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EQUILIBRIUM AND DYNAMIC PROPERTIES OF SIDE-CHAIN LIQUID-CRYSTALLINE POLYMERS IN DILUTE NEMATIC SOLUTIONS

by

STEVEN RICHARD SMITH

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Thesis Advisors:
Professors Alex M. Jamieson and Shi-Qing Wang

Department of Macromolecular Science
CASE WESTERN RESERVE UNIVERSITY
January, 1995
CASE WESTERN RESERVE UNIVERSITY

GRADUATE STUDIES

We hereby approve the thesis of

STEVEN RICHARD SMITH

candidate for the PhD

degree.*

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SQUILIBRIUM AND DYNAMIC PROPERTIES OF SIDE-CHAIN LIQUID-CRYSTALLINE POLYMERS IN DILUTE NEMATIC SOLUTIONS

Abstract

by

STEVEN R. SMITH

Using a combination of depolarized dynamic light-scattering, electric and magnetic Frederickscz transition, and rheological characterization techniques, we have measured various combinations of the anisotropic viscoelastic coefficients of dilute nematic mixtures of a number of side-chain liquid-crystalline polymers (LCPs) in low-molecular-weight liquid-crystalline (LC) solvents. Comparison of solution and solvent values of the elastic constants characterizing splay, twist, and bend curvature distortions of the nematic director in aligned monodomains of these materials indicates that the dissolved mesogenic polymers induce modest changes in the elasticity of the solvent. On the other hand, it is observed that the anisotropic viscosity coefficients of the LCs are strongly increased by the addition of small amounts of polymer.

In the effort to establish functional correlations between various structural attributes of the LCPs and the nature and extent of their conformational coupling to the orienting influence of a nematic solution environment, the anisotropic hydrodynamic dimensions of the dissolved polymers parallel and perpendicular to the director have been estimated in each case using either of two interpretive approaches. It has been shown that evaluation of $R_{II}$ and $R_{II}$ as equivalent hydrodynamic sphere radii from either of the anisotropic reduced viscosity pairs [$\eta_1$] and [$\eta_{bend}$], or [$\eta_e$] and [$\eta_b$], respectively, yields interpretations that are consistent with expectations deriving from
the theoretical model of Warner and Wang. In contrast, quantitative evaluation of the 
experimental data via the "anisotropic dumbbell" model proposed by Brochard leads to 
contradictory implications for the conformational anisotropy of the LCPs. Empirical 
modifications to Brochard’s expressions that admit self-consistent interpretation of the 
experimental results have been proposed.

The observed trends in the anisotropic viscous increments of the LCP solutions 
evaluated in this study suggest generally that the length of the flexible linkages 
connecting the mesogenic moieties to their polymeric backbones plays a predominant 
role in determining the strength and character of conformational coupling of a side-
chain LCP to the nematic matrix. Both the thermodynamic rigidity of the backbone and 
the polarity of the mesogens appear to exert a secondary influence in this regard. 
Auxiliary direct measurements of the solvated dimensions of the materials by small-
angle scattering techniques is suggested as a means of confirming the results deduced 
from the present viscometric study.
The author wishes to express his appreciation to Professor Alex Jamieson for his sponsorship, advice, and not least of all his enduring patience throughout the course of this project.

Recognition and thanks are due as well to those members of Professor Jamieson's group whose technical training and assistance were instrumental to the progress of this work. In this regard, the author is particularly indebted to the experimental advice and insights contributed by his working peers and close friends, Dongfeng Gu and Fulung Chen.

The author wishes lastly to acknowledge Professor Virgil Percec and his students in the Department of Macromolecular Science, as well as Dr. L. C. Chien of the Liquid Crystal Institute of Kent State University, for their contributions of the liquid-crystalline polymers studied in this work.
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1. Reduced temperature variation of the estimated hydrodynamic volumes of the various side-chain LCPs studied in this work.
A. OVERVIEW

By their nature as both polymeric and mesophase materials, thermotropic side-chain liquid crystal polymers (LCPs) -- alternately referred to in the literature as comb-like LCPs -- possess inherently competing conformational tendencies. On the one hand, the polymeric backbones connecting pendant mesogenic units in side-chain LCPs, being typically comprised of repeat units whose catenation through single-bond covalent linkages results in flexible or semi-flexible chains, imparts an entropically favorable tendency toward three-dimensional conformational isotropy to the molecules. On the other hand, packing constraints among the pendant rod-like moieties of a side-chain LCP in any of its accessible mesophases has the opposite tendency to impose lesser-dimensional anisotropic order on the global conformation of the molecules, the coefficient of dimensionality depending on the symmetry attributes of the mesophase -- i.e., one-dimensional order among the mesogens in the case of simple nematics, and two-dimensional order in the case of smectic phases. Resolution of this conflict in conformational tendencies imparted respectively by the backbone and mesogenic constituents of these materials is mediated intramolecularly by the introduction of variable length flexible spacer segments connecting the two. The generic architecture of side-chain LCPs implied by this description, as well as the basic structural characteristics of representative nematic and smectic mesophases, are illustrated schematically in Figure I-1.

From a more general standpoint, global resolution of the competition that exists between the separate conformational tendencies of the backbone and
mesogenic moieties of side-chain LCPs is an interdependent function of 1) the specific chemical identities of each of these two constituents, 2) the extent to which connecting flexible spacer linkages act to decouple their opposing organizational tendencies, 3) the intermolecular environment of the molecules -- i.e., whether the molecules are in their pure state as in a melt phase, or isolated in a solution environment -- and 4) in all of the above cases, on the independent thermodynamic variables of temperature and pressure. It is to various subsets of this general list of parameters that the work of this thesis addresses itself. More specifically, it is the intent of this work to contribute greater insight into the functional interrelationships governing the nature and extent of coupling between mesomorphic order in low-molar-mass liquid crystal materials (LCs) and anisotropic chain conformational order in side-chain LCPs. To this end, a variety of experimental techniques has been used to measure the anisotropic viscoelastic behavior of nematic monodomains of dilute mixtures of various side-chain LCPs in nematic LC solvents.

As will be elaborated on in some detail intermittently in subsequent sections of this document, anisotropic liquid crystal polymer/solvent coupling effects are observable and, in principle, interpretable through measurement of induced increments to the anisotropic viscosity coefficients of the LC solvents in which the side-chain LCPs are dissolved. The latter are a direct consequence of the expanded hydrodynamic dimensions of the solvated LCP molecules, and relationships among the various viscosity increments permit the extraction of estimates as to the anisotropy in chain conformation of the molecules. These effects may in turn be related to specific aspects of the molecular architecture of the side-chain LCPs, and their dependence on the nature of the LC solvent and on the degree of mesophase order in the solution -- i.e., on its temperature relative to characteristic mesophase transition temperatures -- demonstrated.
Figure 1-1A: Schematic illustration of a typical side-chain LCP.

Figure 1-1B: Depiction of the progress of increasing mesomorphic order in side-chain LCPs as temperature decreases. The nematic phase is characterized by net alignment of the long axes of the mesogenic cores along the uniaxial director \( \hat{n} \). In the lower-temperature smectic phases, two-dimensional order results from organization of the mesogens in planes either perpendicular to the director, in the case of smectic A phases, or at an inclined angle in the case of smectic C mesophases.
B. EXPERIMENTAL AND THEORETICAL BACKGROUND ON THE CONFORMATIONAL BEHAVIOR OF SIDE-CHAIN LCPs

The equilibrium conformational behavior of side-chain LCPs, both as pure materials in various mesophase melt states and in nematic mixtures with low-molar-mass liquid crystal solvents, has been the subject of considerable theoretical and experimental study within the field of liquid crystal polymer research for well over a decade now. For instance, a theoretical model predicting the dependence of backbone and side-chain conformational order in the nematic melt phase of side-chain LCPs on reduced temperature and on various phenomenological intramolecular coupling coefficients has been developed by Warner and Wang [1-3]. Furthermore, there exists a theoretical analysis of the effect of polymer chain conformational anisotropy on the anisotropic viscosity coefficients of dilute nematic LC polymer/solvent mixtures attributable to Brochard [4]. These two theoretical approaches will be discussed separately, following the present brief review of the results of representative experimental investigations into chain conformational order in side-chain LCPs. Finally, the remainder of this chapter will be devoted to a more detailed introduction to the specific experimental techniques which have been used in this author's study of the subject.

1. LITERATURE REVIEW OF EXPERIMENTAL STUDIES

A number of experimental techniques have been used to examine the separate packing arrangements and dynamic behavior of the mesogen, backbone, and flexible spacer moieties of side-chain LCPs in both their melt and solution states. To this end,
Various NMR (3-7), small- and wide-angle X-ray (8-11) and neutron diffraction (11-19), infrared dichroism (20), and dielectric relaxation (21-23) techniques have all been employed, the nature of the information obtained in each case varying with the technique. Perhaps the most important of these methods from the standpoint of addressing the issue of global LCP chain conformation are the small-angle neutron (SANS) and X-ray (SAXS) scattering techniques, since they are uniquely capable of providing direct measurement of the anisotropic chain dimensions in LCPs, given the appropriately designed structural basis for scattering contrast.

In particular, neutron scattering experiments on selectively deuterated samples have yielded information on the average dimensions and orientation of the polymer backbones of a variety of side-chain LCPs in their isotropic, nematic, and smectic melt phases. By virtue of their relative ease in being prepared as deuterated backbone homologues, the majority of reported SANS studies of this type have been performed on high-molecular-weight polymethacrylate (12,14,17) and polyacrylate (11,19) side-chain LCPs. As illustrated by the series of structures I and II depicted in Figure 1-2, the mesogenic moieties of these materials have consisted of phenyl hydroxybenzoate cores linked to the polymeric mainchain via hexyl spacer groups. Individual members of this group of LCPs were further chemically distinguished by the nature of para substituent groups attached to the terminal phenyl rings of the mesogen cores. Also shown in Figure 1-2 are the chemical structures of two additional acrylate backbone side-chain LCPs (16,18) and a methyl siloxane backbone LCP (17) whose mesophase conformations have been investigated by SANS. The results obtained from these studies are summarized in Table I-1, in which the orientation and magnitude of global conformational anisotropy at various reduced temperatures in each case has been indicated by the ratio of the particular polymer's experimentally measured radii of gyration perpendicular ($R_L$) and parallel ($R_H$) to the
Figure 1-2: Chemical structures of various side-chain LCPs whose melt-phase conformation have been studied by SANS. The results of these studies are summarized in Table 1. Selective angle-dependent scattering contrast in these materials was accomplished by deuteration at the sites of the bolded hydrogens.
<table>
<thead>
<tr>
<th>Structure</th>
<th>N (1)</th>
<th>Phase</th>
<th>$R_L/R_\parallel$ (2)</th>
<th>Reference</th>
</tr>
</thead>
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<tr>
<td>Ia</td>
<td>~1.030</td>
<td>nematic</td>
<td>1.25</td>
<td>[12]</td>
</tr>
<tr>
<td></td>
<td>~700</td>
<td>nematic</td>
<td>1.10</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>smectic</td>
<td>1.35 - 1.55</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>glass</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
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<td>~890</td>
<td>nematic</td>
<td>1.10</td>
<td>[14]</td>
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<tr>
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<td></td>
<td>smectic</td>
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<td></td>
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<tr>
<td>Ic</td>
<td>~240</td>
<td>nematic</td>
<td>1.05 - 1.10</td>
<td>[17]</td>
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<tr>
<td></td>
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<td>1.25 - 1.35</td>
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<td></td>
<td>glass</td>
<td>1.40</td>
<td></td>
</tr>
<tr>
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<td>nematic</td>
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<td>[19]</td>
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<td>smectic</td>
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<tr>
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<td>0.90</td>
<td>[11]</td>
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<td>nematic</td>
<td>1.05</td>
<td>[16]</td>
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<td></td>
<td>smectic</td>
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<td></td>
<td></td>
<td>re-entrant</td>
<td>0.80 - 0.60</td>
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<td></td>
<td></td>
<td>nematic</td>
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<td></td>
<td>smectic</td>
<td>1.05 - 1.60</td>
<td></td>
</tr>
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</table>

(1) Obtained from light-scattering or GPC molecular weight determinations.
(2) Anisotropy ratios designated by a range of values correspond to the trend with decreasing temperature within the mesophase.
Figure I-3: Illustration of average global chain dimensions, parallel and perpendicular to the nematic director, measured by small-angle scattering techniques.
preferred orientation of its mesogenic units, as illustrated in Figure 1-3. Oriented monodomains of the various LCPs were obtained by slowly cooling thin films of the materials maintained as isotropic melts below their isotropic-to-nematic transition temperatures ($T_{NI}$) in the presence of strong magnetic fields.

Several trends are evident in the results from these studies. First, under the influence of the anisotropic mean field environment imposed by their pendant mesogens, all of the polymers were found to acquire some degree of conformational anisotropy on traversing $T_{NI}$. Among the methacrylate backbone LCPs studied, the trend was consistently toward oblate (i.e., $R_L/R_\parallel > 1$) anisotropies whose extent was relatively small, but increased with the degree of nematic order as the temperature decreased. Furthermore, all of the materials possessing smectic phases assumed more pronounced oblate anisotropic conformations below their nematic-to-smectic transition temperatures ($T_{AN}$), the magnitude of the anisotropy again increasing with decreasing temperature within the smectic phase. Consistent with these observations are the wide-angle neutron scattering results obtained in several of the studies [13,14,17] implying that the backbone segments of side-chain LCPs in the smectic phase laterally segregate in microphase-separated fashion within layers normal to the nematic director, which in turn alternate with the smectic layers of the mesogenic portions of the molecules.

On the other hand, except for the Structure III material, all of the polyacrylate and methyl siloxane LCPs listed in Table I-1 were found to adopt globally prolate (i.e., $R_L/R_\parallel < 1$) conformations in at least the high temperature nematic region if not throughout their entire nematic temperature range. Furthermore, although the anisotropic conformation of the Structure IIa polymer inverted from prolate to oblate within the nematic phase as temperature decreased, similar to the tendency of the methacrylate backbone materials, the conformational anisotropy of polymers IIb, IV,
and V became more prolate with decreasing temperature, opposite to this trend. The behavior of the Structure III polyacrylate LCP is anomalous in that its conformation, determined to be increasingly oblate as temperature decreased through the nematic and smectic phases, inverted in a lower-temperature re-entrant nematic phase to being increasingly prolate as temperature decreased.

The generally contrasting behavior of the methacrylate and of the acrylate and methyl siloxane LCPs was at first ascribed to the influence of polymer backbone rigidity. This interpretation had been fostered by the results of an early deuterium NMR study [5], in which comparison of the nematic phase behavior of a polymethacrylate and a polyacrylate side-chain LCP had yielded the similar finding that the local orientation of the acrylate unit roughly paralleled the nematic director, whereas that of the methacrylate unit was on average perpendicular to the director. The more recent results of the SANS studies suggest further refinement of this rationalization, taking into account whether or not the polymer exhibits strong pre-smectic density fluctuations in the nematic phase. This revised interpretation can in fact be generalized to the statement that, lacking pre-smectic layer-like ordering tendencies characterized by a correlation length significantly greater than the mean radius of gyration of the polymer, a particular side-chain LCP should adopt a globally prolate conformation in the nematic melt phase in order to accommodate the highest possible packing density of the mesogenic units [18]. In this regard, it is clear that the specific chemical nature of the LCP's mesogenic units may exert a more significant effect than that of its backbone structure in determining the global conformation of the polymer.

A number of studies of the conformation of side-chain LCPs in nematic solution have also been reported, principally using viscometric director relaxation techniques [24-26], the analysis of whose results have relied on the Brochard
theoretical model yet to be discussed. However, there exists at least one published study in the literature [8] making use of small-angle X-ray scattering (SAXS) to directly determine the conformational anisotropy of a series of methyl siloxane backbone side-chain LCPs at various reduced temperatures within the nematic range of their dilute solutions in a solvent chemically similar to the mesogens of the polymer. As indicated in Figure 1-4, the various polymers in this study were differentiated by the lengths of their flexible spacer groups and their molecular weights. While the experimental results were insufficient to resolve the conformation of the lower-molecular-weight six-spacer material, the anisotropies of the remaining higher-molecular-weight materials were determined to be uniformly prolate, the ratios $R_{\|}/R_{\perp}$ falling within the range

$$R_{\|}/R_{\perp} = 1.3 - 1.6$$

which increased weakly with decreasing temperature.

Two aspects of the results of this study are particularly noteworthy. The first is that they contradict the findings of an earlier study of two of the same polymer/solvent mixtures (namely, those using polymers with $n = 4$ and $n = 6$), in which oblate conformational anisotropies of the LCPs had been inferred by Brochard model analysis of dynamic Fredericksz transition measurements [24]. Given the greater experimental certainty in measuring anisotropic chain dimensions by the techniques used in the more recent X-ray study, this discrepancy seems to imply the need for theoretical refinement in the Brochard model. Secondly, the trend that emerged in the SAXS study in regard to the dependence of LCP chain anisotropy in the nematic state on side-chain spacer length is qualitatively similar to that found in another study by Mitchell et. al. [27], who investigated spacer length effects in a series of lightly cross-linked copolymeric elastomers whose non-juncture constituents were homologues of structure IIb in Figure 1-2 having flexible spacer lengths ranging
Figure 1-4: Chemical structures of side-chain LCPs whose conformation in nematic solution in the indicated solvent were obtained by SAXS in Ref.[8].
from two to six methylene units. In the latter study, the orientation of each sample’s
mesogenic side groups with respect to the direction of uniaxial mechanical alignment
of its backbone network was obtained via wide-angle X-ray scattering measurements.

Specifically, although the various LCPs of the SAXS study were all found to
exhibit prolate configurational anisotropy on dilution in a nematic solvent,
additionally observed was a slight but consistent even/odd effect favoring greater
prolate anisotropies among the even-spacer polymers which damped off with
increasing spacer length. A resemblance to this trend was found in the results of the
study of the mechanically aligned copolymeric elastomers, with the exception that
perpendicularity rather than a lesser degree of parallelism between the polymer
backbone and the mesogenic side groups was demonstrated in the odd-spacer
materials [27]. Compared to the results of the SAXS study, the peculiarity of this
alternation in backbone/mesogen alignment tendencies within the LCP elastomer
series (which, when translated to the case of an isolated LCP chain in a nematic
environment implies an odd/even alternation between oblate and prolate
configurations of the polymer backbone) can be regarded as deriving from the overall
differences in chemical structure between the two groups of polymers and in the
nature of the aligning field. It seems unlikely, notwithstanding the previously stated
generalization, that the results of the elastomer study manifest an underlying
even/odd alternation in non-pre-smectic/pre-smectic behavior in the chemically
equivalent free LCP chains. In any case, the results of both sets of experiments
demonstrate a measurable influence of flexible spacer length on the coupling of
nematic order between the backbone and mesogenic constituents of side-chain LCPs,
whether imposed by a molecular mean field or by uniaxial mechanical extension.
Moreover, the trend found in both of these studies is similar, in that a greater
tendency toward backbone/mesogen parallelism was evidenced when the connecting
linkages between these two portions of the LCP contained an even number of flexible bonds.

