioned in a refractive index matching liquid bath in which temperature was controlled within 0.1°C variation.

We also performed magnetic Freedericksz transition measurements on homeotropic samples with the magnetic field perpendicular to the director.[7] This determines $K_{33}/\Delta\chi$, where $\Delta\chi$ is the magnetic susceptibility anisotropy. By carrying out simultaneous birefringence measurements we are able to extract $\Delta\chi(T)$ and hence $K_{33}(T)$.[7]

RESULTS AND DISCUSSION

Measured decay rates, Γ_2 based on single exponential fits to photon correlation spectroscopy in configuration B of pure 5CB and MSHMA/570-5CB mixtures at polymer concentrations from 1.5% w/w to 15% w/w are shown in Figure 1 at scattering angles in the range $18° < \theta < 54°$. Clearly Γ_2 decreases markedly with increasing polymer concentration at all scattering angles. For instance, at $\theta = 18°$, Γ_2 decreases from 11760 $\sec^{-1}$ to 164 $\sec^{-1}$; at $\theta = 36°$, from 37530 $\sec^{-1}$ to 553 $\sec^{-1}$, and, at $\theta = 54°$, from 64180 $\sec^{-1}$ to 1140 $\sec^{-1}$. Similar decreasing trends were found for configurations A and C. Values of the elastic constants and viscosity coefficients were computed from the light scattering data on the mixtures are based on a trial and error fit to Equations (1)–(3), subject to several known constraints. First, the K_{ii} must be smaller than the known values for pure 5CB, and must decrease monotonically with LCP concentration, behavior which was confirmed in the Freedericksz measurements.[7] Likewise, the viscosity coefficients of the mixtures must be larger than the values for pure 5CB and increase monotonically with LCP

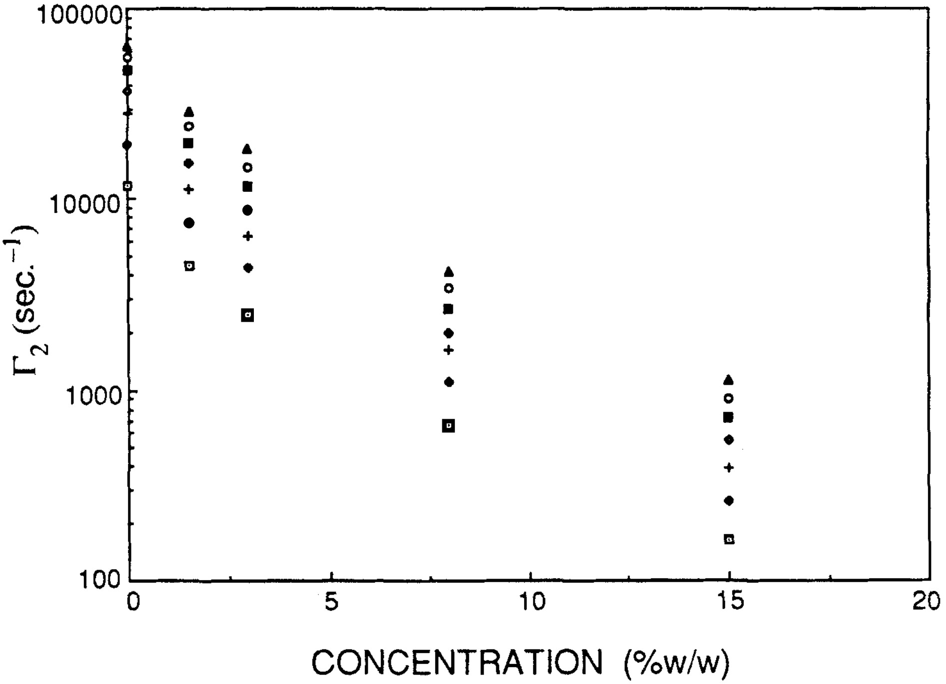

FIGURE 1 Decay rates Γ_2 at seven scattering angles (18° ~ 54°) for pure 5CB and MSHMA/5CB mixture. ⊡: ø = 18°, ◆: ø = 24°, +: ø = 30°, ◇: ø = 36°, ■: ø = 42°, ○: ø = 48°, ▲: ø = 54°.

tonically with LCP concentration. Also, by carrying out scattering experiments in all three geometries over a wide range of angles we are able to uniquely define the ratios of the elastic constants. Calculated and experimental values of the decay rate in all three configurations agree to within 3% at all scattering angles. In configuration A, the single exponential fits are accurate only in the range $18° < \theta < 33°$. Outside this, deviations occur due to contributions from mode 2.

In Table I, we list the experimental values of the intrinsic decay rates for light scattering from the splay, twist and bend distortions: $\Gamma_{\text{splay}} = K_{11}/\eta_{\text{splay}}$, $\Gamma_{\text{twist}} = K_{22}/\gamma_1$, and $\Gamma_{\text{bend}} = K_{33}/\eta_{\text{bend}}$. Also listed are the values of the individual elastic and viscosity coefficients deduced based on the fits according to Equations (1)–(3). The numerical values of the computed parameters are specified to within the errors shown by the requirement of matching the calculated and experimental decay rates over the entire range of scattering angles.

