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Dynamic Light Scattering from Nematic Monodomains Containing Mesogenic Polymers of Differing Architectures

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ABSTRACT: Dynamic light scattering studies of nematic monodomains which contain side-chain and main-chain liquid crystal polymers dissolved in a low molar mass nematogen, 4′-*n*-pentyl-4-cyanobiphenyl (5CB), are described. The relaxation rates of the splay, twist, and bend director distortions have been measured and compared with those of pure 5CB at comparable temperature decrements $T_{\mathrm{N-I}} - T$ from the nematic to isotropic transition. Addition of both side-chain and main-chain polymers results in substantial decreases in the relaxation rates of all three modes. However, for the side-chain polymers, the relative decrease in the relaxation rate of the bend mode is comparable to or larger than those of the twist and splay modes and is strongly dependent on backbone flexibility and spacer length. In contrast, for main-chain polymers, the relative decrease in relaxation rates is large for splay and twist and small for the bend mode. This dynamical behavior is consistent with the expectation that the chain backbone orients perpendicular to the director for side-chain polymers and extends parallel to the director for main-chain polymers.

Introduction

Dynamic light scattering analysis of the depolarized light scattered by thermally-driven director orientation fluctuations in a nematic monodomain is an effective method to characterize the viscoelastic properties of the nematic matrix.[1] The director distortions give rise[1] to two scattering components: mode 1, a combination of splay and bend; and mode 2, a combination of twist and bend. The scattered intensity of each mode is inversely proportional to the Frank elastic constants, K_{ii}, where $i = 1, 2, 3$ corresponds to splay, twist, and bend:

$$I_\nu(q) = \sum^{\nu=1,2}\left[\frac{G_\nu}{K_{33}q_\parallel^2 + K_{\nu\nu}q_\perp^2}\right] \qquad (1)$$

Here G_ν is a geometric factor,[1] and $q_\parallel$ and $q_\perp$ are the components of the scattering vector $\bar{q}$ parallel and perpendicular to the director. The relaxation rates of each mode are proportional to ratios of the various elastic constants to the corresponding viscosity functions:

$$\Gamma_\nu(q) = \frac{K_{33}q_\parallel^2 + K_{\nu\nu}q_\perp^2}{\eta_\nu} \qquad (2)$$

where

$$\eta_1(q) = \gamma_1 - \frac{(q_\perp^2\alpha_3 - q_\parallel^2\alpha_2)^2}{q_\perp^4\eta_b + q_\perp^2 q_\parallel^2(\alpha_1 + \alpha_3 + \alpha_4 + \alpha_5) + q_\parallel^4\eta_c} \qquad (3)$$

$$\eta_2(q) = \gamma_1 - \frac{q_\parallel^2\alpha_2^2}{q_\perp^2\eta_a + q_\parallel^2\eta_c} \qquad (4)$$

In eqs 3 and 4, the α_i refer to the five Leslie viscosity coefficients,[2] γ_1 is the twist viscosity,[1] and η_a, η_b, and η_c are the Miesowicz viscosities.[3] By utilizing particular combinations of scattering vector, polarization states of the incident and scattered light, and director orientations, it is possible to isolate scattering contributions from pure splay, pure twist, and pure bend.

The viscoelastic behavior of nematic monodomains containing polymers has been investigated using dynamic light scattering. One class of systems studied are lyotropic materials consisting of concentrated solutions of stiff-chain polymers such as helical poly(γ-benzylglutamate) (PBG)[4,5] and poly(1,4-phenylene-2,6-benzobisthiazole) (PBT).[6] The relaxation rates for the twist and splay modes in these systems are much slower than those of low molar mass nematics, whereas the bend relaxation rates are more comparable to low molar mass values. This is in qualitative agreement with theory[7,8] since twist and splay involve molecular rotations, whereas bend corresponds principally to a sliding motion for long rods.