In summary, the results of the various studies reviewed in this section imply that the phenomenon of coupling of mesophase order and main-chain conformational anisotropy in side-chain LCPs is jointly dependent on each of the three main architectural features of the polymer's structure -- i.e., mesogen type, polymer backbone, and flexible spacer length. If the phenomenon is viewed in terms of transference of anisotropic order from the mesogens to the LCP backbone, mediated by the flexible spacer moieties, it appears that the specific free energy constraints dictating the nature of inter- and intra-molecular organization of the mesogenic units of the LCP, whether as a pure melt or on dilution in a mesogenic solvent, plays a dominant role. It appears further that, lacking either long-range pre-smectic ordering tendencies among the LCP mesogens or the imposition of backbone/mesogen perpendicularity by connecting spacer groups, the backbones of side-chain LCPs are likely to adopt prolate anisotropic conformations in a nematic environment. The magnitude of this anisotropy is in turn influenced both by absolute temperature, through the entropically elastic configurational response of the LCP backbone, and by reduced temperature, reflecting the degree of nematic order among the mesogenic units. The results of the LCP elastomer study serve to illustrate the reciprocity of these coupling interactions.

2. WARNER-WANG THEORY

As has been both postulated and repeatedly demonstrated in the various experimental studies which have been cited, the development of uniaxial order
among the mesogens of a side-chain LCP in the nematic state imposes configurational constraints on the main-chain of the material, distorting the entropically favored 3D random-coil conformation adopted by the latter in the isotropic phase. Thermodynamic account of this coupled side-chain/main-chain nematic interaction as it applies to the nematic melt phase behavior of side-chain LCPs has been formulated within the general framework of Maier-Saupe mean-field theory by Warner and Wang [1-3]. These authors identify five structure-derived competitive influences on internal molecular order whose relative magnitudes determine, as a function of reduced temperature, which of several alternative global chain conformations should theoretically be assumed by a particular side-chain LCP.

Figure I-5A provides schematic illustration of the various parameters invoked in the Warner/Wang model. These consist of 1) the dimensionless lengths x and n, representing length-to-diameter ratios of the LCP's mesogenic units and backbone linkages separating successive side-chains, respectively; 2) the angles $\theta_A$ and $\theta_B(s)$ specifying the orientation of individual mesogen and backbone units (located at positions s along the contour of the polymer main-chain) with respect to the average uniaxial director $\hat{n}$; 3) the energetic coupling coefficients, $v_i$, which scale the orientation-dependent interaction potentials between the various LCP constituents and the nematic mean field as follows:

(i) $v_A$ is a measure of the nematic drive toward parallel order among the mesogenic side-chains resulting from the net influence of anisotropic steric and vander Waals forces acting between these elements.

(ii) $v_B$ characterizes the same nematic tendency acting between sections of the polymer backbone, and can be expected to vary in magnitude in proportion to backbone rigidity.
Figure I-5A: Schematic illustration of significant dimension and interaction parameters invoked in the Warner-Wang theory of side-chain LCP nematic phase conformation.

$N_i$: $S_A > 0, S_B < 0$

$N_{II}: S_A < 0, S_B > 0$

$N_{III}: S_A > 0, S_B > 0$

Figure I-5B: Various nematic conformational phases theoretically predicted for side-chain LCPs.
(iii) $v_c$ characterizes the same parallel ordering tendency acting between mesogen and backbone elements, and can similarly be expected to scale with the stiffness of the backbone.

(iv) $v_f$ measures the degree to which interconnecting spacer groups act to impose perpendicular alignment between mesogen and backbone moieties, and is therefore opposite in its influence compared to $v_c$. In fact, a single effective side-chain/backbone nematic cross-coupling coefficient, $v_m$, results on combining the appropriately weighted competitive ordering tendencies represented by $v_c$ and $v_f$, namely

$$v_m = v_c - v_f / \chi n$$

where $\chi = x / x+n$ is the volume fraction of mesogenic groups per polymer repeat unit. The complementary volume fraction of backbone elements per repeat unit is then taken to be $1-\chi$. It will be noted that the volume fraction occupied by the spacer groups is unaccounted for in this definition. Rather, the effect of the spacers in promoting order between mesogen and backbone elements as a function of their length and stiffness is indicated merely by the sign and magnitude of $v_f$, positive values being assumed to indicate a net tendency of the spacers to maintain backbone/mesogen perpendicularity.

(v) Finally, although not depicted in Figure I-5A, the theory takes explicit account of energetic resistance to bending and torsion of the polymer backbone by incorporation of the parameter $\varepsilon$, an effective modulus whose value therefore also increases in proportion to backbone stiffness.

Given this set of parameters, Warner and Wang formulate the mean-field potentials governing the free energy of the LCP's mesogens and backbone, respectively, as
\[
U_A = -\left(\chi v_A S_A + (1-\chi) v_m S_B\right) P_2(\cos \theta_B(s))
\]

and

\[
U_B = \int_0^{L_B} ds \left[ \frac{1}{2} \left( \frac{\delta u}{\delta s} \right)^2 - \left( (1-\chi) v_B S_B + \chi v_m S_A \right) P_2(\cos \theta_B(s)) \right]
\]

where \(\mathbf{\hat{u}}(s)\) is the unit vector tangent to the LCP backbone at position \(s\) whose orientation relative to \(\mathbf{\hat{n}}\) is given by \(\theta_B(s)\), \(P_2\) represents the second Legendre polynomial of either angle cosine,

\[
P_2(\cos \theta) = \frac{3}{2} \cos^2 \theta - \frac{1}{2}
\]

and the mesogen and backbone order parameters \(S_A\) and \(S_B\) are obtained as the respective ensemble averages of these functions, namely

\[
S_A = \left\langle P_2(\cos \theta_A) \right\rangle
\]

and

\[
S_B = \left\langle P_2(\cos \theta_B(s)) \right\rangle
\]

In the case of \(S_B\), this averaging procedure requires summation over all possible configurations of the assumed worm-like LCP backbone. The integral expression for \(U_B\) in Eq. 1-3, which is evaluated over the contour length \(L_B\) of the polymer backbone, demonstrates the antagonistic competing drives of backbone entropy and nematic order, since the terms accounting for the bend/torsion elastic energy and the nematic interaction energy enter the argument of the integral with opposite sign.

Equations 1-2 and 1-3 represent a coupled set of conditions on the simultaneous state of orientational order that exists among the mesogens and backbone of a side-chain LCP at any given reduced temperature. Solutions to these
equations yielding mutually self-consistent sets of values for $S_A$ and $S_B$ may be obtained either perturbatively and numerically [1], or by graphical and analytical analysis [2]. Warner and Wang have demonstrated using the former approach that the problem reduces to the mathematically equivalent task of evaluating the eigenfunctions of the differential equation representing diffusion of a unit tangent vector on the surface of a unit sphere under the influence of a nematic mean-field potential.

A characteristic variable emerging from this analysis is the dimensionless coupling coefficient $\Delta$.

$$\Delta = \frac{3\beta}{2Dl} - (1 - \chi)\nu_B S_B + \chi\nu_m S_A$$  \hspace{1cm} 1-7

where $\beta = 1/k_BT$, $l$ represents the cross-sectional diameter of the LCP backbone, and the parameter $D$, whose relationship to the backbone bending modulus is given by

$$D = \frac{1}{2\beta e}$$  \hspace{1cm} 1-8

represents an effective persistence length for the presumed worm-like backbone in the absence of the nematic field. The mathematical significance of $\Delta$ is that its sign and magnitude indicate the tendency for the unit vector to reside preferentially in regions either near the poles or near the equator of the unit sphere. Negative values of $\Delta$ infer the former tendency, positive values the latter. The corresponding physical interpretation in application to the conformational behavior of a side-chain LCP is that negative values of $\Delta$ are associated with prolate chain conformations, whereas positive values of the coefficient are associated with oblate chain conformations.

Jointly considering Eqs. 1-1, 1-7, and 1-8, the interplay among the various parameters of the model in their effect on $\Delta$ may be summarized as follows:
1) The condition $\Delta < 0$ obtains generally whenever $v_m > 0$, i.e., so long as $v_c > \bar{v}_f / \chi n$. In this case, there is a mutually parallel nematic ordering tendency among the LCP side chains and backbone, and the conformationally prolate $N_{III}$ phase illustrated in Figure 1-5B results. $N_{III}$ phase behavior would be expected to be favored in side-chain LCPs where the mesogenic units are particularly long or bulky, or in which the side-groups are infrequently spaced along the polymer backbone, either structural attribute being accompanied by an increase in the magnitude of the product $\chi n$.

2) If $v_m < 0$, indicating perpendicularity between the LCP mesogens and backbone, $\Delta$ may be either positive or negative, depending on the relative magnitudes of the bracketed A and B terms in Eq. 1-7. $\Delta > 0$ corresponds to the oblate $N_1$ conformational phase shown in 1-5B, and obtains if nematic ordering of the LCP side-chains predominates over that of the backbone. Compared to the $N_{III}$ case, this phase behavior would be expected of polymers having shorter, more frequently spaced mesogenic groups. A reduction in length of the interconnecting flexible spacer groups would similarly promote the $N_1$ phase relative to the $N_{III}$ phase by increasing the relative magnitude of $v_f$.

3) The third alternative, namely the prolate $N_{II}$ phase illustrated in 1-5B for which both $v_m$ and $\Delta$ are negative, arises if the backbone nematic ordering tendency predominates over that of the mesogenic side-chains. This case is realistically conceivable only for side-chain LCPs having mesogenic units incorporated as well into their polymeric backbones, thereby conferring a large value to the coupling coefficient $v_B$.

4) Aside from the qualitative propensity of the worm-like polymer backbone to couple either negatively or positively to the nematic mean field environment of the
LCP matrix, the magnitude of the conformational anisotropy that obtains is influenced by the intrinsic flexibility of the LCP backbone. This is evidenced by the direct proportionality that exists between $\Delta$ and $\varepsilon$. Hence, the extent of anisotropy exhibited in any of the three nematic conformational phases is diminished as the rigidity of the LCP backbone is decreased. As any explicit temperature dependence of $\Delta$ cancels in the prefactor term of Eq. 1-7, variations in the degree of LCP conformational anisotropy with temperature are instead implicitly accounted for by the temperature dependence of the parameters $\varepsilon$, $v_m$, $v_B$, $S_A$, and $S_B$.

Although the Warner/Wang model was developed strictly in application to predicting the conformational tendencies of side-chain LCPs in the nematic melt state, its extension to the case of dilute solutions of the polymers in nematic solvents is readily obtained by suitable redefinition of appropriate parameters of the model. In particular, if one merely subsumes account of the mean field contribution of the solvent molecules in the parameter $\chi$, it is evident that a nematic solvent environment should generally enhance the tendency for a dissolved side-chain LCP to exhibit $N_{III}$ phase prolate anisotropy, owing to the increased $\chi$-weighted influence of $v_e$ relative to that of $v_f$. It may furthermore be argued on the basis of excluded volume considerations that the magnitude of conformational anisotropy displayed in any of the three possible phases should be reduced for a particular side-chain LCP in solution compared with the melt, inasmuch as excluded volume effects are negligible in polymer melts. The influence of intramolecular excluded volume is similarly expected to play a role in the absolute temperature dependence of the nematic solution conformational anisotropy of side-chain LCPs.
The utility of the theoretical approach of Warner and Wang in regard to predicting the nematic phase conformational anisotropy of side-chain LCPs is restricted, in the sense that quantitative application of the theory requires *a priori* knowledge of the various phenomenological parameters $e$ and $v_1$ characterizing the LCP structure. On the other hand, Brochard [4] has formulated a theoretical model which is interpretive, as opposed to predictive, in its approach to elucidating the anisotropic chain dimensions of nematic-solvated LCPs. Compared with the Warner and Wang model, the Brochard model is therefore more immediately capable of serving as a theoretical guide for evaluating the results of experimental studies of the viscoelastic behavior of LC/LCP mixtures. In order to be in a position to meaningfully discuss the theoretical origins of this model, as well as the experimental techniques used in this work, it is first necessary to review certain fundamental relationships in terms of which the anisotropic viscoelastic behavior of nematic fluids can be quantitatively described.

Briefly stated, the unidirectional order characteristic of nematic liquid crystals reflects the existence of orientation-dependent attractive forces acting between the constituent molecules of the liquid. Such forces impart inherently anisotropic viscous and elastic properties to these materials. According to the fluid mechanical model first developed by Frank [28], the free energy density change accompanying elastic deformations of the director $\mathbf{n}$ in a bulk nematic sample is a linear function of the potential energies associated with three geometrically distinct types of curvature distortion. Illustrated in Figure 1-6, these three distortion modes are referred to as splay, twist, and bend, whose corresponding elastic constants are conventionally designated $K_{11}$, $K_{22}$, and $K_{33}$, respectively. As indicated in the figure, the
Figure I-6: Illustration of the three principal types of curvature distortion occurring in aligned monodomains of a nematic liquid crystal.
The mathematical form of the director curvature in each case is given by the relationships
\[ \nabla \cdot \hat{n} \neq 0 \quad \text{for splay}, \]
\[ \hat{n} \cdot (\nabla \times \hat{n}) \neq 0 \quad \text{for twist}, \]
and
\[ |\hat{n} \times (\nabla \times \hat{n})| \neq 0 \quad \text{for bend}. \]

In analogy with Hooke's law, the three \( K_{ii} \) thus represent proportionality force constants linking the squared amplitude of appropriate combinations of the spatial derivatives of \( \hat{n} \) specifying the curvatures of the distortions with their respective potential energies.

Dynamically related to the potential energy changes associated with static deformations of the director profile in a nematic LC are the kinetic energy changes incurred on subjecting the fluid to macroscopic flow. The behavior of a nematic liquid in a flow field is distinguished from that of conventional isotropic liquids, in that momentum fluxes accompanying translational motions of the molecules are coupled to their average state of alignment -- i.e., to the nematic director. Consequently, in most cases, the application of flow will disturb the molecular alignment, causing the director to rotate. Taking a macroscopic fluid mechanical approach wherein the fluid is regarded as a continuous medium, equations for the time rate of change of the free energy density in a flowing nematic, applicable to the regime of slow flows, were first formulated by Ericksen [29], Leslie [30], and Parodi [31]. For a more thorough discussion of the derivation of these authors' results (hereafter referred to as ELP hydrodynamic theory), the interested reader is referred to authoritative reviews given in References [32-34]. It suffices for present purposes to present the main features of their analysis.

Summarily stated, ELP theory assumes that the net rate of change in the free
energy density of an isothermal nematic liquid due to hydrodynamic frictional processes is given by the relationship

$$TS = \int_V \left\{ A : \sigma^s + \vec{h} \cdot \vec{N} \right\} \, d^3r \quad 1-9$$

where $T$ and $\dot{S}$ are the temperature and time derivative of the entropy of the sample, respectively, $A$ represents the symmetric portion of the velocity gradient tensor, expressed in component form by

$$A_{\alpha\beta} = \frac{1}{2} \left( \frac{\delta v_\beta}{\delta x_\alpha} + \frac{\delta v_\alpha}{\delta x_\beta} \right) \quad \alpha, \beta = x, y, z \quad 1-10$$

$\sigma^s$ represents the corresponding symmetric portion of the total stress tensor acting on the fluid, $\vec{h}$ is the nematic molecular field, expressing the effect of the net elastic torque experienced by the director on being rotated away from its equilibrium alignment direction, and the vector $\vec{N}$ represents the rate of change in the orientation of $\vec{n}$ with respect to rotation of the surrounding fluid as a whole,

$$\vec{N} = \frac{\delta \vec{n}}{\delta t} - (\vec{\omega} \times \vec{n}) \quad 1-11$$

In Eq. 1-11, $\vec{\omega}$ represents the vorticity of the bulk sample, whose components are given by the antisymmetric portion of the velocity gradient tensor, i.e.,

$$\vec{\omega} = - (W_{y\alpha} W_{\alpha\beta} W_{\beta\gamma}) \quad 1-12$$

where

$$W_{\alpha\beta} = \frac{1}{2} \left( \frac{\delta v_\beta}{\delta x_\alpha} - \frac{\delta v_\alpha}{\delta x_\beta} \right) \quad \alpha, \beta = x, y, z \quad 1-13$$

The total viscous stress acting on the nematic is therefore accounted for as the sum of a symmetric contribution, originating in the coupling between $A$ and $\sigma^s$, and an
antisymmetric portion, represented in Eq. 1.9 by the term $\vec{h} \cdot \vec{N}$.

In an incompressible nematic liquid, it can be shown that the most general form for the components of the total viscous stress tensor, $\sigma'$, compatible with the presumed uniaxial symmetry of $\vec{n}$ as well as the requirement that the model be invariant on rotation of the inertial reference frame, is given by the expression

$$
\sigma'_{\alpha\beta} = \alpha_1 n_{\alpha} n_{\beta} n_{\mu} n_{\mu} A_{\mu\rho} + \alpha_4 A_{\alpha\beta} \\
+ \alpha_5 n_{\alpha} n_{\mu} A_{\mu\beta} + \alpha_6 n_{\beta} n_{\mu} A_{\mu\alpha} \\
+ \alpha_2 n_{\alpha} N_{\beta} + \alpha_3 n_{\beta} N_{\alpha}
$$

where the Einstein convention of summing over repeated indices has been assumed. Eq. 1.14 defines six coupling coefficients, each having the dimension of a viscosity, which are referred to as the Leslie coefficients. Parodi's contribution to the theory, based on consideration of Onsager's reciprocal theorem [35] expressing the time reversal invariance of the microscopic flow phenomena, was to demonstrate that

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5$$

1-15

Thus, only five of the six $\alpha_i$ are linearly independent. By assuming a balance is achieved in the flow field between elastic and viscous torques acting on the director, it can furthermore be shown within the context of the theory that the components of $\vec{h}$ are expressible in the form

$$h_{\mu} = \gamma_1 N_{\mu} + \gamma_2 n_{\alpha} A_{\alpha\mu}$$

1-16

where $\gamma_1$ and $\gamma_2$ represent shear torque coefficients relating $\vec{h}$ to the antisymmetric and symmetric portions, respectively, of the velocity gradient field. With the aid of the Parodi relationship, one can additionally derive the identities

$$\gamma_1 = \alpha_3 - \alpha_2$$

1-17

and

$$\gamma_2 = \alpha_3 + \alpha_2$$

1-18
Inherently by their definition, the Leslie coefficients characterize the rate of nematic viscous free energy density dissipation in flow situations where the director orientation is permitted to evolve in response to the stresses associated with the flow field, the only constraint on \( \hat{n} \) being the retarding influence of the molecular field. Considering the alternative possibility that the director is instead forced to maintain a fixed alignment, as for example by the application of a strongly orienting external field, one can envision three orthogonal alignment states of \( \hat{n} \) relative to the flow and velocity gradient directions of a shear flow field that are of immediate practical interest. These are illustrated in Figure I-7.