For pure 5CB, our experimental results are in good agreement with selected literature values. The intrinsic twist decay rate K_{22}/γ_1 agrees very well with the published data of Sefton *et al.*[5] The viscosity values determined in our study are numerically similar to those reported for 5CB by Skarp *et al.*[16] Likewise K_{11} and K_{33} values obtained by us for 5CB agree very well with results reported by several groups. K_{22} values computed from our light scattering data yield ratios K_{33}/K_{22} which are reasonably consistent with corresponding values obtained by Hara *et al.*[17]

The addition of polymer MSHMA-45 to 5CB results in a substantial decrease in

TABLE I

Temperature dependence of viscoelastic parameters for 5CB and 3% w/w LCP/5CB mixture (M_n = 4500)

	T = 25°C		T = 30°C		T = 33°C	
	5CB	LCP/5CB	5CB	LCP/5C	5CB	LCP/5CB
K_{11}x10^6dyne±5%	62	58	45	41	30	26
K_{22}x10^6dyne±3%	43	36.5	30.5	25	20.5	193
K_{33}x10^6dyne±3%	81	61	54	45	41	32.7
η_{splay}(poise)±1%	.83	.89	.48	.52	.29	.35
γ_1(poise)±1%	.83	.91	.50	.53	.30	.36
η_{bend}(poise)±2%	.14	.18	.12	.18	.11	.12
K_{11}/η_{splay} (x10^7cm^2/s)±5%	7.47	6.52	9.38	7.89	10.3	7.43
K_{22}/γ_1 (x10^7cm^2/s)±3%	5.18	4.01	6.10	4.72	6.83	5.36
K_{33}/η_{bend} (x10^7cm^2/s)±3%	57.9	33.9	45.0	25.0	37.3	27.2

all three intrinsic decay rates. In Table I, we can see this is due to a decrease in the associated elastic constants coupled with an increase in the corresponding viscosity coefficients. We also note that the K_{33} values computed from our dynamic light scattering data for the polymer mixtures are numerically consistent with values independently obtained via the Freedericksz method, verifying the utility of our analytical methods.

The influence of polymer concentration and molecular weight on the viscoelastic parameters can be seen in Table II. These light scattering measurements were carried out on the highest molecular weight polymer, MSHMA-570, at T = 30.2°C. We find a similar pattern of behavior to that seen for the lower molecular weight LCP (Table I), i.e. the addition of polymer has a largest effect on the decay rates of the bend mode, and smallest on the splay mode. Specifically, we find $\Gamma_{\text{splay}}:\Gamma_{\text{twist}}:\Gamma_{\text{bend}} = 1.5:1.0:8.6$ for 5CB whereas $\Gamma_{\text{splay}}:\Gamma_{\text{twist}}:\Gamma_{\text{bend}} = 4.0:1.0:2.2$ for the 15% w/w MSHMA/570-5CB mixture (Table II). Note that the magnitude of the decrease in decay rates is substantially larger for the high molecular weight LCP. As for MSHMA/45, the major contribution to the decrease in decay rates stems from increases in the viscosity coefficients. We find from Table II that the change is largest for the bend viscosity. To see this, we utilized the intrinsic viscometric quantity $[\eta] = \delta\eta_i/\eta_i^o c$, where $\delta\eta_i = \eta_i(\text{mixture}) - \eta_i^o$, c is the concentration in units g/g, and the superscript o refers to pure 5CB. Thus $[\eta_{\text{bend}}] =$

TABLE II

Concentration dependence of the viscoelastic parameters for MSHMA/5CB (M_n = 57,000) at 30°C

LCP conc. (%wt)	0	1.5%	3.0%	8.0%	15%
$K_{11} \times 10^8$dyne ± 5%	47	40	47	44	27.5
$K_{22} \times 10^8$dyne ± 3%	31.5	28.7	25.0	13.7	7.0
$K_{33} \times 10^8$dyne ± 3%	56	50	41	19	9.6
K_{33}/K_{11} ± 8%	1.2	1.3	0.87	0.43	0.35
η_{splay} (poise) ± 1%	0.496	0.643	0.790	1.39	2.09
γ_1 (poise) ± 1%	0.498	0.646	0.795	1.40	2.10
η_{bend} (poise) ± 2%	0.103	0.240	0.343	0.650	1.33
K_{11}/η_{splay} $\times 10^7$ cm^2/sec ± 5%	9.48	6.22	5.95	3.16	1.32
K_{22}/γ_1 $\times 10^7$ cm^2/sec ± 3%	6.32	4.44	3.14	0.979	0.333
K_{33}/η_{bend} $\times 10^7$ cm^2/sec ± 3%	54.4	20.8	11.9	2.92	0.722

80 g/g, $[\eta_{splay}]$ = 21 g/g ~ $[\gamma_1]$. All three elastic constants show a significant decrease on addition of polymer. We observe $\Delta K_{11}:\Delta K_{22}:\Delta K_{33}$ = 13:16:31, indicating that the change is again largest for the bend distortion. A slightly different pattern of behavior was observed by Coles and Sefton[12] for mixtures of a side-chain LCP with a siloxane backbone in 5CB, viz. $\Delta K_{22} < \Delta K_{11} << \Delta K_{33}$.

CONCLUSION

The results of our dynamic light scattering study indicate that the dissolution of a side-chain LCP in a low molar-mass nematic decreases the relaxation rates of the nematic director distortions in the order of $|\Delta\Gamma_{bend}/\Delta c| >> |\Delta\Gamma_{twist}/\Delta c| > |\Delta\Gamma_{splay}/\Delta c|$. Increase of polymer molecular weight and concentration amplifies the decrease in decay rates. The main contribution arises from a large increase in the viscosity coefficients. Our results also suggest that the presence of the side-chain LCP substantially restricts the mean square amplitude and viscosity of the bend distortion, which requires motions normal to the backbone, relative to the twist and splay distortions, which involve relatively unhindered motions around the backbone.

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