A second class of systems comprise miscible mixtures of liquid crystal polymers (LCP) dissolved in low molar mass nematogens.[9-14] The addition of LCP causes a substantial decrease in the relaxation rates of the director fluctuation modes.[9-14] Our previous studies[13] of a side-chain LCP in 4′-*n*-pentyl-4-cyanobiphenyl (5CB) established that the relative decrease of the relaxation rate of the bend mode was substantially larger than those of the twist and splay modes. This appears qualitatively in accord with a theory[15] of the viscosity of such systems, which assumes that the pendant mesogenic groups align with the director and hence the chain backbone is oriented perpendicular to the director.

Here we report further dynamic light scattering studies of such nematic mixtures, involving a second chemically-distinct side-chain LCP and a main-chain LCP which has mesogenic groups in the backbone, separated by flexible alkyl spacers. It is of particular interest to contrast the main chain versus the side-chain LCP since experiment[16,17] and theory[18] indicate that, in the former, the interaction of the nematic field with the mesogenic groups aligns the backbone parallel to the director.

Experimental Section

Light scattering experiments were performed using photon correlation analysis on planar and homeotropic monodomains prepared between clean microscope slides separated by 25-μm Mylar spacers by means of methods described elsewhere.[13] Although extensive measurements of the angle dependence of the dynamic light scattering were carried out, we confine ourselves here to reporting numerical values of relaxation rates in three VH scattering configurations which detect pure splay, pure twist, and pure bend distortion modes. These are, respectively, (a) planar monodomain, director perpendicular to the scattering

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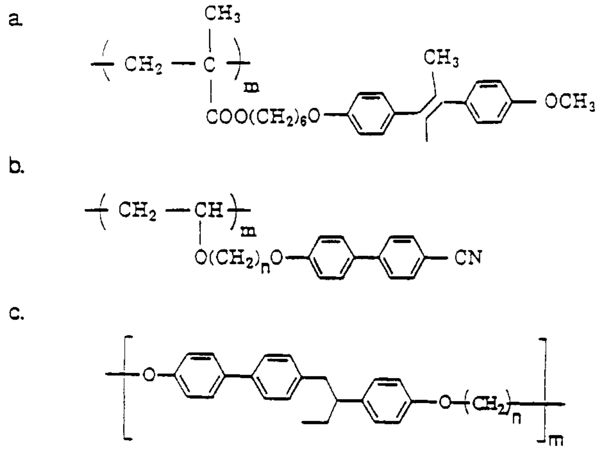

Figure 1. Molecular structures of the liquid crystal polymers studied in this investigation: (a) MSHMA, (b) *n*-PVE, and (c) TPB-*n*-polyether.

plane ($q_{\parallel} = 0$) and scattering angle $\theta = 24°$; (b) homeotropic monodomain, director parallel to the incident wave vector, scattering angle $\theta = 15$–$24°$; and (c) planar monodomain, director in the scattering plane and perpendicular to the incident wave vector, scattering angle $\theta = 24°$. The selection of these scattering configurations is based on the analysis described in detail elsewhere.[13]

We have studied nematic solutions of three liquid crystal polymer species, each dissolved in 4′-*n*-pentyl-4-cyanobiphenyl (5CB). The chemical structures of the polymers are shown in Figure 1. A detailed dynamic light scattering study of the side-chain LCP poly[6-[(4-methoxy-α-methylstilben-4-yl)oxy]hexyl methyacrylate] (MSHMA) in 5CB has been described elsewhere.[13] Here we compare these data with results of similar experiments on nematic solutions in 5CB of a second side-chain LCP with variable spacer lengths, poly[ω-[(4-cyano-4′-biphenyl)oxy]*n*-alkyl vinyl ether] (*n*-PVE), and of a main-chain liquid crystalline polyether consisting of the mesogenic group 1-(4-hydroxy-4′-biphenyl)-2-(4-hydroxyphenyl)butane, separated by flexible spacers of variable length (TPB-*n*-polyethers). Each of these polymers has been extensively characterized by Percec and co-workers,[19-21] and each was found to be miscible at low concentrations with 5CB in the isotropic state. On cooling into the nematic region, the side-chain LCPs remained miscible. However, the main-chain LCP showed a striking odd–even effect, only the odd spacer lengths showing miscibility in the nematic state with 5CB. This effect is presumably due to the higher degree of order in the main-chain LCP with even spacers which have higher $T_{\text{N-I}}$ than the odd-spacer species.[21,22] 5CB was obtained from BDH Chemicals and used as received. Dynamic light scattering measurements were performed using a photon correlation spectrometer (Brookhaven Instruments Corp., Ronkonkoma, NY) equipped with a 15-mV He/Ne laser and a BI 2030 AT 256-channel digital correlator.