Given that any particular orientation of \( \hat{n} \) in the flow field is specified by the angles \( \theta \) and \( \phi \) indicated in the figure, the fixed alignment directions imposed on \( \hat{n} \) and the sensible viscosities one would measure in these three cases are given by

\[
\begin{align*}
\eta_1: & \quad \hat{n} \text{ is maintained parallel to the velocity gradient, with } \phi = 0^\circ \text{ and } \theta = 90^\circ; \\
\eta_2: & \quad \hat{n} \text{ is maintained parallel to the flow direction, with } \phi = 0^\circ \text{ and } \theta = 0^\circ; \\
\eta_3: & \quad \hat{n} \text{ is maintained normal to the shear plane, with } \phi = 90^\circ \text{ and } \theta = 90^\circ.
\end{align*}
\]

The coefficients \( \eta_1, \eta_2, \) and \( \eta_3 \) are referred to as the Miesowicz viscosities of a nematic, after their original investigator [36], and are more commonly designated in the literature by the notations \( \eta_c, \eta_b, \) and \( \eta_a \) respectively. As Figure I-7 also depicts, a physical analogy exists between the coefficient pairs - \( \alpha_2 \) and \( \eta_c, \alpha_3 \) and \( \eta_b, \) and \( \alpha_4 \) and \( \eta_a, \) in the sense that the director assumes a common orientation with respect to the governing coefficient in all three cases. In fact, if the ELP relationship between the component of the hydrodynamic stress tensor and the velocity gradient pertinent to the simple shear flow field specified in Figure I-7 is compared with the definitions of the Miesowicz viscosities, it can be shown that
Figure 1-7: Illustration of the nematic director orientation with respect to the shear plane in general, and specifically in the three cases defining the Miesowicz viscosities and their counterparts among the Leslie coefficients.
\[ \eta_c = \frac{1}{2} \left( -\alpha_2 + \alpha_4 + \alpha_5 \right) \tag{1-19} \]

\[ \eta_b = \frac{1}{2} \left( \alpha_3 + \alpha_4 + \alpha_6 \right) \tag{1-20} \]

and

\[ \eta_a = \frac{1}{2} \alpha_4 \tag{1-21} \]

A final set of nematic viscosity coefficients can be associated with the free energy density dissipation rates encountered on relaxation of splay, twist, and bend curvature distortions of the director profile as defined above. It will be demonstrated subsequently in this chapter that analysis of the long-wavelength viscous response of the director on relaxing from any of these three types of distorted profiles toward its average equilibrium alignment direction yields the relationships

\[ \eta_{\text{splay}} = \gamma_1 - \frac{\alpha_3}{\eta_b} \tag{1-22} \]

\[ \eta_{\text{twist}} = \gamma_1 \tag{1-23} \]

and

\[ \eta_{\text{bend}} = \gamma_1 - \frac{\alpha_2}{\eta_c} \tag{1-24} \]

Considering the identities on \( \gamma_1, \eta_b, \) and \( \eta_c \) given above, it is clear that all three distortion relaxation viscosity coefficients are implicitly functions of the Leslie coefficients. The non-linear subtractive terms in \( \eta_{\text{splay}} \) and \( \eta_{\text{bend}} \) reflect the fact that, in contrast to twist distortions of the director, relaxations of splay and bend distortions necessarily engender macroscopic backflow effects in the surrounding fluid. As will be shown, the significance of these three viscosity functions is that, like the Miesowicz viscosities, they are amenable to direct measurement by various experimental techniques.
Attention may now be re-focused on the Brochard model. In analogy with the behavior of dilute isotropic solutions of random-coil polymers, this model specifically postulates that increments to the anisotropic viscosity coefficients of a nematic solvent incurred by small additions of LC polymers can be expressed as functions of the solvated chain dimensions and the polymer-solvent frictional coefficients of the polymers. In a nematic medium, these characteristic parameters may each be viewed as having components $R_{||}$ and $R_{\perp}$, and $\lambda_{||}$ and $\lambda_{\perp}$, respectively parallel and perpendicular to the solvent director orientation. The general procedure involved in derivation of the Brochard relationships for the nematic solution viscosity increments in terms of these four anisotropic coefficients consists of calculating the appropriate stress increments obtained in shear flow due to the average projection of the LCP chain dimensions on the flow field. Expressions for the shear plane projections of the LCP dimensions can in turn be obtained in each case by steady-state evaluation of appropriate dynamical equations for the time rate of change of the net extensions of the LCP in the two orthogonal directions defining the shear plane. The latter expressions result on equating the internal elastic resistance and frictional drag forces acting on the polymer in the flow field.

For the geometry of the shear flow illustrated in Figure 1-7, application of these procedures to solve for the increment to the Miesowicz viscosity $\eta_a$ yields

$$\delta \sigma_{xz} = -\frac{c}{N} \langle f_z x \rangle = \left( \frac{ck_BT}{N} \right) \left( \frac{<f_z>}{R_{\perp}} \right)^2$$  \hspace{1cm} 1-25

where $c/N$ represents the number density of LCP chains having degree of polymerization $N$, the brackets $\langle \rangle$ denote a rotational time average, and use has been made of the fact that $f_z$, representing the elastic restoring force of the LCP resisting extension in the flow direction, is given by
where \( k_B T \) is the Boltzmann thermal energy. The stress increment \( \delta \sigma_{xz} \) is therefore viewed as the product of the stress associated with shear distortion of the \( xz \) cross-sectional area of a single polymer chain times the volumetric concentration of chains. This statement implicitly restricts the applicability of the Brochard model to the dilute solution regime, wherein it can be assumed that the incremental effects of the dissolved LCP chains is linearly additive -- i.e., the chains do not mutually interact with one another.

Next, the average projection \( \langle xz \rangle \) emerges from steady-state evaluation of the dynamical equations of the system, which as previously stated result on equating for each of the \( x \)- and \( z \)-directions the frictional drag force on the LCP with the appropriate component of the elastic restoring force. Given that the drag force is generally of the form

\[
\phi = \lambda \left( \frac{d\vec{r}}{dt} - \vec{v}_{loc} \right)
\]

where \( \vec{r} \) represents the extension of the polymer in a given direction and \( \vec{v}_{loc} \) is the local solvent velocity, one obtains in the present case the simultaneous equations

\[
\frac{dx}{dt} = \frac{x}{\tau_\perp}
\]

and

\[
\frac{dz}{dt} - \gamma x = \frac{z}{\tau_\perp}
\]

where \( \gamma \) is the macroscopic shear rate, and \( \tau_\perp \) is the characteristic relaxation time of the chain, given by

\[
\frac{1}{\tau_\perp} = \frac{k_B T}{\lambda_\perp R_\perp^2}
\]
Under conditions of steady flow, it is assumed that \( \langle xz \rangle \) attains a constant value, i.e.,

\[
\frac{d\langle xz \rangle}{dt} = -\frac{dx}{dt} + x \frac{dz}{dt} = 0
\]

1-31

Substitution of Eqs. 1-28 and 1-29 into this equation yields for the LCP cross-sectional projection

\[
\langle xz \rangle = \left( \frac{y}{z} \right) \tau_\perp \langle x^2 \rangle = \left( \frac{y}{z} \right) \tau_\perp R_\perp^2
\]

1-32

Hence, from Eq. 1-25,

\[
\delta \sigma_{xz} = \left( \frac{y}{z} \right) \frac{ck_BT}{N} \tau_\perp
\]

1-33

and finally

\[
\delta \eta_a = \left( \frac{\delta \sigma_{xz}}{\gamma} \right) = \frac{1}{2} \left( \frac{ck_BT}{N} \right) \tau_\perp = \frac{1}{2} \left( \frac{c}{N} \right) \lambda_\perp R_\perp^2
\]

1-34

In the case of the director orientation defining the Miesowicz viscosity \( \eta_a \), on the other hand, one obtains for the stress increment

\[
\delta \sigma_{xz} = \frac{c}{N} \langle xz \rangle = \left( \frac{ck_BT}{N} \right) \frac{\langle xz \rangle}{R_{||}^2}
\]

1-35

The dynamical equations for the extensions of the polymer in the \( x \)- and \( z \)-directions in this case are given by

\[
\frac{dx}{dt} = -\frac{x}{\tau_\perp}
\]

1-36

and

\[
\frac{dz}{dt} - \gamma x = -\frac{z}{\tau_\parallel}
\]

1-37

Hence, steady-state evaluation of the cross-section \( \langle xz \rangle \) yields

\[
\langle xz \rangle = \gamma \left( \frac{\tau_\perp}{\tau_\perp + \gamma} \right) \langle x^2 \rangle = \gamma \tau_\parallel R_\perp^2
\]

1-38
where $\tau_R$, expressing the reduced mean value of $\tau_i$ and $\tau_L$, represents an effective relaxation time for rotation of the LCP chain in the shear plane. The relationship of $\tau_R$ to the frictional coefficients $\lambda_i$ and $\lambda_L$ is given by

$$\tau_R = \frac{\lambda_i \lambda_L R^2 \tau^2}{\lambda_i R^2 + \lambda_L |R^2|}$$  \hfill (1-39)

Combining Eqs. 1-35 and 1-39, one therefore obtains for the increment to $\eta_b$

$$\delta \eta_b = \frac{\delta \sigma_{xz}}{\gamma} = \left(\frac{ckB}{N}\right) \tau_R \left(\frac{R^2}{R^2_{||}}\right)$$  \hfill (1-40)

Analogous implementation of these procedures to the task of evaluating the increment to the Miesowicz viscosity $\eta_c$ yields the result

$$\delta \eta_c = \left(\frac{ckB}{N}\right) \tau_R \left(\frac{R^2_{||}}{R^2_{\perp}}\right)$$  \hfill (1-41)

Four additional viscosity increment relationships may be obtained by evaluating the shear torque increments experienced by the nematic director in consequence of projection of the hydrodynamic dimensions of the LCP chains on the flow field. For a flow in the $xz$ plane, the component of the director torque along the positive $y$-direction is given by

$$\Gamma_y = -\sigma_{zx} + \sigma_{xz}$$  \hfill (1-42)

The increments to the two stress components due to the presence of the chains are in turn given by

$$\delta \sigma_{zx} = \frac{c}{N} \langle x \cdot z \rangle = \left(\frac{ckB}{N}\right) \left(\frac{\langle x \cdot z \rangle}{R^2_{\perp}}\right)$$  \hfill (1-43)

and
\[ \delta \sigma_{xz} = - \frac{c}{N} \langle \zeta_x \rangle = \left( \frac{ckB}{N} \right) \langle xz \rangle \frac{1}{R_{||}^2} \]

Therefore, one obtains for the shear torque increment

\[ \delta \Gamma_y = \left( \frac{ckB}{N} \right) \langle xz \rangle \left( \frac{1}{R_{||}^2} - \frac{1}{R_1^2} \right) \]

For any particular orientation of the director with respect to the flow and gradients of the shear field, the steady-state expression for \( \langle xz \rangle \) yields

\[ \frac{d\langle xz \rangle}{dt} = x \frac{dz}{dt} + z \frac{dx}{dt} = xv_z + zv_x - \frac{xz}{\tau_R} = 0 \]

where \( v_x \) and \( v_z \) are the components of the local velocity of the solvent. Assuming the flow to be in the \( z \)-direction as before, if \( \hat{n} \) is aligned in the \( x \)-direction, Eq. 1-46 yields

\[ \langle xz \rangle = \dot{y} \tau_R \langle x^2 \rangle = \dot{y} \tau_R R_{||}^2 \]

whereas if \( \hat{n} \) is aligned in the \( z \)-direction,

\[ \langle xz \rangle = \dot{y} \tau_R R_1^2 \]

Furthermore, given that the shear torque coefficients \( \gamma_1 \) and \( \gamma_2 \) are defined in ELP theory [32] by the relationship

\[ \Gamma = \hat{n} \times \left[ \gamma_1 \left( \frac{dn}{dt} - (\omega \times \hat{n}) \right) + \gamma_2 (\hat{n} \cdot A) \right] \]

whenever the director is oriented along the \( x \)-direction, a shear flow in the \( z \)-direction will exert a torque

\[ \Gamma_y = \frac{\dot{y}}{2} (\gamma_1 + \gamma_2) \]

On the other hand, if \( \hat{n} \) is along \( z \), Eq. 1-49 yields
If the incremental counterparts to Eqs. 1-50 and 1-51 are associated with the expression given by Eq. 1-45, substitution of the appropriate relationship for \( \langle \alpha \rangle \) in these two cases therefore yields

\[
\frac{1}{2} \left( \delta \gamma_1 + \delta \gamma_2 \right) \delta \alpha_2 = \left( \frac{ckB}{N} \right) \tau_R \left( 1 - \frac{R_{\parallel}^2}{R_\perp^2} \right)
\]

and

\[
\frac{1}{2} \left( \delta \gamma_1 + \delta \gamma_2 \right) \delta \alpha_3 = \left( \frac{ckB}{N} \right) \tau_R \left( \frac{R_\perp^2}{R_{\parallel}^2} - 1 \right)
\]

where use has been made of Eqs. 1-17 and 1-18. Adding and subtracting these two equations, one obtains the additional relationships

\[
\delta \gamma_1 = \left( \frac{ckB}{N} \right) \tau_R \left( \frac{R_\perp^2 - R_{\parallel}^2}{R_\perp^2 R_{\parallel}^2} \right)^2
\]

and

\[
\delta \gamma_2 = \left( \frac{ckB}{N} \right) \tau_R \left( \frac{R_\perp^4 - R_{\parallel}^4}{R_\perp^2 R_{\parallel}^2} \right)
\]

It will be noted from Eqs. 1-34, 1-40, and 1-41 that, as expected, the LCP solution increments to the Miesowicz viscosities are predicted to be uniformly positive, with relative magnitudes that depend on the temperature- and solvent-dependent anisotropic chain dimensions and friction factors of the particular solvated polymer. In contrast, Eqs. 1-52, 1-53, and 1-55 indicate that the solution increments \( \delta \alpha_2, \delta \alpha_3, \) and \( \delta \gamma_2 \) are unrestricted in their value. Specifically, all three increments are
predicted to be positive if \( R_\perp > R_\parallel \), zero if \( R_\perp = R_\parallel \), and negative if \( R_\perp < R_\parallel \). Finally, Brochard’s analysis implies that the solution increment to \( \delta \gamma_1 \) will be zero in the event the LCP chains assume an isotropically random, spherical conformation, being otherwise positive with a quadratic relationship to the difference \( R_\perp^2 - R_\parallel^2 \).

Taking ratios of the various increments to isolate their dependence on the purely geometric influence of LCP chain anisotropy, one sees for instance that

\[
\frac{\delta \eta_b}{\delta \eta_c} = \left( \frac{R_\perp}{R_\parallel} \right)^4
\]

Hence, for globally oblate chain conformations, it is expected that \( \delta \eta_b > \delta \eta_c \), whereas the reverse inequality should be observed if the chains are conformationally prolate. Similarly comparing the increments \( \delta \alpha_2 \) and \( \delta \alpha_3 \), since

\[
\frac{\delta \alpha_3}{\delta \alpha_2} = \left( \frac{R_\perp}{R_\parallel} \right)^2
\]

it is apparent that the relationship \( \delta \alpha_3 > \delta \alpha_2 > 0 \) is predicted for \( R_\perp > R_\parallel \), whereas one expects \( \delta \alpha_3 < \delta \alpha_2 < 0 \) if \( R_\perp < R_\parallel \). Next, comparison of \( \delta \gamma_1 \) to \( \delta \eta_b \) and \( \delta \eta_c \) respectively reveals that

\[
\frac{\delta \gamma_1}{\delta \eta_b} = \left( 1 - \frac{R_\parallel^2}{R_\perp^2} \right)^2
\]

and

\[
\frac{\delta \gamma_1}{\delta \eta_c} = \left( \frac{R_\perp^2}{R_\parallel^2} - 1 \right)^2
\]

The quadratic form of these two viscosity increment ratios implies that they each have double-valued solutions within certain ranges of the dependent variable. Equivalently stated, the ratio \( \frac{\delta \gamma_1}{\delta \eta_b} \) can in principle be uniquely associated with prolate coil conformations only if \( R_\parallel/R_\perp > 1 \), whereas unique identification of the ratio \( \frac{\delta \gamma_1}{\delta \eta_c} \)
with oblate coil conformations is possible only if $R_{\perp}/R_{||} > \sqrt{2}$.

Lastly, in spite of the fact that the dependence of the splay and bend nematic viscosities on the squared magnitude of $\alpha_3$ and $\alpha_2$ algebraically excludes the possibility of expressing the ratios $\delta\eta_{\text{splay}}/\delta\gamma_1$ and $\delta\eta_{\text{bend}}/\delta\gamma_1$ solely as functions of the chain anisotropy ratio $R_{\perp}/R_{||}$, it can rigorously be argued on the basis of typical pure nematic solvent values for $\gamma_1$, $\alpha_2$, $\alpha_3$, $\eta_b$, and $\eta_c$ that both $\delta\eta_{\text{splay}}$ and $\delta\eta_{\text{bend}}$ should be larger than or equal to $\delta\gamma_1$ in the event $R_{\perp} > R_{||}$, whereas both of these solution viscosity increments should be smaller than $\delta\gamma_1$ if $R_{\perp} < R_{||}$. The qualitative and quantitative implications of the various viscosity increment relationships derived in the Brochard model will subsequently be drawn on in the context of interpreting the body of experimental results obtained in studying the viscoelastic behavior of the side-chain LCP/LC mixtures investigated in this work.

C. EXPERIMENTAL METHODS FOR MEASURING THE ANISOTROPIC VISCOELASTIC COEFFICIENTS OF DILUTE NEMATIC LCP SOLUTIONS

1. DYNAMIC LIGHT-SCATTERING TECHNIQUES

Compared with conventional isotropic liquids, one of the most distinguishing features of nematic liquid-crystalline fluids is their turbidity. Early in the study of this phenomenon, Chatelain [37] demonstrated that the light which is scattered by an oriented nematic sample is strongly depolarized and exhibits a marked angular variation in its intensity. It is now well established that the intense, depolarized scattering of light by nematic LCs originates from Brownian fluctuations in the orientation of the nematic director $\hat{n}$. Furthermore, these fluctuations are dynamic in
nature, and therefore possess characteristic relaxation spectra whose long-wavelength components are describable by the equations of nemato-hydrodynamics. The fundamental relationships interrelating the angular dependence of the intensity and long-wavelength relaxation frequency distribution of depolarized light scattered by oriented nematic monodomains were first derived by the Orsay liquid crystal group headed by deGennes [38,39]. The main features of their work will now be summarized.