The sample temperature was controlled by a refrigerated circulating bath accurate to 0.1 °C, $\Delta T \equiv T_{\text{N-I}} - T = 5$ °C for all the LCP mixtures. The transition temperature $T_{\text{N-I}}$ for the monodomain samples was monitored by a Carl Zeiss optical polarizing microscopy (magnification 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor. The $T_{\text{N-I}}$ for pure 5CB is 35.0 °C. The $T_{\text{N-I}}$'s for the LCP mixtures were found to be slightly higher than that of 5CB (0.2–2 °C), depending on the polymer concentration. The concentrations of the LCP mixtures, the spacer length *n* of the LCP, and the degrees of polymerization as determined by GPC analyses, using polystyrene standards, are listed in Table I. The refractive indexes for 5CB and LCP mixtures were measured using ABBE refractometer Model 60/HR equipped with a Fisher isotemperature refrigerated circulator, Model 9100.

Results and Discussion

We report here measurements of the mean relaxation rates of light scattered by dilute nematic mixtures of all three polymers in 5CB. By selecting the three scattering configurations described above, we isolate the pure splay, twist, and bend modes:

$$\Gamma_{\text{splay}} = K_{11}q_{\perp}^{2}/\eta_{\text{splay}} \tag{5}$$

$$\Gamma_{\text{twist}} = K_{22}q_{\perp}^{2}/\gamma_{1} \tag{6}$$

and

$$\Gamma_{\text{bend}} = K_{33}q_{\parallel}^{2}/\eta_{\text{bend}} \tag{7}$$

These values are tabulated in Table I. Since we are dealing with dilute polymer mixtures, it is a reasonably accurate approximation[13] to assume that the refractive indexes of the mixtures are identical to those of pure 5CB $n_e = 1.690$, $n_o = 1.533$ at 30 °C. This assumption was confirmed by our experimental measurements of ordinary and extraordinary refractive indexes, n_o and n_e for LCP mixtures. At $\Delta T = 5$ °C, the largest change in $n_e - n_o$ for LCP mixtures up to 8% (w/w) concentration is 0.0079 (MSHMA, DP = 140). This causes only 0.9% relative change in the relaxation rate for the splay mode and no change in that of the twist and bend modes. Therefore, we can compute $q_{\parallel}$ and $q_{\perp}$ and hence determine the ratios $K_{11}/\eta_{\text{splay}}$, K_{22}/γ_1, and $K_{33}/\eta_{\text{bend}}$. These values are also listed in Table I. To facilitate comparison of the different polymer species, we have also tabulated the intrinsic decay rate decrement quantities:

$$[\Gamma] = \frac{\Gamma(\text{5CB}) - \Gamma(\text{polymer mixture})}{\Gamma(\text{polymer mixture})c} \tag{8}$$

where *c* is polymer concentration. This quantity provides a quantitative measure of the effectiveness of the polymer in increasing the relaxation time of the director orientation fluctuation. Note that in our previous study of MSHMA in 5CB we established that the addition of polymer causes comparatively small changes in the elastic constants and large changes in the viscosities.[13] Under such circumstances, the intrinsic decay rate decrement is equivalent to an intrinsic viscosity.

Considering first the side-chain polymers, we present new experimental data on MSHMA polymers with DP = 29 and DP = 140 dissolved in 5CB at 0.08 g/g concentration. These results confirm our previous observations[13] that MSHMA shows a comparatively large decrease in the intrinsic decay rate for bend, relative to splay and twist. Specifically, $[\Gamma_{\text{bend}}] \gg [\Gamma_{\text{twist}}] > [\Gamma_{\text{splay}}]$. In our earlier study,[13] we established that these changes are due principally to changes in the associated viscosities. The effect is strongly enhanced by an increase in molecular weight[13] and is qualitatively consistent with the theoretical expectation[15] that in such systems the bend mode will be especially impeded if the chain backbone is extended perpendicular to the director and there is incomplete decoupling of the mesogen motion.

Our studies of the side-chain LCP *n*-PVE were designed principally to investigate the influence of spacer length on viscoelastic properties. We found that, for $n > 3$, very little change is evident in the magnitude of elastic or viscosity coefficients. In Table I, we exhibit the results for 0.08 g/g nematic solutions of 2-PVE and 7-PVE. A somewhat different pattern of behavior is observed from that seen in MSHMA. The relative change in Γ_{bend} is again larger than that in Γ_{twist}, but is comparable to that in Γ_{splay}. Thus, $[\Gamma_{\text{bend}}] \sim [\Gamma_{\text{splay}}] > [\Gamma_{\text{twist}}]$. The magnitude of the intrinsic relaxation rate decrements are substantially larger for 2-PVE in comparison to 7-PVE, indicative that

Table I
Relaxation Rates of Director Fluctuations in Nematic Mixtures[a]

	$10^4\Gamma_{splay}$, s^{-1}	$10^{-7}K_{11}/\eta_{splay}$, $cm^2\ s^{-1}$	$[\Gamma_{splay}]$, g/g	$10^3\Gamma_{twist}$, s^{-1}	$10^{-7}K_{22}/\eta_{twist}$, $cm^2\ s^{-1}$	$[\Gamma_{twist}]$, g/g	$10^3\Gamma_{bend}$, s^{-1}	$10^{-7}K_{33}/\eta_{bend}$, $cm^2\ s^{-1}$	$[\Gamma_{bend}]$, g/g
pure 5CB	4.20	9.48	x	2.47	6.32	x	19.4	53.5	x
3% MSHMA (DP = 11)	3.49	7.89	6.78	1.93	4.72	9.33	10.9	25.0	26
8% MSHMA (DP = 29)	1.84	4.20	16	1.00	2.7	19	4.36	12.0	43
8% MSHMA (DP = 140)	1.44	3.30	24	0.40	1.1	65	1.10	3.00	208
8% *n*-PVE (DP = 22, *n* = 2)	1.16	2.60	33	0.91	2.5	21	5.30	14.6	33
8% *n*-PVE (DP = 30, *n* = 7)	2.10	4.80	13	1.40	3.9	10	9.04	24.9	14
3% TPB-*n*-PE (DP = 42, *n* = 5)	0.41	0.92	310	0.27	0.73	270	7.90	21.8	48
3% TPB-*n*-PE (DP = 37, *n* = 7)	0.43	0.96	290	0.33	0.92	220	9.01	24.0	41
3% TPB-*n*-PE (DP = 60, *n* = 9)	0.21	0.47	630	0.13	0.37	600	9.12	25.2	38
3% TPB-*n*-PE (DP = 44, *n* = 11)	0.29	0.65	450	0.15	0.42	520	9.75	27.0	32
3% TPB-*n*-PE (DP = 71, *n* = 13)	0.18	0.40	750	0.12	0.33	660	9.24	25.5	37

[a] M_w/M_n for all *n*-PVE is about 1.10 and for TPB-*n*-PE is about 2.00.