If the average orientation of the nematic director, \( \hat{n} \), is assumed to be along the z-axis of a spatially fixed Cartesian coordinate system, then slowly varying, periodic fluctuations in this orientation at any position \( \vec{r} \) in a sample may be described by non-zero components \( \delta n_{x}(\vec{r}) \) and \( \delta n_{y}(\vec{r}) \) in either of the two directions orthogonal to \( \hat{n} \). In the absence of any additional applied field, the total Frank curvature free energy per unit volume of the nematic sample, \( V \), associated with such rotational perturbations of the director is given by

\[
F_d = \frac{1}{2} \int_V \left\{ K_{11} \left( \frac{\partial n_x}{\partial x} + \frac{\delta n_x}{\delta y} \right)^2 + K_{22} \left( \frac{\partial n_x}{\partial y} - \frac{\delta n_x}{\delta x} \right)^2 + K_{33} \left[ \left( \frac{\partial n_x}{\partial x} \right)^2 + \left( \frac{\delta n_x}{\delta z} \right)^2 \right] \right\} d\vec{r} \tag{1-60}
\]

The director fluctuations may be more readily analyzed in terms of parameters which are intrinsic to light-scattering experiments by alternatively expressing the components \( \delta n_{u}(\vec{r}) \) as their Fourier inverse quantities,

\[
\delta n_{u}(\vec{q}) = \int_V \delta n_{u}(\vec{r}) e^{i(\vec{q} \cdot \vec{r})} d\vec{r} \quad u = x, y \tag{1-61}
\]

where the scattering wave-vector \( \vec{q} \) represents the vectorial difference between the propagation wave-vectors, \( \vec{k}_{i} \) and \( \vec{k}_{f} \), of the incident and scattered light beams, i.e.,
\( \mathbf{q} = \mathbf{k}_i - \mathbf{k}_f \)

The polarization states of \( \mathbf{k}_i \) and \( \mathbf{k}_f \) are given by the unit vectors \( \hat{i} \) and \( \hat{r} \), respectively. It is furthermore convenient to refer the orthogonal components of the distortions to a coordinate frame such that, at any particular scattering angle, one of the components lies in the plane defined by \( \mathbf{q} \) and \( \hat{n} \), the other component being oriented perpendicular to this plane. This procedure defines two rotationally invariant, decoupled distortion eigenmodes whose basis vectors are given by

\[
\hat{e}_2 = \hat{n} \times \mathbf{q} / |\hat{n} \times \mathbf{q}| \quad 1-63
\]

and

\[
\hat{e}_1 = \hat{e}_2 \times \hat{n} \quad 1-64
\]

Transformed in this manner, the components \( \delta n_1(\mathbf{q}) \) along \( \hat{e}_1 \) and \( \delta n_2(\mathbf{q}) \) along \( \hat{e}_2 \) account respectively for admixtures of splay and bend, and twist and bend contributions to the director fluctuations, as Figure 1-8 illustrates. Equation 1-60 is accordingly re-expressed in the transformed coordinate frame as

\[
F_d = \frac{1}{2} \sum_q \left[ |\delta n_1(\mathbf{q})|^2 (K_{11}q_1^2 + K_{33}q_3^2) + |\delta n_2(\mathbf{q})|^2 (K_{22}q_2^2 + K_{33}q_3^2) \right] \quad 1-65
\]

where \( q_\parallel \) and \( q_\perp \) represent the magnitudes of the components of \( \mathbf{q} \) respectively parallel and perpendicular to \( \hat{n} \). Since the director fluctuations are Brownian in origin, thermal averages of the quantities \( |\delta n_1(\mathbf{q})|^2 \) may be obtained by invoking the Boltzmann equipartition theorem of classical thermodynamics, which states that the average free energy per degree of freedom at thermal equilibrium is equal to \( \frac{1}{2} k_B T \), \( k_B \) being the Boltzman constant. Applying this principle to Eq. 1-65, one obtains the result
Figure I-8: (a) Illustration of the two director distortion eigenmodes observable by DLS techniques; (b) Components of the deformation in the $\delta n_1$ mode: bend and splay; (c) Components of the deformation in the $\delta n_2$ mode: bend and twist.
\[
\left\langle \Delta n_\nu(\mathbf{q}) \right\rangle = \frac{k_B T}{K_{\nu \nu} A_1 + K_{33} A_1^2} \quad \nu = 1, 2 \tag{1-66}
\]

where the brackets \( \langle \rangle \) denote a thermal average at the temperature \( T \).

The intensity of depolarized light that is scattered in consequence of thermally driven fluctuations in \( \hat{n} \) represents the average square magnitude of the outgoing electric field \( \mathbf{E}_{\text{out}}(\mathbf{r'}) \), observed at \( \mathbf{r} \) and polarized along \( \hat{\mathbf{r}} \), which is emanated by oscillating dipoles \( \mathbf{P}(\mathbf{r}) \) within the illuminated sample volume. The latter are induced by interaction of the nematic medium with the electric field \( \mathbf{E}_{\text{in}}(\mathbf{r}) = iE_0 e^{i(\mathbf{k}_i \cdot \mathbf{r})} \) of the incident light beam of magnitude \( E_0 \) polarized along \( \hat{i} \), and are given by

\[
\mathbf{P}(\mathbf{r}) = \left( \frac{1}{4\pi} \right) \left[ \mathbf{\varepsilon}(\mathbf{r}) - \mathbf{I} \right] \cdot \mathbf{E}_{\text{in}}(\mathbf{r}) \tag{1-67}
\]

where \( \mathbf{\varepsilon}(\mathbf{r}) \) represents the local dielectric tensor of the medium, and \( \mathbf{I} \) is the unit tensor. From classical electrodynamic theory, the electric field radiated in the direction \( \mathbf{R} = \mathbf{r} - \mathbf{r} \) by a dipole at \( \mathbf{r} \), oscillating at angular frequency \( \omega \), is known to be

\[
\mathbf{E}(\mathbf{r}) = \left( \frac{2}{\mathbf{R}} \right) \frac{\omega^2}{\mathbf{c}^2 R} e^{i(\mathbf{k}_f \cdot \mathbf{R})} \tag{1-68}
\]

where \( \mathbf{R} = |\mathbf{R}|, \mathbf{E}(\mathbf{r}) \) is the component of \( \mathbf{P}(\mathbf{r}) \) normal to \( \mathbf{R} \), and \( c \) is the speed of light in a vacuum.

At a point of observation \( \mathbf{r} \) suitably distant from \( \mathbf{r} \), assuming that the scattered radiation propagates in a nearly isotropic medium, the magnitude of the depolarized field at \( \mathbf{r} \) is obtained as the projection on \( \mathbf{r} \) of each of the contributions \( \mathbf{E}(\mathbf{r}) \) originating from the various differential elements of the scattering volume, namely
\[ \hat{r} \cdot \mathbf{E}_{\text{out}}(\hat{r}) = \left[ \frac{E_0}{R} \right] e^{i \mathbf{k} \cdot \hat{r}} \cdot \alpha \]  

where the factor

\[ \alpha = \left( \frac{\omega}{4\pi c^2} \right)^2 \int_V \hat{r} \cdot [\varepsilon(\hat{r}) \cdot \mathbf{I}] \cdot \hat{r} e^{-i(\mathbf{q} \cdot \hat{r})} \, d\hat{r} \]  

defines a quantity referred to as the scattering length. For non-zero \( \mathbf{q} \), the term - \( \mathbf{I} \) does not contribute to the integral in Eq. 1-70, and may be disregarded. Furthermore, taking into account the fact that

\[ \varepsilon(\mathbf{q}) = \int_V \varepsilon(\hat{r}) e^{-i(\mathbf{q} \cdot \hat{r})} \, d\hat{r} \]  

it is clear that the scattering length may be equivalently expressed as

\[ \alpha = \left( \frac{\omega}{4\pi c^2} \right) \hat{r} \cdot \varepsilon(\mathbf{q}) \cdot \hat{r} \]  

The thermally-averaged square magnitude of \( \alpha \) in turn defines the related quantity \( \sigma \), referred to as the scattering cross-section, i.e.,

\[ \sigma = \langle |\alpha(\mathbf{q})|^2 \rangle \]  

It remains to evaluate the fluctuating components of \( \varepsilon(\mathbf{q}) \), deriving from the orientational fluctuations in \( \hat{n} \), which couple the incident and scattered radiation electric fields. For a uniaxial nematic medium, the relevant element of \( \varepsilon \) interrelating these two fields is

\[ \hat{r} \cdot \varepsilon \cdot \hat{r} = \varepsilon_{\text{if}} - \varepsilon_{\text{a}} \left( n_i n_f \cdot \frac{1}{3} \right) \]  

where \( \varepsilon \) represents the rotationally-averaged magnitude of \( \varepsilon \), \( \varepsilon_{\text{a}} = \varepsilon_\parallel - \varepsilon_\perp \) is the dielectric anisotropy of the nematic medium, and \( n_i = \hat{n} \cdot \hat{r} \) and \( n_f = \hat{n} \cdot \hat{r} \) are the components of \( \hat{n} \) along the polarization directions of the incoming and scattered light.
rays, respectively. Substitution into Eq. 1-74 of the expression for the fluctuating Fourier components of $\hat{n}$, resolved in terms of the two distortion eigenmodes defined above, yields the result

$$\hat{\mathbf{r}} \cdot \mathbf{e}(q) \cdot \mathbf{i} = \delta e_{\mathbf{i},d}(q) = \varepsilon_2 \sum_{v=1,2} \delta n_{\mathbf{v},d}(q) |i_{\mathbf{v},f_{\parallel}} + i_{\mathbf{v},f_{\perp}}|$$  \hspace{1cm} (1-75)

where the terms

$$|i_{\mathbf{v},f_{\parallel}} + i_{\mathbf{v},f_{\perp}}| = (\hat{\mathbf{r}} \cdot \mathbf{e}_v)(\hat{\mathbf{r}} \cdot \hat{n}) + (\hat{\mathbf{r}} \cdot \hat{n})(\hat{\mathbf{r}} \cdot \mathbf{e}_v)$$  \hspace{1cm} (1-76)

in the summation represent appropriate geometric weighting factors for each of the eigenmodes.

Combining Eqs. 1-66, 1-72, 1-73, and 1-75, one finally obtains as an expression for the scattering cross-section per unit scattering volume, per unit solid angle, $\Omega$, in the direction of the scattered beam, the relationship

$$\frac{d\sigma}{d\Omega} = \left(\frac{\pi \varepsilon_2}{\lambda}\right)^2 k_B \sum_{v=1,2} \frac{(i_{\mathbf{v},f_{\parallel}} + i_{\mathbf{v},f_{\perp}})^2}{K_{\mathbf{v},f_{\parallel}^2} + K_{\mathbf{v},f_{\perp}^2}}$$  \hspace{1cm} (1-77)

where use has been made of the substitute variable $\lambda = \omega/2\pi c$. Since the scattered light intensity measured in any particular direction is proportional to $d\sigma/d\Omega$, Eq. 1-77 demonstrates that the intensity associated with either distortion mode is an inverse function of the angularly-weighted sum of the Frank elastic constants appropriate to the mode. Equivalently stated, the larger the magnitude of the torque on $\hat{n}$ exerted by the restoring force of the molecular mean field which is responsible for the existence of nematic orientational order in the liquid crystal, the smaller will be the thermally-averaged magnitude of the various types of curvature distortion.

If the energetic resistance to these distortions is increased by applying an electric or magnetic field along the average alignment direction in the sample (i.e.,
parallel to \( \hat{n} \), Eq. 1-77 must be accordingly modified. Augmentation of the nematic mean-field potential of a particular sample by the application of a supplementary aligning field has the effect of reducing the intensity of light scattered by the sample according to either

\[
\frac{d\sigma}{d\Omega} = \left( \frac{\alpha \pi n_0}{\lambda} \right)^2 k_B T \sum_{\nu = 1,2} \frac{(i_m f_{\|} + i_m f_{\perp})^2}{K_{\nu n} A_{\perp}^2 + K_{33} Q_{\|}^2 + \varepsilon \varepsilon_r E^2}
\]

or

\[
\frac{d\sigma}{d\Omega} = \left( \frac{\alpha \pi n_0}{\lambda} \right)^2 k_B T \sum_{\nu = 1,2} \frac{(i_m f_{\|} + i_m f_{\perp})^2}{K_{\nu n} A_{\perp}^2 + K_{33} Q_{\|}^2 + \chi_a H^2}
\]

1-78

1-79

depending on the nature of the aligning field. In these equations, \( E \) and \( H \) represent the magnitudes of the applied electric and magnetic fields, respectively, and \( \chi_a = \chi_{\|} - \chi_{\perp} \) is the anisotropy in the diamagnetic susceptibility of the sample.

The frequency distribution of the scattered light is obtained by Fourier analysis of the time dependence of the director fluctuations. Since a full description of director relaxation processes via Leslie-Erickson hydrodynamic theory is quite mathematically involved and lengthy, it suffices here merely to indicate the main results of this analysis. As discussed by deGennes [40], derivation of appropriate expressions for the frequency bandwidth of light scattered in consequence of fluctuations in \( \hat{n} \) proceeds from the assumption that, conjugate to either of the eigenmode distortions \( \delta n_{\|}(\vec{q}) \) is an effective restoring 'force' representing the corresponding component of the nematic mean field. If attention is restricted to director relaxation processes which occur on a time scale amenable to instrumental detection by DLS measurement techniques, the Leslie-Erickson equations then predict that the distortions will relax toward equilibrium under the influence of this
restoring force in a purely viscous manner – i.e., they diffusively dissipate with time rather than oscillate.

In this event, the frequency distribution of the scattered light at any given angle of observation is predicted to be described by a single Lorentzian peak of halfwidth $\Delta \omega_v(q)$ centered on the incident light frequency, $\omega_0$. This half-width represents the inverse of the characteristic time, $\tau_v(q)$, for relaxation of the director distortions, or equivalently, their relaxation rate, $\Gamma_v(q)$, i.e.,

$$\Delta \omega_v(q) = \frac{1}{\tau_v(q)} = \Gamma_v(q) = \frac{K_{0v}a_{\perp}^2 \pm K_{3v}a_{\parallel}^2}{\eta_v(q)} \quad u = 1, 2 \quad 1-80$$

The effective viscosity functions defined by Eq. 1-80, relating the two eigenmode distortion relaxation rates to their respective restoring forces, $K_v(q)$, are given as explicit functions of the components of $q$ by the relationships

$$\eta_1(q) = \gamma_1 \cdot \frac{(\alpha_3q_{\perp}^2 - \alpha_2q_{\parallel}^2)^2}{\eta_1 a_{\perp}^4 + (\alpha_1 + \alpha_3 + \alpha_4 + \alpha_5)q_{\parallel}^2 + \eta_2 a_{\parallel}^4} \quad 1-81$$

and

$$\eta_2(q) = \gamma_1 \cdot \frac{\alpha_2q_{\parallel}^2}{\eta_1 a_{\perp}^2 + \eta_2 a_{\parallel}^4} \quad 1-82$$

In the following chapter, it will be explained in greater detail how decay rates specifically characterizing viscoelastic relaxations of splay, bend, and twist director distortions in a nematic monodomain sample can be obtained by DLS techniques from time-domain analysis of the depolarized scattered light intensity autocorrelation functions measured at certain angles, using appropriate combinations of sample director orientation with respect to the polarization states of the incident and scattered light rays.
2. FREDERICKSZ TRANSITION TECHNIQUES

Fredericksz transition techniques offer perhaps the simplest, most direct method for measurement of the Frank elastic constants for splay, bend, and twist director distortions in a nematic LC monodomain. These methods consist of determining the critical value of an electric or magnetic field, applied normal to \( \hat{n} \) in an appropriately aligned monodomain sample, above which the director alignment distorts in response to the torque exerted by the applied field [41-43]. Generally stated, the Fredericksz transition threshold response in a thin nematic layer reflects a condition of thermodynamic balance between the competitive influences of the orientation imposed on \( \hat{n} \) by the external field and that imposed by the bounding surfaces of the layer. The importance of the phenomenon from an experimental point of view is that the critical fields, \( E_c \) or \( H_c \), can be related to the particular Frank elastic constant corresponding to the deformation mode at the transition.

In more precise mathematical detail, the application of an electric or magnetic field to an aligned LC monodomain increases the free energy density of the unperturbed sample by amounts

\[
\Delta F_d = \frac{1}{2} \left( \varepsilon_1 \left| \mathbf{E} \right|^2 - \varepsilon_a \left( \mathbf{n} \cdot \mathbf{E} \right)^2 \right)
\]

and

\[
\Delta F_d = \frac{1}{2} \left( \chi_1 \left| \mathbf{H} \right|^2 - \chi_a \left( \mathbf{n} \cdot \mathbf{H} \right)^2 \right)
\]

respectively. Equations 1-83 and 1-84 imply that, for nematics with positive dielectric or diamagnetic susceptibilities, \( \varepsilon_a \) and \( \chi_a \), neglecting energetic boundary constraints, the net free energy density of the sample will be minimized if \( \hat{n} \) is aligned collinear with \( \mathbf{E} \) or \( \mathbf{H} \). However, the unperturbed alignment state of the
sample in the absence of an applied field is in fact determined by the existence of surface layer forces, whose imposition of unidirectional alignment in the bulk sample is mediated by the elasticity of the sample.

As Figure 1-9 illustrates for each of the three geometrically distinct orientations of an applied field with respect to the surface-imposed preferred alignment direction, at less-than-critical applied field strengths, the mean-field elastic torque on \( \vec{n} \) exceeds that due to the external field, and the director will retain its unperturbed configuration. Above \( E_c \) or \( H_c \), on the other hand, the competition between these opposing torques will give rise to curved conformations of the director within the sample. Taking the case illustrated in Figure 1-9A with a normally-incident magnetic field as a specific example, one may derive appropriate relationships for \( H_c \), as well as for the distorted director profile at \( \vec{H} > H_c \), by minimizing the expression for the total free energy density of the sample with respect to variations in the director pattern as follows.

In a nematic slab of thickness \( d \), a static distortion of the director in any plane normal to the z-axis can be described by the tilt angle \( \theta(z) \), whence the director profile assumes the form

\[
\vec{n}(z) = [\cos \theta(z), 0, \sin \theta(z)]
\]

1-85

Neglecting the orientation-independent contribution of the term \( \chi_1 |\vec{H}|^2 \) in Eq. 1-84, combination of Eqs. 1-60, 1-84, and 1-85 then yields for the total free energy density of the nematic sample in this case

\[
F_d^{\text{tot}} = F_d + \Delta F_d = \frac{1}{2} \int_0^d \left[ (K_{11} \cos^2 \theta + K_{33} \sin^2 \theta) \left( \frac{\delta \theta}{\delta z} \right)^2 - \chi_4 |\vec{H}|^2 \sin^2 \theta \right] dz \quad 1-86
\]

If the director alignment is assumed to be rigidly maintained at the boundaries of the
Figure I-9: The three principal types of Fredericksz deformation occurring on application of a magnetic field perpendicular to the unperturbed alignment direction of the nematic director.
slab (i.e., $\theta = 0$ at $z \pm d/2$, corresponding to the condition of strong surface anchoring),
minimization of $F_d^{tot}$ leads to the result

$$\left(K_1 \cos^2 \theta + K_{33} \sin^2 \theta \right) \left(\frac{\delta \theta}{\delta z}\right)^2 + \chi_d |\mathbf{H}|^2 \sin^2 \theta = C$$  \hspace{1cm} 1-87

where the constant $C$ is determined by the fact that $\theta(z)$ has a maximum value, $\theta_{\text{max}}$, in the center of the slab. Hence, $\delta \theta/\delta z|_{z=0} = 0$, and

$$C = \chi_d |\mathbf{H}|^2 \sin^2 \theta_{\text{max}}$$  \hspace{1cm} 1-88

Substituting this result into Eq. 1-87, one obtains the equation

$$|\mathbf{H}| \int_0^{\theta_{\text{max}}} \frac{d\theta}{\left[\frac{K_1 \cos^2 \theta + K_{33} \sin^2 \theta}{\chi_a (\sin^2 \theta_{\text{max}} - \sin^2 \theta)}\right]^{1/2}}$$  \hspace{1cm} 1-89

whose solution in the limit $\theta_{\text{max}} \rightarrow 0$ yields for the threshold field at the onset of the
Frederickscz distortion

$$H_c = \frac{\pi}{d} \left(\frac{K_{11}}{\chi_a}\right)^{1/2}$$  \hspace{1cm} 1-90

For $|\mathbf{H}| < H_c$, small changes in the director configuration of the sample are
unstable with respect to the free energy minimum, and therefore relax to the
equilibrium profile $\theta(z) = 0$ for all values of $z$. For $|\mathbf{H}| > H_c$, on the other hand, $\theta(z)$
at any arbitrary point in the sample can be computed from the expressions [42,43]

$$\frac{|\mathbf{H}|}{H_c} = \frac{2}{\pi} \int_0^{\theta_{\text{max}}} \left(\frac{1 + \kappa \sin^2 \theta}{(\sin^2 \theta_{\text{max}} - \sin^2 \theta)}\right)^{1/2} d\theta = 1 + \frac{1}{4} (\kappa + 1) \theta_{\text{max}}^2 + ..., \hspace{1cm} 1-91$$
and

\[
\frac{\mathcal{Z}}{d} = \frac{H_c}{\pi l H_1} \int_0^\theta \left( \frac{1 + \kappa \sin^2 \theta}{\sin^2 \theta_{\text{max}} - \sin^2 \theta} \right)^{1/2} d\theta
\]

\[
= \frac{1}{\pi} \sin^{-1} \left( \frac{\theta}{\theta_{\text{max}}} \right) - \theta (\theta_{\text{max}}^2 - \theta^2)^{1/2} \frac{1 + 3\kappa + ...}{12\pi \left[ 1 + \frac{1}{4}(\kappa + 1) \theta_{\text{max}}^2 + ... \right]}
\]

where

\[
\kappa = (K_{33} - K_{11})/K_{11}
\]

Thus, in this geometric arrangement, the Frederickscz threshold condition can be used to directly determine the splay modulus $K_{11}$ of the sample, whereas the director profile at applied fields exceeding $H_c$ depends on the ratio $K_{33}/K_{11}$.