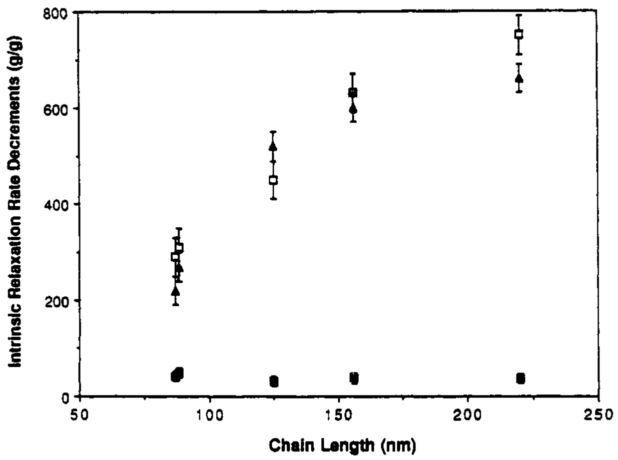

Figure 2. Chain length (nm) dependence of the intrinsic relaxation rate decrements for nematic mixtures of main-chain LCP (TPB-*n*-PE) in 5CB: (□) $[\Gamma_{splay}]$, (▲) $[\Gamma_{twist}]$, and (■) $[\Gamma_{bend}]$. The spacer length *n* varies from 5 to 11.

the longer spacer produces a substantial degree of decoupling of the mesogen motion from the polymer backbone. Note that 2-PVE does not, by itself, form a stable nematic mesophase, indicating strong coupling of the mesogen mobility with the polymer backbone.[20] A more complete analysis of the effect of spacer length and backbone flexibility on the viscoelastic parameters of *n*-PVE will be published elsewhere.

Comparing the intrinsic relaxation rates for the splay, twist, and bend distortions of mixtures of the side-chain LCPs 7-PVE and MSHMA in 5CB, one finds that the decrements in relaxation rates of 7-PVE are smaller than those of MSHMA at similar molecular weights and concentrations. Thus the difference between these side-chain LCP mixtures is presumably due to their different chemical structures. The pendant methyl group vicinal to the mesogenic side chain in MSHMA will substantially reduce the flexibility of the backbone relative to 7-PVE and hence produce an enhanced dynamical anisotropy (see Figure 1a and b). On the other hand, 7-PVE has an ether linkage between the side chain and backbone in comparison to the ester linkage in MSHMA. This makes the spacer more flexible, and consequently, a more complete decoupling of the mesogen motion from the backbone is expected.

Turning to the main-chain LCP, quite distinct behavior is observed, with a very large decrease in the twist and splay relaxation rates, and a small decrease in the bend relaxation rate. Thus, $[\Gamma_{twist}] \sim [\Gamma_{splay}] \gg [\Gamma_{bend}]$. We remark that our results for splay are in agreement with those of Devanand,[14] who observed a large decrease in the splay decay rate of *p*-azoxyanisole (PAA) when a small amount of a main-chain liquid crystal polymer was added. This pattern of behavior appears qualitatively consistent with that anticipated if the LCP backbone aligns parallel to the nematic direction since splay and twist involve rotations of the backbone whereas bend involves a sliding displacement in the long rod limit.[7,8] Our results shown in Figure 2 represent the first experimental demonstration of the dynamical anisotropy predicted by theory[15] for main-chain LCP dissolved in a nematic solvent, due to the alignment of the polymer backbone by the nematic field.[16-18]

It is of interest to discuss the dependence of the viscoelastic parameters on polymer molecular weight or chain length. By combining our present data on MSHMA with previous observations[13] on a low molecular weight specimen (DP = 11), viz. $[\Gamma_{splay}] = 6.78$ g/g, $[\Gamma_{twist}] = 9.33$ g/g, and $[\Gamma_{bend}] = 26.0$ g/g, we find, for MSHMA

$$[\Gamma_{splay}] = 2.54(\mathrm{DP})^{0.47} \qquad (9a)$$

$$[\Gamma_{twist}] = 1.48(\mathrm{DP})^{0.76} \qquad (9b)$$

and

$$[\Gamma_{bend}] = 3.13(\mathrm{DP})^{0.84} \qquad (9c)$$

Recognizing that eqs 9 are based on fits to only three sets of data, we infer from the substantial dependence on LCP molecular weight that dynamics of the pendant mesogens in MSHMA are coupled to the backbone motion and that this coupling is strongest for bend ($[\Gamma_{bend}]$ largest) and weakest for splay ($[\Gamma_{splay}]$ smallest). As has been noted previously,[11,13] this is consistent with the notion that the bend distortion requires translational displacements normal to the backbone whereas splay and twist involve relatively unhindered rotations around the backbone.