Similar analysis can be applied to the other two geometries shown in Figure 1-9, yielding comparable expressions for $H_c$ which are instead functions of the twist and bend elastic constants of the sample. The threshold transition measurements may also be made using an electric field. In fact, there is a complete analogy between electric and magnetic fields as far as the Frederickscz threshold is concerned [43]. Above the threshold field, however, important differences between these two types of distorting fields may arise. Specifically, since the magnetic susceptibilities of nematic liquids and their anisotropies are typically small, it is generally valid to assume that a magnetic field applied to a monodomain film is spatially homogeneous within the film. By contrast, nematic dielectric permittivities and their anisotropies tend characteristically to be much larger in value, with the result that the dielectric field strength across a sample film will be non-uniform. In addition, precautions have to be taken in the case of electric field Frederickscz measurements to avoid ionic sample impurities, inasmuch as these can lead to the development of conduction-induced instabilities above the Frederickscz threshold [44].
Attention must finally be called to the effect of surface anchoring conditions on the behavior of a sample. The derivation of Eq. 1-90 and its analogues is predicated on the assumption that, at super-critical applied fields, the director retains its unperturbed alignment orientation at the boundaries of the sample. If this is not the case, the actual field strengths inducing the appropriate Frederickscz distortion will be correspondingly reduced. Generalized expressions for the Frederickscz threshold fields, accounting for variable surface anchoring strengths, are given by [45-47]

\[ H_c = \pi \left( \frac{K_{ii}}{\chi_a} \right)^{1/2} \beta \]  

and

\[ V_c = \pi \left( \frac{K_{ii}}{\varepsilon_a} \right)^{1/2} \beta \quad i=1,2,3 \]  

where the proportionality factor \( \beta \) is related to a characteristic sample dimension \( b \), referred to as the extrapolation length, by

\[ \pi \beta \tan \left( \frac{\pi \beta}{2} \right) = \frac{d}{b} \]  

The extrapolation length serves as a measure of the anchoring strength, and is defined in terms of the ratio between the bulk and surface nematic interaction potentials, \( U \) and \( U_{WN} \), namely

\[ b = \frac{U}{U_{WN}} a \]  

where the length \( a \) represents a typical molecular dimension of the nematic. Strong anchoring conditions will prevail if \( U_{WN} \) is comparable in magnitude to \( U \), in which case \( b = a \), and \( \beta \) approaches unity. If on the other hand \( U_{WN} \leq U \), \( b \) becomes
appreciable in magnitude compared to the sample film thickness, and the director alignment at the boundaries of the film becomes subject to the distorting influence of the applied field in the same manner as in the bulk sample. Equations 1-94, 1-95, and 1-96 then imply that reducing in the surface anchoring strength leads, via progressive reduction in the value of $\beta$, to lowering of either $V_c$ or $H_c$.

Determination of the average state of alignment of the director in a Fredericksch transition experiment can in principle be accomplished by monitoring the value of any anisotropic property of the nematic sample as a function of the applied field. Optical birefringence measurements and capacitance measurements represent two commonly used techniques well-suited to the use of magnetic and electric distorting fields, respectively. In the former method, one detects the polarization state of linearly polarized incident light transmitted by the sample. The intensity of the transmitted light, subsequently passed through a 90° crossed analyzer, shows a discontinuity at the Fredericksch threshold. A pattern of sequential interference maxima and minima is observed on further increasing the applied field, indicative of the phase retardation angle acquired by the light on traversing the distorted director profile. Capacitance detection methods, on the other hand, consist of measuring the average dielectric permittivity of the nematic sample, which similarly varies in response to field distortions of the director orientation. As both of these methods were used in this work to determine the splay and bend elastic constants of various monodomain samples, more extensive descriptions of the experimental aspects of the techniques will be given in the following chapter.
The depolarized dynamic light-scattering and Frederickscz transition techniques theoretically outlined in the previous two sections of this chapter represent complementary methods for probing the anisotropic viscoelastic behavior of nematic monodomain samples under conditions of thermal and mechanical equilibrium. An alternative route for investigating the anisotropic properties of nematic fluids is provided by studying their non-equilibrium hydrodynamic stress response on being subjected to a shear flow field. In this regard, it is well known that nematic liquid crystals may be broadly divided into two classifications based on the sign of the ratio of their Leslie coefficients $\alpha_2$ and $\alpha_3$. Given that $\alpha_2$ is invariably negative in low-molecular-weight rod-like nematic LCs [48], this classification scheme therefore qualitatively distinguishes the sign of the coefficient $\alpha_3$.

In both instances, the stresses associated with a shear flow field couple with the director orientation in a nematic monodomain via hydrodynamic torques which act to rotate the director away from its equilibrium alignment direction. As demonstrated below, however, the shear flow response of a nematic in which both $\alpha_2$ and $\alpha_3$ are negative is such that the director orientation with evolve, asymptotically approaching a steady-state alignment angle with respect to the flow direction at which a balance of hydrodynamic torques is achieved. In a nematic characterized by $\alpha_3 > 0$, on the other hand, the hydrodynamic torque on $\vec{n}$ remains unbalanced at any orientation within the shear plane. In this case, neglecting the influence of elastic restoring forces, the director is predicted to rotate indefinitely in shear flow, resulting in an oscillatory response of the material functions of the fluid. These two characteristic responses of a nematic monodomain in shear flow are accordingly referred to as "shear-aligning" and "shear-tumbling", respectively.
On condition that certain simplifying assumptions are made, one may derive an analytical model for the shear flow evolution of the director in an initially homeotropic monodomain film within the context of Leslie-Erickson-Parodi (ELP) continuum hydrodynamic theory [32,49,50]. As Figure 1-10 illustrates, this model assumes first that motions of the nematic director in the shear flow field are restricted to the plane defined by the shear velocity (x-direction) and the velocity gradient (y-direction). It is further assumed that, at sufficiently high values of the characteristic dimensionless ratio $V_0 = v_0 \alpha z_0 / K_{11}$ (the Erickson number), elastic torques exerted on the director by the maintenance of homeotropic alignment at the boundary layers of the film are negligible in comparison with hydrodynamic shear torques.

Given these assumptions, ELP theory yields the following expressions for the linear momentum balance and the torque balance on the director:

\[
\tau_{yx} = \left[ \alpha_1 \sin^2 \theta \cos \theta + \eta_b - (\alpha_2 + \alpha_3) \cos^2 \theta \right] \frac{\delta v_x}{\delta y} + \left( \alpha_2 \cos^2 \theta - \frac{\delta \theta}{\delta t} \right) \frac{\alpha_3 \sin^2 \theta}{\gamma_1} \quad 1-98
\]

and

\[
\frac{\delta \theta}{\delta t} = \frac{\left( \alpha_3 \sin^2 \theta - \alpha_2 \cos^2 \theta \right)}{\gamma_1} \frac{\delta v_x}{\delta y} \quad 1-99
\]

where $\theta(y,t)$ is the angle that the director makes with respect to its initial alignment normal to the limiting surfaces at $y = 0$ and $y = d$. A constitutive relationship between the hydrodynamic portion of the applied shear stress and the local velocity gradient results on substituting Eq.1-99 into Eq.1-98, from which an angle-dependent apparent viscosity function may be defined:

\[
\eta_{\text{app}}(\theta) = \left[ \alpha_1 \sin^2 \theta \cos \theta + \eta_b - (\alpha_2 + \alpha_3) \cos^2 \theta - \frac{\left( \alpha_3 \sin^2 \theta - \alpha_2 \cos^2 \theta \right)}{\gamma_1} \right]^2 \quad 1-100
\]
Figure I-10: Schematic representation of the director response of a homeotropic nematic monodomain to a simple shear flow field, as assumed in the 2-D ELP hydrodynamic model described in the text.
The characteristic difference in the transient shear flow response of aligning and tumbling nematics is made evident by considering the bracketed right-hand term in Eq. 1-99. Assuming $\alpha_2 < 0$, one sees that if $\alpha_3 < 0$, a flow-alignment angle exists for which the torque on the director vanishes. Moreover in this case, it can be shown by differentiating Eq. 1-100 with respect to $\theta$ that, following an initial increase with increasing strain, the apparent viscosity of the sample will exhibit a single maximum, corresponding to a director orientation of $\theta = \pi/4$. With further increase in the strain, $\eta_{app}$ is predicted to decay to its steady-state value, attained at the flow-alignment angle. Finally, if the velocity gradient across the thickness of the sample is assumed to be uniform, hence equal to the macroscopic strain rate, $\dot{\gamma}$, an explicit expression for the director orientation as a function of the net applied strain obtains on integrating Eq. 1-99 with respect to time, i.e.,

$$\tan \theta = \left( \frac{\alpha_2}{\alpha_3} \right)^{1/2} \tanh \left[ \frac{\alpha_2 \alpha_3}{\alpha_3 - \alpha_2} ^{1/2} \right] \dot{\gamma}$$  \hspace{1cm} 1-101

whose asymptotic solution thus yields as the value of the flow-alignment angle

$$\theta_{f,a} = \tan^{-1} \left( \frac{\alpha_2}{\alpha_3} \right)$$  \hspace{1cm} 1-102

Returning to Eq. 1-99, one sees on the other hand that if $\alpha_2$ and $\alpha_3$ are of opposite sign (i.e., $\alpha_2 < 0$ and $\alpha_3 > 0$), no such flow-alignment angle exists, and the director is predicted to execute continual rotary motion with a periodic oscillation in the apparent viscosity. Differentiation of Eq. 1-100 in this case reveals that $\eta_{app}$ is repeatedly maximized for director orientations which are odd-integer multiple of $\pi/4$, whereas sequential minima occur whenever $\theta$ is an integer multiple of $\pi/2$. The analogous expression for the strain dependence of the director orientation in a shear-
tumbling sample is given by

\[
\tan \theta = \left( \frac{-\alpha_2}{\alpha_3} \right)^{1/2} \tan \left[ \frac{(-\alpha_2 \alpha_3)^{1/2}}{\alpha_3 - \alpha_2} \gamma \right]
\]

from which one obtains as an expression for the strain period of the oscillations

\[
\gamma_p = \frac{\pi (1 + \delta^2)}{\delta}
\]

where \(\delta = (-\alpha_3/\alpha_2)^{1/2}\).

The interpretive accuracy of this model will clearly be limited in the event the director moves out of the shear plane. In fact, the susceptibility of low-molecular-weight tumbling nematics to out-of-plane hydrodynamic instabilities has been previously shown by Leslie and Zuniga [51] to occur at relatively low Erickson number. Although full three-dimensional calculations are lacking, following the onset of an out-of-plane instability, it is reasonable to expect that the director orientation would tend to evolve toward alignment along the vorticity axis of the shear flow (i.e., perpendicular to the shear plane) in order to avoid experiencing further hydrodynamic torques. Depending on the rate of such an out-of-plane motion, one would in turn expect to observe either a concomitant damping or a complete suppression of the tumbling response of the fluid.

The presumption of negligible influence of Frank elasticity on the stress response of a tumbling nematic represents yet another potential source of quantitative inaccuracy in the proposed model. However, Burghardt and Fuller [49] have demonstrated via numerical modelling techniques that, when the transient shear stress contribution of elastic director torques is properly taken into account, the basic qualitative features of the present model are preserved in shear flow fields for which the Erickson number is sufficiently high. Specifically, these authors have
demonstrated that stress oscillations progressively approaching the periodic behavior predicted by the present model become apparent in the transient shear flow response of a hypothetically tumbling nematic when the Erickson number exceeds ~100 - 200. On the other hand, an important qualitative feature emerging from their work which differs from the predictions of the model proposed here is that, with increasing strain, the maximum and minimum intensity of the stress oscillations exhibited by tumbling nematics display a tendency to damp, whereas the cycle-averaged magnitude of the stress steadily increases. Both of these effects manifest the progressive elastic free energy penalty incurred by rotation of the director against the constraining influence of the alignment state maintained at the boundaries of the sample.

Taking into account the above remarks, it can be expected that the simplified model proposed in this section should be capable of providing at least a semi-quantitative description of the stress response of a nematic monodomain sample in simple shear flow. Accepting the restriction on the applicability of the model to shear flows for which the Erickson number is sufficiently large, so long as out-of-plane tumbling instabilities are either absent or occur on a time scale that is slow compared to the oscillation period of a shear-tumbling sample, one might expect readily to be able to discern from the rheological response of the sample the sign of the Leslie coefficient \( \alpha_3 \). Furthermore, if in shear-tumbling samples the strain period over one or more oscillation cycles is measurable, the ratio \( -\alpha_2 / \alpha_3 \) can in principle be uniquely determined. Coupled with DLS determination of the difference between these two coefficients, via \( \gamma_1 \), one can therefore obtain their values individually. In view of the predictions of the Brochard model, the significance of the ability to obtain even rough experimental estimates of \( \alpha_2 \) and \( \alpha_3 \) is immediately apparent.
CHAPTER II.
EXPERIMENTAL TECHNIQUES

A. MONODOMAIN SAMPLE PREPARATION AND TRANSITION TEMPERATURE MEASUREMENT

All of the experimental techniques used to measure viscoelastic distortions of the nematic director in the various solvents and side-chain LCP solutions characterized in this work required that the sample fluids be prepared as thin monodomain films having either homeotropic or homogeneous (planar) alignment. Specifically, the determination of sample bend elastic constants via magnetic field-induced Fredericksz transition measurements, the twist distortion-weighted Mode 2 DLS decay rate measurements, and viscometric characterization of director rotations in shear flow all necessitated that the nematic director in the sample films be homeotropically aligned at thermal equilibrium. In these cases, bulk orientation of the director perpendicular to the bounding surfaces either of a ~1 cm² ITO-coated glass cell, or of the cone-and-plate fixture of a Rheometrics RMS-300 rheometer, was accomplished by preliminary surface treatment with lecithin. (Monodomain preparation of one of the LCP mixtures in a glass cell alternatively coated with dimethyl silane was found to result in oblique pre-tilt of the director alignment. Further use of silane surface treatments was therefore abandoned.) The lecithin was applied as a dilute solution (~3% w/v) in ethanol. Following evaporation of the solvent, the deposited surfactant was lightly polished using a cotton swab until the residual film of the material was sufficiently uniform and thin as to no longer be visually evident.

Nematic phase homeotropic director alignment was verified for the various
samples introduced to the lecithin-treated glass cells by observation of characteristic angle-dependent emitted light intensity when viewed between crossed polars by light microscopy. While the state of alignment of samples introduced to the rheometer could not similarly be ascertained by polarized optical examination, these were likewise assumed to form homeotropic monodomains following a sufficient period of annealing. The basis for this conviction rests not only on having identically pre-treated the cone and plate surfaces with lecithin but, as will be demonstrated in the following chapter, on conformance of the initial stress-strain behavior of the fluids with the predictions of the anisotropic fluid dynamic theoretical model outlined in Chapter I.

The electric field Fredericksch transition determinations of splay elastic constants, and the Mode 1 and bend-weighted Mode 2 DLS relaxation measurements, on the other hand, were performed on homogeneously aligned monodomain samples. Uniform homogeneous alignment of the nematic director in sample films contained between the parallel surfaces of ITO glass sample cells used for these measurements was effected by laminating the glass surfaces with a rubbed polyimide coating. The material was spin-coat applied to the ITO glass as a polyamic acid solution. The latter was subsequently dehydrated in an elevated-temperature cure cycle, yielding a thin film (~0.2 - 0.5μ) of high-molecular-weight polyimide. The surface of the film was then unidirectionally rubbed using velvet fabric. It was verified that the director field within samples subsequently introduced to these cells was uniformly oriented in the rubbing direction by polarized microscopic observation of minimum light transmission through the samples at either of the extinction angles of the crossed polars.

Apart from their surface treatment, the various ITO glass cells prepared for containment of the monodomain samples were constructed in accord with the specific
measurement technique to be applied to a particular sample. Common to all the cells was the distance separating opposite glass faces (assumed to be the same as the resultant film thickness of the filled nematic samples). This distance was uniformly maintained at ~25μ by shimming outer edges of the glass pieces with 1 mil thick Mylar strips. The shimmmed cells were glued together under pressure using a two-part epoxy adhesive. The latter was allowed to cure, either for 24 hours at room temperature or for several hours in a 100°C drying oven, to high modulus prior to filling the cells with the various sample fluids by capillary flow.

In the case of the homeotropic cells intended for making electric field-dependent relaxation rate measurements, the cell thicknesses were determined precisely by an interferometric technique, illustrated in Figure II-1. This enabled calculation of the electric field strength acting on the director within a sample film at any given applied voltage. These cells required the additional attachment of copper electrode strips to the exposed ITO/lecithin-coated edges of opposing glass faces, in order to permit insertion of the cells in the index-matching quartz vat of the light-scattering instrument. The copper strips were adhered to the ITO faces of these cells using electrically conductive silver paint, then secured with an overcoating of epoxy adhesive.

Finally, parallel lines were scored with a diamond-tipped scribe through the ITO surfaces of the polyimide-coated glass pieces intended for use in cells for electric field-induced splay Fredericksocz transition measurements. This procedure accomplished electrical insulation of the regions of the glass plates between which the Mylar spacers were placed from those which were ultimately intended for containment of sample fluid whose capacitance was to be measured. Were it not for this procedural step, the capacitance of the Mylar strips would have been averaged into the values of the anisotropic dielectric permittivities, ε₁ and ε₁₁, obtained from
Figure II-1: Set-up for interferometric measurement of sample cell thicknesses. On rotation of the goniometer-mounted cell, interference among the parallel rays of the laser light, reflected at the air/glass interfaces on either side of the unfilled gap in the cell, leads to a series of primary maxima and minima in the exiting light intensity which is observed on a paper screen. The thickness, $d$, of the air gap is related to the angular separation of sequential maxima or minima in the reflected beam intensity by the relationship
\[
d = \frac{\lambda}{2} (\cos \theta_i - \cos \theta_{i+1})
\]
In practice, one measures ~10 - 15 interference maxima or minima and computes an average value of $d$, thus achieving a typical RMS measurement precision of $\pm 0.01\mu$. 
Phase transition temperatures in the monodomain samples were established by polarized microscopic examination. Appropriately filled and sealed sample cells were placed in a Mettler FP82 hot stage and observed through several heating and cooling cycles to determine the pertinent transition temperatures. As for the solvents, 5CB and 8CB exhibited discrete, reproducible $T_{NI}$ values of $34.9 \pm 0.1$ °C and $39.8 \pm 0.1$ °C, respectively, in both homeotropic and planar cells. Discrete, apparent first-order nematic-to-smectic transitions were also detectable for 8CB and its LCP solutions in the planar cells due to the divergent increase in the twist and bend Frank elasticity of the fluids at $T_A N$, which led to the obliteration of birefringent surface-layer alignment imperfections in the samples. Based of this criterion, $T_A N = 32.8 \pm 0.1$ °C was determined for 8CB. The N→A transition of the 8CB/LCP mixture whose viscoelastic properties are discussed in the following chapter (3-PVE-30) was similarly determined to occur at $T_A N = 30.6 \pm 0.1$ °C.

On the other hand, all of the 5CB and 8CB LCP solutions exhibited phase-separated biphasic temperature regions on traversing the N→I transition. The effect was specific to the particular dissolved polymer, although the lower phase inversion temperature was typically ~ 0.3 - 0.8 °C below the $T_{NI}$ of the pure nematic solvent. Furthermore, in those cases where several concentrations of a given LCP/solvent mixture were prepared, the temperature interval of the biphasic region was observed to be ~ 0.5 - 1.5 °C, relatively independent of LCP concentration. Since meaningful comparison of LCP solution and pure solvent viscoelastic coefficients requires temperature reference of the experimental data to a common scale of reduced temperature, it was necessary in the case of the polymer mixtures to determine equal-order-parameter "pseudo-transition" temperatures within their biphasic regions.

Brochard has demonstrated theoretically [52] that the pseudo-transition
temperature of an LCP/LC mixture whose upper and lower biphasic region temperatures bracket \( T_{NI} \) of the pure solvent is indicated by equal volume coexistence of polymer-rich nematic and polymer-poor isotropic phases. The various pseudo-transition temperatures determined in this manner were in every case found to coincide within measureable error with the solvent \( T_{NI} \) values, presumably a consequence of the dilute range of LCP concentrations studied. This observation served to justify the use of a common absolute temperature scale in computing solution/solvent differences in the anisotropic viscoelastic constants. Any systematic errors in model interpretation of the experimental data resulting from inadequacies in the assumptions of this practice therefore remain unaccounted for.

B. DETERMINATION OF DIRECTOR ORIENTATIONAL DIFFUSIVITIES BY DEPOLARIZED DYNAMIC LIGHT-SCATTERING

The basic theoretical expressions describing the frequency distribution of depolarized scattered light by nematic liquid-crystalline fluids were presented in the previous chapter. Presentation is made in this section of the specific experimental techniques exploited in this work in order to extract values of the diffusivity ratios \( K_{11}/\eta_{splay} \), \( K_{22}/\gamma_1 \), and \( K_{33}/\eta_{bend} \) characterizing the dynamical behavior of the three independent types of curvature distortion of the director field in a nematic monodomain sample. It is shown that, given knowledge of the ordinary and extraordinary refractive indices of a particular sample, the diffusivity ratios are individually obtainable from photon correlation analysis of the sample's scattered light intensity by appropriate manipulation of its director alignment relative to the plane defined by the incoming and depolarized scattered light beams, and to the
Recalling from Chapter I the fundamental equation for the mean relaxation frequencies of the two orthogonal director deformation eigenmodes,

\[
\Gamma_v(q) = \frac{K_{\nu}q^2 + K_3q^2}{\eta_v(q)} \quad v = 1, 2
\]

1-80

where \(\eta_v(q)\) are the two viscosity functions

\[
\eta_1(q) = \gamma_1 \cdot \frac{(\alpha_1 q_1^2 - \alpha_2 q_2^2)^2}{q_2^2 + q_1^2 + \eta_1 q_1^2 + \eta_1 q_2^2}
\]

1-81

and

\[
\eta_2(q) = \gamma_1 \cdot \frac{q_2^2}{q_2^2 + \eta_2 q_2^2}
\]

1-82

it is clear that if the alignment of the nematic director \(\hat{n}\) is chosen such that \(q_\parallel = 0\), the Mode 1 and Mode 2 relaxation frequencies characterize pure splay and pure twist deformations, respectively. This condition on the geometric relationship between the scattering wave-vector \(\vec{q}\) and \(\hat{n}\) is attained in the sample configuration designated Geometry A in Figure II-2. As the figure implies, the experimental set-up in this case employs a homogeneous monodomain sample whose director is aligned simultaneously parallel to the incoming vertically polarized light beam and perpendicular to the scattering plane defined by the incoming and scattered light wave-vectors \(\vec{k}_i\) and \(\vec{k}_s\). The magnitude of the component of \(\vec{q}\) perpendicular to \(\hat{n}\) in this geometry is given by

\[
q_\perp = (2\pi/\lambda)[n_0^2\sin^2\theta_0 + (n_e - n_0\cos\theta_0)^2]^{1/2}
\]

2-1

It is further evident on consideration of the general expression for the intensity of the depolarized scattered light,
Geometry A: Homogeneous monodomain sample, director perpendicular to scattering plane

Geometry B: Homogeneous monodomain sample, director in scattering plane

Geometry C: Homeotropic monodomain sample, director in scattering plane

Figure II-2: The three orthogonal nematic monodomain director configurations exploited in the DLS technique for measurement of the diffusivity ratios characterizing splay, twist, and bend director distortions.
\[ \frac{d\sigma}{d\Omega} = \left( \frac{\pi e_a}{\lambda} \right)^2 k_B \Gamma \sum_{\nu=1,2} \frac{(i\nu f_1 + i\nu f_0)^2}{K_{33}q_1^2 + K_{33}q_1^2} \] 

1-77

that if the scattered light is detected at an angle such that one or the other of the eigenmode geometric weighting factors in Eq.1-77 is negligibly small, then the contribution of that mode to the director relaxation frequency measured in the experiment is similarly negligible. Evaluation of the two weighting factors appropriate to Geometry A yields

\[ (i\nu f_1 + i\nu f_0)^2 = \frac{n_0^2 \sin^2 \theta_0}{n_0^2 \sin^2 \theta_0 + (n_0 - n_0 \cos \theta_0)^2} \] 

2-2

and

\[ (i\nu f_1 + i\nu f_0)^2 = \frac{(n_0 - n_0 \cos \theta_0)^2}{n_0^2 \sin^2 \theta_0 + (n_0 - n_0 \cos \theta_0)^2} \] 

2-3

The second of these expressions demonstrates that if the scattered light in this configuration is measured at an angle such that the condition \( \cos \theta_0 = n_0/n_e \) is met, then only splay deformations of the director within the sample will be detected in the experiment. Equation 1-80 reduces in this case to

\[ \Gamma_1(q) = \frac{K_{33}q_1^2}{\gamma_1 - \alpha y / \eta_b} = \frac{K_{11}q_1^2}{\eta_{\text{splay}}} \] 

2-4

It therefore suffices to know the value of \( q_1 \) at \( \theta_0 = \cos^{-1}(n_0/n_e) \) in order to obtain the splay diffusivity ratio from the measured value of \( \Gamma_1(q) \) at this angle.

Two additional, mutually orthogonal configurations of the director alignment were employed in determining the twist and bend diffusivity ratios of the samples. Schematically illustrated as well in Figure II-2, these are designated as Geometries B
and C, respectively. The Geometry B configuration makes use of the same homogeneously aligned sample characterized in Geometry A, but the orientation of the director in this case is in the scattering plane, perpendicular to the incoming light beam wave-vector \( \vec{k}_p \). Geometry C, on the other hand, employs a homeotropically aligned monodomain sample whose director is oriented parallel to \( \vec{k}_p \) hence also in the scattering plane. In both of these geometries, only Mode 2 director distortions are sampled in the scattered light, since the weighting factor for the scattering intensity of Mode 1 distortions reduces to zero in each instance.

Selectivity in the discrimination of twist and bend contributions to the Mode 2 decay rates measured in Geometries B and C is obtained in consequence of differences in the angle dependence of the scattering vector components \( q_\perp \) and \( q_\parallel \) between these geometries. Evaluation of the \( \vec{q} \) components of the depolarized scattered light measured in Geometry B yields

\[
q_\perp = (2\pi/\lambda)[n_e \cos \theta_0 - n_o]
\]

and

\[
q_\parallel = (2\pi/\lambda)[n_e \sin \theta_0]
\]

whereas for Geometry C, these relationships are reversed, i.e.,

\[
q_\perp = (2\pi/\lambda)[n_e \sin \theta_0]
\]

and

\[
q_\parallel = (2\pi/\lambda)[n_e \cos \theta_0 - n_o]
\]

It will be noted that, in all of the above expressions, \( n_o \) and \( n_e \) designate the ordinary and orientation-dependent effective extraordinary refractive indices of the nematic sample at the measurement temperature, and \( \theta_0 \) refers to the angle of the scattered light within the sample. Modification of the various equations for the components of the scattering vector and for the Mode 1 and Mode 2 intensity weighting factors appropriate to measurement angles \( \theta_{lab} \) in the laboratory frame is accomplished by application of Snell's law.
where \( n \) and \( n_T \) are the refractive indices experienced by the scattered light respectively within the nematic sample, and in the index matching liquid surrounding the sample cell. In Geometry A, \( n = n_o \), and \( n_e \) at any measurement angle is equal to the maximum value of the refractive index of the nematic sample along the director, \( n_{II} \). In Geometry B, on the other hand, \( n = n_e \), the latter index being expressed as a function of \( \theta_0 \) by the relationship
\[
\frac{1}{n_e^2} = \frac{\sin^2 \theta_0}{n_o^2} + \frac{\cos^2 \theta_0}{n_{II}^2}
\]

2-10

Again in Geometry C, \( n = n_e \), but the angle dependence of \( n_e \) in this case is given by
\[
\frac{1}{n_e^2} = \frac{\cos^2 \theta_0}{n_o^2} + \frac{\sin^2 \theta_0}{n_{II}^2}
\]

2-11

Equations 1-80, 1-82, and 2-5 together imply that the same condition on \( \theta_0 \) which isolates the splay diffusivity ratio in Geometry A applies to isolation of the bend diffusivity ratio in Geometry B. Thus, at \( \theta_0 = \cos^{-1}(n_o/n_e) \) in the latter configuration, \( q_\perp = 0 \), and Eqs. 1-80 and 1-82 reduce to
\[
\Gamma_\chi^2(q) = \frac{K_{33}^2}{\gamma_1 - \frac{\alpha_2}{n_e} \eta_{bend}}
\]

2-12

Taking into account Snell's law correction to \( \theta_0 \) and the above-indicated relationships for the effective refractive indices in the two geometries, it can furthermore be shown that \( K_{11}/\eta_{splay} \) and \( K_{33}/\eta_{bend} \) are uniquely characterized in Geometries A and B, respectively, at the same finite laboratory measurement angle
\[
\theta_{lab} = \sin^{-1} \left[ \frac{n_o}{n_T} \sqrt{1 - \left( \frac{n_o}{n_T} \right)^2} \right]
\]

2-13
which varies implicitly with variations in the temperature-dependent parameters $n_0$, $n_||$, and $n_T$. As before, given knowledge of $q_\perp = f(n_0, n_||, n_T)$ at this angle, $K_{2y}/\eta_{\text{bend}}$ is obtained from $\Gamma_2(q)$ via Eq. 2-12.

Finally, it follows from consideration of Eqs. 2-7, 2-8, 2-9, and 2-11 that, in Geometry C, $q_\perp$ and $q_\parallel$ simultaneously approach zero as the scattering measurement angle approaches zero. However, in this same limit, the ratio $q_\perp/q_\parallel$ becomes infinite. Therefore, the expression given by Eq. 1-80 for the Mode 2 decay rate in this third configuration is highly weighted in favor of the twist diffusivity ratio at low measurement angles. In practice, one extracts accurate estimates of $K_{2y}/\gamma_1$ in Geometry C as the least-squares limiting slopes of the curves that result on plotting the values of $\Gamma_2(q)$ measured over the angular range $15^\circ \leq \theta_{\text{lab}} \leq 30^\circ$ versus $q_\perp^2$. The latter quantities are obtained for known values of $n_0$, $n_\parallel$, $n_T$, and $\theta_{\text{lab}}$ by manipulation of Eqs. 2-7, 2-9, and 2-11.

Figure II-3 illustrates the measurement angle dependence of $q_\perp$ and $q_\parallel$ appropriately evaluated for the depolarized DLS spectrum of pure SCB at $T = 30^\circ\text{C}$ in each of Geometries A, B, and C. The various scattering wave-vector components were computed using literature values of the refractive indices $n_0$ and $n_\parallel$ of SCB [53], and the measured index $n_T$ of toluene for HeNe laser light ($\lambda = 6328$ Å) at this temperature. Each of the curves shifts slightly in a calculable fashion with changes in temperature, reflecting variations in the three temperature-dependent refractive indices. Given the dilute concentration regime of the LCP solutions studied in this work, it was a generally assumed approximation that LCP mixture values of $n_0$ and $n_\parallel$ matched those of pure SCB at equal temperatures. The validity of this assumption was experimentally verified by Gu in the case of one of the SCB/LCP mixtures [54]. By implication, $q_\perp$ and $q_\parallel$ were therefore known in every case to within measurable
Figure II-3: Variation with laboratory measurement angle of the components of the scattering vector parallel and perpendicular to the nematic director for SCB at $T = 30^\circ C$ in each of the three director configurations employed in the DLS determination of the splay, bend, and twist diffusivity ratios of the samples. In Geometry A, $q_{\parallel} = 0$ at all measurement angles.
The substantial differences in magnitude and curvature of $q_L$ and $q_\parallel$ among the three director configurations evident from Figure II-3 suggest that, in addition to the use of DLS decay rate measurements made at particular angles to resolve the respective curvature distortion diffusivity ratios, it should be possible to individually evaluate the various elastic and viscous coefficients of the nematic samples by least-squares curve-fitting their intensity correlation decay rates measured over a wide angular range. This procedure was in fact followed in the case of data collected in Geometries B and C, for which only Mode 2 director distortions (i.e., twist and bend) are characterized. The utility of the method is complicated in the case of Geometry A, on the other hand, by the fact that the depolarized scattered light intensity in this configuration manifests a significantly-weighted admixture of Mode 1 (splay) and Mode 2 (twist) director distortions at measurement angles significantly different from $\theta^*_{\text{lab}}$.

Even in the former case, however, it was demonstrated by trial-and-error that the variational stability of the viscoelastic parameter sets obtained by least-squares fitting $\Gamma_2(q)$ measurements made over the range $15^\circ \leq \theta_{\text{lab}} \leq 60^\circ$ was strongly influenced by the values selected as initial estimates for the various coefficients, and by the upper and lower bounds imposed on these as constraints. This curve-fitting procedure was therefore not entirely objective, nor were the resultant solution sets unique except within the range of the imposed constraints. Since precise characterization of the anisotropic viscous behavior of the various monodomains remained a primary goal of this work, it was deemed necessary to independently measure certain of the viscoelastic coefficients using auxiliary techniques yet to be discussed.

Having outlined the general techniques for determining the three director
distortion diffusivity ratios, a description of certain details of the DLS experimental set-up, as well as of several important aspects of the raw data acquisition and processing steps not previously discussed, is in order. Figure II-4 schematically illustrates the basic components of the photon correlation apparatus (Brookhaven Instruments Corporation, Ronkonkoma, N.Y.) used in collecting and analyzing the depolarized light scattered by the various monodomain samples. These consisted of:

1) A vertically polarized 15mW HeNe laser light source (Spectra-Physics, Model 120S) whose output was focussed on passage through a condensing lens (L₁) positioned between two narrow-diameter pinholes (P₁ and P₁'), thereby irradiating an essentially point-source scattering volume within the monodomain sample;

2) A cylindrical quartz vat containing the refractive index-matching liquid (either toluene or tert-butyl toluene) in which the monodomain sample cells were immersed. The matching liquid temperature immediately adjacent to the cell was monitored with a thermocouple (Barnant, Model 90) and controlled to within 0.1°C by means of a recirculating heating/refrigeration unit (Neslab, Model RTE-5DD);

3) A rotatable goniometer arm along which were mounted a horizontally oriented polarizing film (P₁'), followed by the photomultiplier detector unit of the apparatus (Brookhaven, Model BI-DS). The diameter setting of an iris aperture (P₂) externally mounted on the detector was manipulated to define the solid angle of the scattered light which, after being re-focussed through a second condensing lens (L₂) and an adjustable pinhole (P₂'), was finally admitted to the photomultiplier grid;

4) A 256-channel digital correlator (Brookhaven, Model BI-2030AT) interfaced with an interactive PC control unit.

The sample cells, adhesively mounted at the end of supporting glass strips, were always positioned in the index-matching vat such that the cell faces were normal to the incoming laser beam. Precise alignment of the cells in this manner,
Figure II-4. Schematic of DLS experimental set-up. While not indicated, the monochromatic light emitted from the laser is vertically polarized by preliminary passage through a Brewster lens.
accomplished by making suitable adjustments using a custom-assembled 3-D micropositioner, was monitored by observation of their low-angle forward scattering patterns. The micropositioner further permitted horizontal and vertical translation the sample cells, so as both to avoid localized imperfections in the samples as well as to constantly maintain the scattering volume in the focal plane of the collecting lens at all scattering angles.

The process of characterizing the frequency distribution of director fluctuations in a monodomain sample consisted first of photomultiplier detection of the intensity of light scattered by the sample as a function of elapsed time. On transmission to the correlator, the time-dependent fluctuating signal from each sample measurement was digitized, cross-multiplied, and stored in time increment-indexed memory registers. This process resulted in the generation of baseline-normalized intensity autocorrelation functions

\[ G_2(t) = \frac{\langle n(0)n(t) \rangle}{\langle n(0)n(0) \rangle} \]  

where \( n(t) \) refers to the detected photon counts at time increment \( t \), and the brackets \( \langle \rangle \) denote the multiple-acquisition time average of the two signal products.