In considering the main-chain LCP, TPB-*n*-PE, since we are dealing with chains of different spacer lengths, it is more pertinent to use contour length as a scaling variable. In Figure 2, we have plotted the intrinsic relaxation rate decrements against contour length *L* (nm) for the fully-extended chain, based on the measured molecular weights. Evidently, $[\Gamma_{splay}]$ and $[\Gamma_{twist}]$ increase rapidly with chain length whereas $[\Gamma_{bend}]$ is essentially independent of chain length. We note that the highest molecular weight specimen shows a somewhat smaller incremental change in $[\Gamma_{splay}]$ and $[\Gamma_{twist}]$. This is likely due to an overestimation of the polymer concentration since, under the cross-polarizing microscope, it is evident that, at $c = 0.03$ g/g, this polymer exhibits only partial miscibility in nematic 5CB. Least-squares fits to the data for the four lower molecular weight samples leads to

$$[\Gamma_{\rm splay}] = 1.07L({\rm nm})^{1.26} \tag{10a}$$

$$[\Gamma_{\rm twist}] = 0.145L({\rm nm})^{1.67} \tag{10b}$$

Equation 10 are qualitatively consistent with the idea that the nematic field orients the chain backbone parallel to the director. Thus splay and twist require reorientational motions of the backbone whereas bend involves principally a sliding displacement parallel to the backbone.[4]

Let us suppose that, for dilute mixtures, our earlier observation, that the decrement in relaxation rate is determined principally by the increase in the associated viscosity, is applicable to the present data. Under such circumstances, we may write $[\Gamma_i] \propto [\eta_i] = \delta\eta_i/\eta_i{}^{\circ}c$ where $[\eta_i]$ is the intrinsic viscosity, subscript i is splay, twist, or bend, $\delta\eta_i$ is the corresponding viscosity increment, and $\eta_i{}^{\circ}$ is the viscosity of the pure solvent (5CB). From the literature, we have, for 5CB, $\eta_{\rm splay}{}^{\circ} \approx \gamma_1 = 0.5$ P and $\eta_{\rm bend} = 0.12$ P.[23] It is then pertinent to make a qualitative comparison of our results for $[\Gamma_{\rm splay}]$, $[\Gamma_{\rm twist}]$, and $[\Gamma_{\rm bend}]$ with the theoretical analysis of the corresponding viscosities of such mixtures by Brochard.[15] The latter leads to the general results

$$\delta\gamma_1 = (ckT/N)((R_{\parallel}^2 - R_{\perp}^2)^2/R_{\parallel}^2R_{\perp}^2)\tau_{\rm R} \tag{11}$$

$$\delta\gamma_2 = (ckT/N)\tau_{\rm R}(R_{\perp}^4 - R_{\parallel}^4)R_{\parallel}^2R_{\perp}^2 \tag{12}$$

$$\delta\eta_{\rm b} = (ckT/N)\tau_{\rm R}(R_{\perp}^2/R_{\parallel}^2) \tag{13}$$

and

$$\delta\eta_{\rm c} = (ckT/N)\tau_{\rm R}(R_{\parallel}^2/R_{\perp}^2) \tag{14}$$

where $\tau_{\rm R}$ is the configurational relaxation time, c and N are polymer concentration and molecular weight, respectively, and $R_{\parallel}$ and $R_{\perp}$ are the radii of gyration parallel and perpendicular to the director, respectively. Using $\alpha_2 = (\gamma_2 - \gamma_1)/2$ and $\alpha_3 = (\gamma_2 + \gamma_1)/2$, we obtain, from eqs 11 and 12

$$\delta\alpha_2 = (ckT/N)\tau_{\rm R}(R_{\perp}^2 - R_{\parallel}^2)/R_{\perp}^2 \tag{15}$$

and

$$\delta\alpha_3 = (ckT/N)\tau_{\rm R}(R_{\perp}^2 - R_{\parallel}^2)/R_{\parallel}^2 \tag{16}$$