Each of the experimentally measured intensity autocorrelation functions is related to an associated electric field correlation function, \( g_1(t) \), by the relationship

\[ G_2(t) = 1 + f(A)g_1(t)^2 \]  

where \( f(A) \) is a parameter which depends of the coherence matching of the scattered radiation at the photomultiplier. (It was found to be routinely possible in the light-scattering measurements to obtain \( f(A) \geq 0.8 \) at all scattering angles by optimally re-positioning monodomain sample cells as needed.) In the general case, the various \( g_1(t) \) are in turn related to relaxation frequency distributions, \( G(\Gamma) \), characterizing the
measurement by

$$g_1(t) = \int_0^\infty G(\Gamma)e^{-\Gamma t} d\Gamma \quad 2-16$$

Frequency distribution analysis of the $g_1(t)$ was finally accomplished by least-squares fitting their logarithmic cumulant expansions,

$$\log_e g_1(t) = -\widetilde{\Gamma} t + \mu_2^2 - ... \quad 2-17$$

where $\widetilde{\Gamma} = \int_0^\infty G(\Gamma)\Gamma d\Gamma$ represents the average decay rate of the frequency spectrum, and $\mu_2 = \int_0^\infty G(\Gamma)(\Gamma - \widetilde{\Gamma})^2 d\Gamma$ is the mean-square variance of the distribution with respect to $\Gamma$. The related, normalized parameter $P = \mu_2/\widetilde{\Gamma}^2$ was taken as a measure of the polydispersity of the director distortion relaxation frequencies reported in this work. Careful restriction of each sample's scattering volume to regions of the cell devoid of defects generally sufficed to permit measurement of $\widetilde{\Gamma}$ for which $P = \mu_2/\widetilde{\Gamma}^2 \leq 0.10$ -- i.e., within measurable error, the acquired $g_1(t)$ typically exhibited single exponential decays. Deviations from this general behavior were occasionally seen in characterizing monodomain samples of the highest molecular-weight LCP solutions, particularly at larger measurement angles or at lower reduced temperatures, suggesting the possibility that internal distortion modes of the LCPs were being monitored in these cases.

In concluding this section, an example is given in Figure II-5 of the quality of agreement between measured and calculated values of the intensity autocorrelation decay functions for SCB at $T = 30^\circ$C in each of the three experimental sample geometries exploited in this work. The curves representing the theoretically predicted dependence of the various $\Gamma(q)$ on laboratory measurement angle were calculated using values of the anisotropic viscoelastic coefficients for SCB at this temperature.
Figure II-5: Comparison between calculated and observed director distortion relaxation rates obtained at T =30°C for SCB and for an illustrative SCB/LCP mixture over a wide range of measurement angles in each of the three sample director configurations. The curve for Geometry A was computed assuming only Mode 1 (pure splay) contributions to the scattered light intensity.
which are consistent with comparable values reported in the literature [55-61]. It will be noted that the theoretical curve for Geometry A assumes only Mode 1 contributions to the predicted decay rates. This accounts for the appearance of systematic deviations from the measured values of $\Gamma(q)$ in this geometry outside the angular range ($15^\circ \leq \theta_{lab} \leq 35^\circ$) where the measured scattered light intensity originates predominantly from Mode 1 director fluctuations.

Within this range, however, and in the case of the Mode 2 decay rates detected in Geometries B and C, the agreement between calculated and observed values of $\Gamma(q)$ is seen to be excellent. While not discounting the statement made previously regarding the inadequacy of multi-parameter least-squares methods to uniquely determine the various nematic viscoelastic coefficients individually from curve-fitting of the experimentally-determined $\Gamma(q)$ alone, the close match between the experimental data and the theoretical curves illustrated in Figure II-5 demonstrates the potential of the DLS techniques discussed in this section to validate the internal consistency of viscoelastic parameter sets whose different coefficients have been determined by a combination of experimental techniques.

Also shown as examples in Figure II-5 are best-fit curves obtained by model parameter fitting the decay rate data obtained from one of the 5CB/LCP mixtures (8\%w/w 3-PVE-30 at $T = 30^\circ C$) studied in this work. The differences between the angle-dependent curves for pure 5CB and for the 5CB/LCP mixture make clear that the effect of the dissolved LCPs is to reduce the rates of splay, bend, and twist director distortions fluctuations. It will be subsequently demonstrated that these observed decrements to the various $\Gamma(q)$ result primarily from LCP-induced increments to the anisotropic viscosity coefficients and, furthermore, that analysis of the viscosity increments provides an indication of the nature and extent of the configurational anisotropy of the dissolved LCPs.
The relationships of the splay, bend, and twist elasticity coefficients of a nematic fluid to the critical value of an applied electric or magnetic field inducing curvature distortion of the director in an aligned monodomain of the material were developed in Chapter I. It was shown that, assuming strong anchoring of the director alignment at the bounding surfaces of the sample, the threshold parameters for the two types of applied field at the onset of the appropriate Frederickscz transition distortion are given by

\[ V_c = \pi \sqrt{\frac{K_{ii}}{\epsilon_a}} \]  

and

\[ H_c = \frac{\pi}{d} \sqrt{\frac{K_{ii}}{\chi_a}} \]

where \( d \) represents the thickness of the sample, \( \epsilon_a \) and \( \chi_a \) are the anisotropies in the dielectric permittivity and diamagnetic susceptibility of the nematic material at its measurement temperature, and selection among the three elastic coefficients is determined by the orientation of the distorting field with respect to the unperturbed director alignment.

Two variants of the Frederickscz transition method were used to independently measure the temperature-dependent splay and bend elastic constants of the LC solvents and LC/LCP mixtures studied in this work. The first of these determined \( K_{11} \) from the critical voltages required to distort homogeneously-aligned monodomain samples of the materials. Experimentally, the net curvature distortion in the director field of a sample was detected by monitoring the change in the sample's capacitance as a function of an increasing applied bias voltage. The details of cell
construction for this method were indicated in Section A of this chapter. A circuit diagram schematically depicting the experimental arrangement is shown in Figure II-6.

Referring to the figure, the sample cells were maintained at their various measurement temperatures by placement in an oven whose temperature was regulated to within ±0.1°C by use of a PID temperature-control unit (YSI, Model 72). A variable-amplitude sinusoidal AC bias voltage, \( V_b \), of frequency \( f_b = 50 \text{ Hz} \) was applied across the central regions of the cells not electrically insulated by the scoring technique previously mentioned. This bias voltage, the transformed output of a Hewlett-Packard Model 200CDR oscillator whose RMS amplitude was monitored by a Digitec Model 2110 voltmeter, provided the electric field source for the Fredericksz distortion in a particular sample. Onto \( V_b \) was superimposed a constant sinusoidal AC probe signal of amplitude \( V_o = 10\text{mV} \) and frequency \( f_s = 6000 \text{ Hz} \). The latter high-frequency signal, supplied by a Wavetek Model 166 signal generator, was used to monitor the voltage drop \( V_s \) across the series probe resistance element, \( R_s \). The RMS amplitudes \( |V_o| \) and \( |V_s| \) were measured using a Keithley Instruments Model 175 voltmeter, and the phase angle of \( V_s \) relative to \( V_o \) at any applied bias voltage, \( \delta \), was determined using an EG&G Model 124A lock-in amplifier.

As indicated by the equivalent circuit diagram insert to Figure II-6, the total impedance \( |Z_C| \) of a sample cell in these experiments may be regarded as having been composed of the parallel capacitance \( C \) and resistance \( r \) of the nematic sample contained within the cell, plus two series contact resistances, \( R_C \), associated with losses across the coated glass cell surfaces. For this equivalent circuit, the ratio of the high-frequency probe voltage \( V_s \) measured across \( R_s \) to its applied value \( V_o \) is given by
Figure II-6: (a) Block diagram of experimental set-up used in the electric Fredericksz transition determination of sample splay elastic constants. (b) Equivalent circuit for the homogeneous nematic sample cells indicated in (a).
\[
\frac{|V_s|}{|V_o|} = \frac{R_s}{R_s + 2R_c + (i2\pi f_s C + 1/r)^{-1}}
\]

Since the resistances \( R_s \) and \( R_c \) were known (\( R_s = 3060\Omega, \ R_c = 300\Omega \)), and the relationship between \( r \) and \( C \) was determined implicitly in measuring \( \delta \), the capacitance of a sample at any applied bias voltage and measurement temperature could be obtained from the relationship

\[
C = \frac{|V_s| \sqrt{1 + \tan^2 \delta}}{2\pi f_s |V_o| R_s (1 + W^2)}
\]

where

\[
W = \tan \delta - \frac{|V_s| R_s + 2R_c}{|V_o| R_s} \sqrt{1 + \tan^2 \delta}
\]

For a given temperature, each of the sample capacitances determined in this manner at incrementally applied \( V_b \) was in turn related to a field-dependent effective dielectric constant \( \varepsilon \) (\( V_{b,T} \)) of the fluid by

\[
\varepsilon = C/C_o
\]

where \( C_o \) represents the capacitance of the unfilled sample cell. At any applied \( V_b < V_c \), sample dielectric constants perpendicular to the director, \( \varepsilon_\perp \), were determined. As the \( \varepsilon-V_b \) data obtained for pure SCB shown in Figure II-7 demonstrates, values of \( V_c \) were obtained by graphical extrapolation of the initial linear increases in sample capacitance beyond the threshold bias voltages to the \( V_b < V_c \) baselines.

Finally, the various sample dielectric constants parallel to the director, \( \varepsilon_\parallel \), were obtained by one of two methods. The first of these, suggested initially by Meyerhofer [62] and found adequate for the pure nematic solvents and some of the LCP mixtures, consisted of extrapolating the experimental data plotted as \( \varepsilon \) versus \( 1/V_b \) to infinite applied bias voltage. In the case of certain other of the LCP mixtures,
Figure II-7: (a) Splay Fredericksz transition variation in ε with applied bias voltage for initially homogeneously aligned pure 5CB at three measurement temperatures. (b) Enlargement of the data in the vicinity of the Fredericksz threshold voltages.
on the other hand, the appearance of convective electrohydrodynamic instabilities intervened at values of $V_B$ only slightly higher than $V_c$, thereby prohibiting use of this extrapolation procedure. The latter instabilities were evidenced by discontinuously increasing, fluctuating values of the phase angle, $\delta$, and presumably resulted from contamination of the samples by ionic impurities. In these cases, $\varepsilon_\| \|$ was obtained from the capacitance of a homeotropically aligned monodomain sample of the material measured at low applied voltage, analogous to the determination of $\varepsilon_\perp$ in the planar cells. Knowing $V_c$ and $\varepsilon_\alpha = \varepsilon_\| - \varepsilon_\perp$ as functions of temperature for a particular nematic sample, associated values of $K_{11}$ were therefore directly calculable using Eq. 1-95. (Dimensional consistency in Eq. 1-95 requires multiplication of $\varepsilon_\alpha$ by $\varepsilon_0$, the dielectric permittivity of light in vacuo, if the former quantities are expressed as dimensionless dielectric anisotropies.) In turn, given knowledge of the diffusivity ratios, $K_{11}/\eta_{splay}$, based on DLS characterization, and of $K_{11}$ from the Fredericksz transition measurements, the viscosity functions $\eta_{splay} = \gamma_1 - \alpha_2^2/\eta_B$ of the various samples were separately calculable.

Bend elastic coefficients of the various nematic samples were measured as a function of reduced temperature by the magnetic Fredericksz transition method schematically illustrated in Figure II-8. The experiments consisted of determining the threshold magnetic fields, $H_c$, required to perturb the director alignment in homeotropic monodomain sample cells, produced as described in Section A. The sample cells, maintained at their measurement temperatures to within $\pm 0.01^\circ$C in a home-built hot stage, were placed between the opposing bores of a 0.7 Tesla electromagnet such that the direction of the applied magnetic field was parallel to the orientation of the sample cell glass plates. (The presumed perpendicularly of $\mathbf{H}$ to the unperturbed director alignment in the monodomain samples could be verified \textit{a posteriori} by the response of the sample to increasing field strength in the vicinity of
Figure II-8: Block diagram of experimental set-up used in the magnetic Fredericksz transition determination of sample bend elastic constants.
The state of director alignment in the samples was monitored by measuring the variation in their birefringence for light incident normal to the films. HeNe laser light was passed consecutively through a polarizing film oriented at 45° with respect to $\vec{H}$, through the sample cell, through an analyzer oriented perpendicular to the polarizer, and finally to a photodiode detector. The output of the photodiode was amplified and recorded using an X-Y plotter whose chart speed had been calibrated against the ramped output of the power supply controlling the current to the electromagnet, so that the magnitude of $\vec{H}$ at any given displacement along the time delay axis of the resulting traces was known. As illustrated in Figure II-9, values of $H_c$ were identified from the extrapolated inflection points of the transmitted light intensity traces.

Given $H_c$ at various reduced temperatures for a particular sample, corresponding values of $K_{33}$ were computed using Eq. 1-94, with the assumption that $\chi_a$ for the dilute mixtures was adequately approximated by its value for the pure nematic solvent at a given measurement temperature. The latter were obtained from the data of Bradshaw and Raynes [56]. This assumption is supported by the experimental observation that the dielectric permittivity anisotropies of the various LCP solutions were found to be minimally different than their pure solvent values at the same temperature. Therefore, as in the case of splay director distortions, having independently determined values of $K_{33}$ for the various samples, the viscosity functions $\eta_{bend} = \gamma_1 - \alpha^2/\eta_c$ could be extracted from the bend diffusivity ratios obtained by DLS characterization.
Figure II-9: Bend Fredericksz transition variation of transmitted light intensity with increasing applied magnetic field strength for a 50μ thick, homeotropically aligned sample of pure 5CB at ΔT = -2°C.
Expressions for the scattering cross-section of a nematic monodomain subjected to an electric or magnetic field were given in the previous chapter. Physically interpreted in the case of nematic materials possessing positive dielectric and diamagnetic anisotropies, Eqs. 1-78 and 1-79 imply that the effect of either type of field applied along the director is to augment the curvature elasticity of the fluid, thereby reducing the thermally averaged magnitude of director fluctuations. Confirming theoretical expectations [63], it has been demonstrated [64,65] that the stabilizing influence of the additional torque exerted on \( \hat{n} \) by an applied electric field manifests itself in light-scattering experiments by a reduction in the intensity of light scattered by a nematic monodomain, and a corresponding increase in the associated relaxation rate of director fluctuations. For the particular case where an electric field is applied parallel to the director of a homeotropic monodomain sample aligned for twist-weighted Mode 2 characterization according to the Geometry C configuration described previously, these two effects are quantitatively described by the relationships

\[
I(q) = \frac{\left( \frac{\pi \varepsilon_r}{\lambda^2} \right)^2 k_B T}{K_{22} q_r^2 + K_{33} q_{\perp}^2 + \varepsilon_a (V/d)^2}
\]

\[
\Gamma_2(q) = \frac{K_{22} q_r^2 + K_{33} q_{\perp}^2 + \varepsilon_a (V/d)^2}{\gamma_1 - \frac{\alpha q_{\perp}^2}{\eta_q q_r^2 + \eta_c q_{\perp}^2}}
\]

where \( V \) is the applied voltage and \( d \) is the sample thickness (known from prior interferometric measurement of the empty sample cell).
The linear dependence of $\Gamma(q)$ on the square of the applied electric field implied by Eq. 2-23 was exploited in this work in order to separately determine $K_{22}$ and $\gamma_1$ values of the samples from analysis of their Geometry C autocorrelation decay rate data collected as a function of applied voltage. The experimental procedure duplicated the conventional DLS characterization technique for this configuration with the exception that the intensity autocorrelation functions were acquired while subjecting the sample to a 6000 Hz AC applied voltage source. The output of the latter was incrementally ramped at various intervals between 0V and 21V RMS. For each sample, field-dependent relaxation rates were measured over the angular range $15^o \leq \theta_{\text{lab}} \leq 30^o$. As Figure II-10 illustrates, least-squares linear fits of $\Gamma(q,V)$ obtained in this manner, plotted against the electric field parameter $\varepsilon_0(V/d)^2$, yielded slope and intercept values (II-10A) whose limits on extrapolation to zero measurement angle yielded values for $\gamma_1$ (II-10B) and $K_{22}/\gamma_1$ (II-10C), respectively. The experimental results therefore provided precise, individual estimates of each sample's twist elastic and viscosity coefficients.
Figure II-10: Summary of results obtained in the field-dependent Geometry C determination of $K_{22}$ and $\gamma_1$ for 5CB and an illustrative SCB/LCP mixture at $T = 30^\circ$C. The significance of each of the three plots is indicated in the text.
Access to knowledge of the viscoelastic coefficients for splay, bend, and twist director distortions in a nematic sample by the techniques outlined thus far in this chapter permits direct evaluation of the viscous parameters $\gamma_1$, $\frac{\alpha_2}{\eta_b}$, and $\frac{\alpha_2}{\eta_c}$.

Invoking the equalities

$$\gamma_1 = \alpha_3 - \alpha_2$$ \hspace{1cm} (1-17)

$$\eta_b = \frac{1}{2} \left( \alpha_3 + \alpha_4 + \alpha_6 \right)$$ \hspace{1cm} (1-20)

and

$$\eta_c = \frac{1}{2} \left( -\alpha_2 + \alpha_4 + \alpha_5 \right)$$ \hspace{1cm} (1-19)

one sees that these three parameters are implicitly functions of the Leslie coefficients $\alpha_2 - \alpha_6$. Despite the fact that only four of these five coefficients are linearly independent due to the constraint imposed by the Parodi relationship, it is nevertheless clear that the DLS and Frederickscz measurements do not collectively generate sufficient information to permit the assignment of unique values to each of the $\alpha_i$ in terms of which the three known quantities are expressed. This motivates the need to obtain at least one additional, experimentally measurable relationship among some subset of the relevant Leslie coefficients.

Gu has demonstrated that the transient shear stress response of homeotropic monodomains of 5CB and 8CB [66], and of dilute LCP solutions in these two solvents [50,67], is amenable to semi-quantitative description by the abridged, two-dimensional hydrodynamic model discussed in Chapter I. It will be remembered that the strain-dependent apparent viscosity function derived in this model is explicitly parametric in the viscosity coefficients $\alpha_1$, $\alpha_2$, $\alpha_3$ and $\eta_b$, and that the sign of a particular sample's viscosity ratio $\alpha_3/\alpha_2$ is evidenced in shear flow by the absence or
presence of an oscillatory stress response with increasing strain. The former case characterizes nematics such as SCB, for which this ratio is uniformly positive, since both \( \alpha_2 \) and \( \alpha_3 \) are negative over the entire nematic temperature range of the solvent. As Figure II-11A illustrates, homeotropically aligned monodomains of this class of nematic fluids exhibit a single stress-overshoot maximum following the onset of shear flow, manifesting rotation of the director toward a stationary flow-aligning angle, \( \theta = \tan^{-1}(\alpha_2/\alpha_3) \), at which hydrodynamic director torques vanish. On the other hand, the application of steady-shear stress to nematic liquids such as 8CB, for which \( \alpha_2 < 0 \) but \( \alpha_3 > 0 \) over the majority of its nematic temperature range, produces a series of damped periodic stress oscillations indicative of director tumbling behavior. Illustrated as well in Figure II-11B, the non-aligning response of this class of nematics derives from the fact that, for negative values of \( \alpha_3/\alpha_2 \), the hydrodynamic torque on the director remains finitely positive at any angular orientation of the director within the shear plane.