These equations may be used, in turn, to estimate the increments in $\eta_{\rm bend} = \gamma_1 - \alpha_2{}^2/\eta_{\rm c}$ and $\eta_{\rm splay} = \gamma_1 - \alpha_3{}^2/\eta_{\rm b}$:

$$\delta\eta_{\rm bend} = \delta\gamma_1 - \frac{2\alpha_2\delta\alpha_2}{\eta_{\rm c}} + \frac{\alpha_2^2\delta\eta_{\rm c}}{\eta_{\rm c}^2} \tag{17}$$

and

$$\delta\eta_{\rm splay} = \delta\gamma_1 - \frac{2\alpha_3\delta\alpha_3}{\eta_{\rm b}} + \frac{\alpha_3^2\delta\eta_{\rm b}}{\eta_{\rm b}^2} \tag{18}$$

Equations 17 and 18 are rigorously applicable only for small viscosity increments.

When $R_{\parallel} \gg R_{\perp}$, these results lead to

$$\delta\eta_{\rm bend} = \delta\gamma_1\left(1 + \frac{\alpha_2}{\eta_{\rm c}}\right)^2 \ll \delta\gamma_1 \tag{19}$$

and

$$\delta\eta_{\rm splay} = \delta\gamma_1 + \frac{2\alpha_3}{\eta_{\rm b}}\frac{ckT\tau_{\rm R}}{N} \leq \delta\gamma_1 \tag{20}$$

The inequalities follow since α_2 and α_3 each have negative values and $\alpha_2/\eta_{\rm c} = -0.58$, $\alpha_3/\eta_{\rm b} = -0.15$ for pure 5CB.[23] Brochard's theory thus predicts, for main-chain LCPs which orient parallel to the director, that $\delta\gamma_1 \sim \delta\eta_{\rm splay} \gg \delta\eta_{\rm bend}$, in qualitative agreement with our dynamic light results for TPB-n-polyether shown in Figure 2 and Table I. Quantitatively, there is a significant discrepancy, since eq 19, again strictly valid only for small viscosity increments, predicts $\delta\eta_{\rm bend}/\delta\gamma_1 = 0.18$ and, since $\gamma_1{}^{\circ}/\eta_{\rm bend}{}^{\circ} = 4.2$ for pure 5CB, $[\eta_{\rm bend}]/[\gamma_1] \sim 0.76$ for main-chain LCP mixtures in 5CB, independent of chain contour length. However, our experimental results (Table I) indicate $[\Gamma_{\rm bend}]/[\Gamma_{\rm twist}]$ decreases from 0.18 for TPB-5-PE (DP = 42) to 0.06 for TPB-11-PE (DP = 44); i.e., we observe a much greater dynamical anisotropy. A corollory to this is that we do not observe, in $[\Gamma_{\rm bend}]$, the chain length dependence predicted in $\delta\eta_{\rm bend}$ by eq 19. It is possible that the chain length dependence is so small that it was masked by the experimental error since $(1 + \alpha_2/\eta_{\rm c})^2 \ll 1$.

By contrast, when $R_{\perp} \gg R_{\parallel}$, eqs 17 and 18 lead to

$$\delta\eta_{\rm bend} = \delta\gamma_1 - \frac{2\alpha_2}{\eta_{\rm c}}\frac{ckT\tau_{\rm R}}{N} \geq \delta\gamma_1 \tag{21}$$

and

$$\delta\eta_{\rm splay} = \delta\gamma_1\left(1 - \frac{\alpha_3}{\eta_{\rm b}}\right)^2 \geq \delta\gamma_1 \tag{22}$$

Thus, for side-chain LCPs whose backbone orients perpendicular to the director, this approximate version of Brochard's analysis predicts $\delta\eta_{\rm bend} \sim \delta\eta_{\rm splay} \sim \delta\gamma_1$; i.e., $[\eta_{\rm bend}] \gg [\eta_{\rm splay}] \sim [\gamma_1]$. From Table I, for MSHMA, we observe $[\Gamma_{\rm bend}] \gg [\Gamma_{\rm twist}] \geq [\Gamma_{\rm splay}]$. Bearing in mind the approximate nature of eqs 21 and 22, and the fact that we have neglected possible small changes in the elastic constants, our observations may be viewed as qualitatively in agreement with theory. A more serious discrepancy is observed in n-PVE, where we find $[\Gamma_{\rm bend}] \sim [\Gamma_{\rm twist}] > [\Gamma_{\rm splay}]$. Clearly our results for side-chain LCP show diverse patterns of behavior not predicted by the Brochard theory.

Finally, to comment on the molecular weight dependence of the director relaxation rates, we utilize Brochard's suggestion for the dependence of the polymer configurational relaxation time on polymer structure:[15]

$$\tau_{\rm R} = [\lambda_{\perp}\lambda_{\parallel}R_{\perp}^2R_{\parallel}^2/(\lambda_{\parallel}R_{\parallel}^2 + \lambda_{\perp}R_{\perp}^2)]\frac{1}{kT} \tag{23}$$

where $\lambda_{\parallel}$ and $\lambda_{\perp}$ are the translational frictional coefficients parallel and perpendicular to the director, respectively. Incorporating this result into eq 11, and with $R_{\parallel} \gg R_{\perp}$ for a fully-extended main-chain LCP which aligns with the director, eq 11 reduces to[15]

$$\delta\gamma_1 = ckT\lambda_{\perp}R_{\parallel}^2/N \tag{24}$$

Assuming $\lambda_{\perp} \propto R_{\parallel}$, which is valid for a rigid rod and, further, that $R_{\parallel} \propto N$, we obtain

$$[\gamma_1] \sim N^2 \tag{25}$$

Thus, the smaller molecular weight exponent, $\nu_{\rm twist} = 1.67$, deduced from our observations embodied in eq 10b may indicate some partial disordering of the spacer groups. Larger deviations between theory and experiment are observed in the molecular weight dependence of $[\Gamma_{\rm splay}]$ and $[\Gamma_{\rm bend}]$, cf. eqs 19 and 20. We note, however, that a clearer picture will require us to determine the individual elastic and viscosity coefficients and to measure the absolute molecular weights of our polymers. At present we limit ourselves to pointing out that the large molecular weight exponent for the twist relaxation rate is qualitatively consistent with the theory.

For a side-chain LCP eq 11 reduces to

$$\delta\gamma_1 = ckT\lambda_{\parallel}R_{\perp}^2/N \qquad (26)$$

If we assume free-draining behavior, $\lambda_{\parallel} \propto N$, and if the polymer backbone executes a self-avoiding two-dimensional random walk perpendicular to the director, $R_{\parallel} \propto N^{0.75}$, and eq 14 indicates $[\gamma_1] \sim N^{1.5}$. Alternatively, if the backbone has no excluded-volume effect, $R_{\perp} \propto N^{0.5}$, and $[\gamma_1] \sim N$. Comparing these results with our smaller experimental exponent, $\nu_{\text{twist}} = 0.76$, eq 9b, it is again apparent that we must allow some partial deviation from a strict, two-dimensional random walk. Note, however, that particularly large errors may be present in molecular weight estimates of side-chain LCP by GPC.

In summary, we have investigated the slowing down of the relaxation rates of director fluctuations in 5CB on addition of side-chain and main-chain LCPs. In the former, as quantified by the intrinsic decay rate decrements, the change in the bend mode is comparable to or larger than that of splay and twist. The reverse is observed for main-chain LCP. These properties and the strong molecular weight dependence of the twist relaxation rate in both types of systems are qualitatively consistent with the idea that the nematic field orients the chain backbone, respectively, perpendicular and parallel to the director. For side-chain LCP, the magnitude of the change in all three director distortion modes is substantially reduced by an increase in spacer length ($n > 3$) or an increase in backbone flexibility. The molecular theory of Brochard[15] is qualitatively consistent with some but not all of our observations. The discrepancies may arise, in part, because of approximations we have made in contrasting theory and experiment, but inadequacies of the dynamical model such as incomplete accounting of decoupling of polymeric mesogen motion may also be involved. Finally, we remark again on the odd–even effect which we observe in the solubility of the main-chain LCP in nematic 5CB, a phenomenon which was not observed in the side-chain LCP.

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