Perhaps the most experimentally significant aspect of shear-tumbling systems is that, regardless of the observed tendency for the magnitude of stress oscillations to decay with increasing strain (in contrast to the indefinitely periodic response predicted by Eqs. 1-98 and 1-99) their periodicity can be assessed quite precisely over only a few cycles. Furthermore, according to Eq. 1-104, the oscillation period \( \gamma_p \) is dependent only on the ratio \( \alpha_3/\alpha_2 \). Given the ratio of these coefficients and their difference, via \( \gamma_1 \), \( \alpha_2 \) and \( \alpha_3 \) are independently obtainable from the relationships

\[
\alpha_2 = \frac{\gamma_1}{K - 1} \quad 2-24
\]

and

\[
\alpha_3 = \frac{\gamma_1}{1 - 1/K} \quad 2-25
\]

where \( K = \alpha_3/\alpha_2 \).
Figure II-11: Illustration of the characteristically different transient stress responses exhibited in steady-shear flow ($\gamma = 16 \text{ sec}^{-1}$) by initially homeotropic monodomain films of director-aligning $5\CB$ (a) and director-tumbling $8\CB$ (b) at various reduced temperatures within the respective nematic ranges of the solvents.
Secondary features of the rheograms of these samples permit one to estimate the viscosity coefficients $\eta_b$ (from the first primary minimum) and $\alpha_1$ (from the initial stress-overshoot maximum). As these latter two parameters are selected interactively, the precision in their determination is less than that of $\alpha_3/\alpha_2$. Nevertheless, modelling of the rheograms of both shear-tumbling and shear-aligning systems via Eq. 1-100 has been shown to provide estimates of $\alpha_1$ and $\eta_b$ which are in satisfactory agreement with results obtained by independent measurement techniques [59-61]. Moreover, the data set of viscosity coefficients is overdetermined in this case, since knowledge of $\gamma_1$, $\alpha_3$, and $\alpha_2$ alone suffices to generate values for $\eta_b$ and $\eta_c$ from the splay and bend viscosity coefficients, respectively.

In view of the distinct, qualitative differences in the shear-stress behavior of 5CB and 8CB, these nematic solvents serve as appropriate reference fluids for indicating the hydrodynamically anisotropic configurations of dissolved LCPs. In particular, the prediction of the Brochard model embodied in Eq. 1-53 leads one to expect that positive increments to $\alpha_3$ resulting on successive additions to 5CB of an LCP whose configuration is oblately ellipsoidal will be evidenced by the progressive transformation of the transient shear stress response of this solvent from director-aligning to director-tumbling. Conversely, if a dissolved LCP has a prolate configuration in 8CB, one expects on the basis of Eq. 1-53 that the director-tumbling behavior of this solvent will be increasingly suppressed, reflecting negative solution increments to $\alpha_3$. These predictions have in fact been borne out by Gu's results testing the effects both of a typical side-chain LCP on the steady-shear rheological response of 5CB [50,67] and of a main-chain LCP on that of 8CB [67].

These same rheological characterization techniques were applied to dilute 5CB solutions of two of the side-chain LCPs studied in this work (MeSi-6-CN and MA-6-OCH$_3$) whose available quantities permitted making adequate volumes of
solution to fill the gap in the cone-and-plate fixture of the rheometer. The steady-shear viscous response of the nematic mixtures at an applied shear rate of 16 sec\(^{-1}\) was measured using a Rheometrics RMS-8400 fluids rheometer. Throughout the course of an experiment, the transient shear stress transmitted to the 0.02 radian, 5 mm diameter cone of the instrument was monitored using a 10 g-cm transducer. As mentioned in Section A of this chapter, homeotropic alignment of the samples was accomplished by pre-treating the cone and plate surfaces with lecithin. Samples were run at various temperatures within their nematic range, controlled to ± 0.1°C by means of a recirculating thermal bath. The results obtained by theoretical modelling of the rheograms resulting from these experiments as previously described will be presented in the following chapter.
A. INTRODUCTION

The side-chain LCPs whose nematic solutions have been characterized by the techniques discussed in the previous chapter present semi-systematic variation on the LCP architectural features of mesogen type, backbone type, flexible spacer length, and molecular weight. Accordingly, comparisons will be drawn in this chapter among subsets of the experimental results which reflect the relative influence of each of these structural elements in determining the elastic (equilibrium) and dissipative (hydrodynamic) behavior of dilute nematic monodomains of these materials. To the extent that the measured anisotropic viscosity increments of the various LC/LCP mixtures admit interpretation via the Brochard theoretical model of the coil configurations of the LCPs, the dependence of this important aspect of side-chain/mainchain conformational coupling on the degree of solvent nematic order will be reviewed. Finally, the interpretive consistency of the Brochard model with the experimental results is a matter that will be discussed in its own right.

B. DYNAMIC LIGHT-SCATTERING STUDIES OF n-PVE-N LCPs

Depolarized DLS measurement of the relaxation rates characterizing splay, twist, and bend distortions of the nematic director was performed as discussed in Chapter II on dilute solutions in either 5CB or 8CB of various members of an homologous series of side-chain LCPs having the generic structure
These polymers, hereafter designated as n-PVE-N, were prepared by members of the research group of V. Percec [68-71]. Owing to their synthesis from precursor n-alkyl monomers by an apparently living cationic mechanism, the molecular weight polydispersities of the n-PVEs were uniformly low (Mₘ/Mₙ ≤ 1.2 by GPC analysis in chloroform, relative to polystyrene standards). The bulk mesophase behavior of the particular PVE homologues used in this study, as determined by DSC and confirmed by polarized light microscopic observation, are summarized in Table III-1. Attention is called to the general trend among the polymers toward greater thermal stability of mesomorphic order with increasing molecular weight and, more dramatically, toward higher-order mesomorphic phase behavior with increasing alkyl spacer length. This trend reflects progressive decoupling of the inherent thermodynamic ordering tendencies of the mesogenic units of the LCPs from the disordering influence of the polymer backbone. In fact, a cooperative packing tendency among the spacer moieties as well appears evident in the ability of the 11-spacer polymer to display a crystalline bulk phase.

It is further noteworthy that the apparent hydrodynamic volume of the n-PVEs at a given degree of polymerization increases with increasing spacer length, confirming that the alkyl spacer groups contribute measurably to the total excluded volume of a PVE molecule in an isotropic solvent environment. For purposes of subsequent comparison of the isotropically solvated dimensions of the n-PVEs with those estimated from their intrinsic viscosity behavior as components of nematic
<table>
<thead>
<tr>
<th>n</th>
<th>N</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>M&lt;sub&gt;w&lt;/sub&gt;/M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>M&lt;sub&gt;r&lt;/sub&gt;</th>
<th>R&lt;sub&gt;h&lt;/sub&gt;.nm</th>
<th>Phase transitions(°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>22</td>
<td>5,020</td>
<td>1.12</td>
<td>5.63</td>
<td>1.65</td>
<td>g 81.0 x 85.7 i</td>
<td>[68]</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>1,570</td>
<td>1.06</td>
<td>2.41</td>
<td>0.84</td>
<td>g 38.2 x 41.3 n 79.6 i</td>
<td>[68]</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>5,080</td>
<td>1.18</td>
<td>5.68</td>
<td>1.66</td>
<td>g 59.5 x 64.5 n 97.8 i</td>
<td>[68]</td>
</tr>
<tr>
<td>3</td>
<td>23</td>
<td>6,040</td>
<td>1.11</td>
<td>6.45</td>
<td>1.83</td>
<td>g 61.7 x 66.4 n 102.7 i</td>
<td>[68]</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>8,090</td>
<td>1.21</td>
<td>7.98</td>
<td>2.17</td>
<td>g 64.4 x 68.4 n 104.5 i</td>
<td>[68]</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>9,490</td>
<td>1.12</td>
<td>8.97</td>
<td>2.38</td>
<td>g 39.3 s&lt;sub&gt;A&lt;/sub&gt; 104.9 n 115.4 i</td>
<td>[69]</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>8,840</td>
<td>1.15</td>
<td>8.51</td>
<td>2.29</td>
<td>g 21.2 s&lt;sub&gt;A&lt;/sub&gt; 140.3 i</td>
<td>[69]</td>
</tr>
<tr>
<td>9</td>
<td>30</td>
<td>11,600</td>
<td>1.12</td>
<td>10.4</td>
<td>2.67</td>
<td>g 14.2 s&lt;sub&gt;A&lt;/sub&gt; 153.8 i</td>
<td>[70]</td>
</tr>
<tr>
<td>11</td>
<td>30</td>
<td>12,000</td>
<td>1.10</td>
<td>10.6</td>
<td>2.73</td>
<td>g 21.3 k 66.5 s&lt;sub&gt;A&lt;/sub&gt; 164.9 i</td>
<td>[71]</td>
</tr>
</tbody>
</table>

(1) Nominal value based on initial [M]/[I] ratio.
(2) Apparent GPC molecular weight relative to polystyrene in CHCl₃.
(3) Computed values of GPC-equivalent PS standards obtained using Mark-Houwink-Sakurada coefficients for PS/CHCl₃ @ 25°C from Reference [72].
(4) Equivalent sphere hydrodynamic radii estimated using Eq. 3-1.
(5) From DSC first heating scans.
monodomains, values of the apparent hydrodynamic radii of the polymers in CHCl₃ are included in Table III-1. These equivalent sphere radii are calculated on the basis of the equation

\[ R_{\text{h eff}} = (3/10 \pi N_A)^{1/3} M_n^{1/3} [\eta]^{1/3} \]  \hspace{1cm} 3-1

adapted from the Einstein viscosity increment relationship for hard-sphere dispersions, where \( N_A \) and \([\eta]\) are respectively Avogadro’s number and the intrinsic viscosity of a GPC-equivalent polystyrene molecular weight reference standard. The latter values were derived from the Mark-Houwink-Sakurada equation

\[ [\eta] = K M_n^a \]  \hspace{1cm} 3-2

using appropriate coefficients \( K \) and \( a \). Reported in Reference [72].

From the DLS relaxation rate measurements of the n-PVE-N monodomain samples obtained at various temperatures below their nematic-to-isotropic transition temperatures, the director distortion diffusivity ratios \( K_{11}/\eta_{\text{splay}}, K_{22}/\gamma_1 \), and \( K_{33}/\eta_{\text{bend}} \) were found by interpolation (splay and bend) or extrapolation (twist) of the raw data to the appropriate measurement angle isolating the respective single-distortion contribution to the decay. Evaluation of the individual elastic and viscous coefficients of the mixtures was subsequently enabled by auxiliary determinations of \( K_{11} \), via electric field-induced Fredericksz transition measurements on planar monodomain samples, and of \( K_{22} \) and \( \gamma_1 \) separately, via electric field-dependent DLS measurements on homeotropic monodomain samples. The remaining coefficients -- \( K_{33}, \eta_{\text{splay}}, \) and \( \eta_{\text{bend}} \) -- were finally extracted as best-fit parameters by least-squares curve-fitting the original angle-dependent relaxation rate data for each of the three previously described director alignment geometries. It will be noted that this particular group of experiments was performed collaboratively with D. Gu, whose
1. SPACER LENGTH EFFECTS

Table III-2 compiles values of the dielectric anisotropies, $\Delta \varepsilon$, threshold voltages, $V_{th}$, and the splay, twist, and bend elastic constants obtained for SCB and for 8% w/w mixtures of the indicated n-PVEs in SCB at a fixed temperature decrement below their respective clearing temperatures of $\Delta T = -5^\circ C$. Comparison with literature values of the elastic constants for SCB is favorable [55-58]. The dielectric anisotropies and threshold voltages of the LCP mixtures are seen to be smaller than the corresponding values for pure SCB, indicating that the solvent order parameter at constant reduced temperature is decreased by the addition of this particular group of side-chain LCPs. Further manifestation of this effect is apparent in the reduced values found for the various elastic constants of the LCP mixtures.

The largest reduction in the splay elastic constant among the mixtures is observed for the 2-PVE solution. Referring to the observed bulk phase behavior of 2-PVE in Table III-1, it is evident that the constraining influence of the short spacer of this material is such that the polymer does not by itself exhibit a thermodynamically accessible liquid crystalline phase. The results obtained here suggest analogously that the stronger the coupling between side-chain mesogen mobility and that of the LCP backbone, the more the solvent director orientation will be disturbed by the configurational disorder of the polymer backbone in the nematic matrix.

With regard to the viscosity coefficients of the samples, Figure III-1 displays as functions of the field strength the electric field-dependent director relaxation rates
<table>
<thead>
<tr>
<th></th>
<th>$\Delta \epsilon \pm 3%$</th>
<th>$V_0 \pm 1%$ (volts)</th>
<th>$K_{11} \pm 5%$ (x $10^{-8}$ dynes)</th>
<th>$K_{22} \pm 5%$ (x $10^{-8}$ dynes)</th>
<th>$K_{33} \pm 5%$ (x $10^{-8}$ dynes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure 5CB:</td>
<td>10.4</td>
<td>0.700</td>
<td>46</td>
<td>31</td>
<td>56</td>
</tr>
<tr>
<td>8% 2-PVE-22</td>
<td>8.19</td>
<td>0.610</td>
<td>27</td>
<td>24</td>
<td>45</td>
</tr>
<tr>
<td>8% 3-PVE-30</td>
<td>8.44</td>
<td>0.680</td>
<td>35</td>
<td>26</td>
<td>46</td>
</tr>
<tr>
<td>8% 5-PVE-30</td>
<td>9.03</td>
<td>0.700</td>
<td>40</td>
<td>26</td>
<td>46</td>
</tr>
<tr>
<td>8% 7-PVE-30</td>
<td>8.87</td>
<td>0.690</td>
<td>38</td>
<td>27</td>
<td>45</td>
</tr>
<tr>
<td>8% 9-PVE-30</td>
<td>8.19</td>
<td>0.700</td>
<td>39</td>
<td>26</td>
<td>45</td>
</tr>
<tr>
<td>8% 11-PVE-30</td>
<td>8.16</td>
<td>0.700</td>
<td>36</td>
<td>26</td>
<td>42</td>
</tr>
</tbody>
</table>
Figure III-1: Electric field dependence of the relaxation rates for the twist distortion mode for pure 5CB and its 8\% w/w mixtures with the indicated n-PVE-N side-chain LCPs at $T_{NI} - T = 5^\circ$C. The error bars on the 5CB data represent typical values for all measurements.
obtained for 5CB and the various n-PVE mixtures, again at $\Delta T = -5^\circ C$. The autocorrelation decay rates of this plot were recorded from homeotropic monodomain samples in the Geometry B configuration at a fixed angle of $\theta_{lab} = 18^\circ$, which very nearly approximates the condition for measurement of pure twist deformation of the nematic director. To this extent, Eq. 2-23 indicates that the slopes of the best-fit lines through the data of this figure approximate the inverse twist viscosities $1/\gamma_1$ of the samples, the intercepts yielding estimates of the ratios $K_{22}/\gamma_1$. (As stated in Section II-D, more refined assessments of these ratios, from which the $K_{22}$ values reported in Table III-2 were computed, were obtained by extrapolation of the zero-field angle-dependent decay rate data to zero angle.) It is clear from the results illustrated in Figure III-1 that addition of the various n-PVEs to 5CB results in a measureable decrease of both the zero-field relaxation rate and the field dependence of the relaxation rate. Furthermore, the values obtained for $\gamma_1$ from these plots, along with those obtained for $\eta_{splay}$ and $\eta_{bend}$ by subsequent curve-fitting of the relaxation rate data for the other two director geometries, confirm that the decreases in the autocorrelation decay rates observed in all three director geometries for the n-PVE polymer mixtures compared to their pure 5CB counterparts result primarily from increments to the solvent viscosity coefficients.

Figure III-2 demonstrates graphically the influence of LCP spacer length on the viscous behavior of the monodomain samples at $\Delta T = -5^\circ C$. Plotted in the figure as a function of side-chain methylene repeat units are the increments to the splay, twist, and bend viscosity coefficients of the solvent for each of the n-PVE/5CB solutions characterized in this study. In every case, it is seen that $\Delta\eta_{splay} \approx \Delta\gamma_1 > \Delta\eta_{bend}$. Furthermore, with the exception of the 11-PVE mixture, the magnitude of all three viscosity increments is seen to systematically decrease with increasing spacer
Figure III-2: Influence of methylene spacer length $n$ on the viscosity increments for the splay, twist, and bend distortion modes measured for 8% w/w solutions in 5CB of n-PVE-N at $T_{NI} - T = 5^\circ$C.
length. This effect is again interpreted as deriving from the mesogen/backbone decoupling influence of the LCP spacer. The reversal of this trend in the case of the 11-PVE solution, on the other hand, may in fact be taken as evidence of enhanced ordering of the solvated LCP side-chains due to increased association of the spacer moieties beyond a critical spacer length, as is observed in the bulk mesophase behavior of the polymer.

From the measured absolute viscosity increments, one may compute reduced anisotropic viscosity increments

\[ [\eta_i] = (\eta_i - \eta_i^0)/\eta_i^0 \quad c = \text{splay, twist, or bend} \]

where \( c \) is the weight/volume solution concentration of the LCP, and the unsuperscripted and superscripted coefficients represent the appropriate viscosities of the various LCP mixtures and of pure SCB, respectively. (The solvent density data required to convert solution concentrations from \( w/w \) to \( w/v \) units were obtained from Reference [56].) In the limit of infinite dilution, the reduced viscosity increments become the equivalent of anisotropic intrinsic viscosity increments. The latter, appropriately combined with LCP molecular weight information, may in turn be taken as a measure of the apparent hydrodynamic dimensions of the dissolved polymers, analogous to their dilute solution behavior in isotropic solvents. Due to the limited availability of the PVE polymers, it was not feasible in this study to attempt measurement of the concentration dependence of the anisotropic viscosity increments. However, assuming that the LCP concentration in the monodomain samples is sufficiently dilute to render negligibly small any numerical differences between the various reduced viscosity increments and their associated anisotropic intrinsic counterparts, comparisons among the former values may be made which yield at least a qualitative indication of the relative configurational anisotropy of the \( n \)-PVEs in a
nematic solution environment. As will be seen, more convincing evidence in support of this interpretative approach is conferred by the dilute solution monodomain behavior of two additional side-chain LCPs investigated in this work.

Given these assumptions, Figure III-3 compares computed values of the reduced twist and bend viscosity increments obtained for the n-PVE/SCB mixtures. (The results for the reduced splay viscosities have been omitted, since they are insignificantly different from the reduced twist viscosities.) Two important trends are evident in this graph. The first of these parallels the behavior displayed by the twist and bend viscosity increments in the preceding figure, both sets of the anisotropic reduced viscosities steadily decreasing as the spacer length of the LCP side-chains increases from two to nine methylene units. This trend provides complementary evidence of the progressive decoupling with increasing spacer length of correlated orientational relaxations of the LCP mesogens and the polymer backbone. That the trend reverses in the case of the 11-PVE mixture is likewise seen as a further manifestation of enhanced mesogen/backbone motional cooperativity due to association among spacer groups exceeding a critical length.

More suggestive of configurational anisotropy within the polymer backbones of the solvated PVE polymers, however, is the generally inverted relationship of the twist and bend reduced viscosities compared to the anisotropic viscosity increments from which they are derived. Specifically, with the exception of the 9-PVE solution, \([\eta_{\text{bend}}] > [\gamma_1]\). If the intuitive assumption is made that \([\eta_{\text{bend}}]\) and \([\gamma_1]\) bear a relationship functionally similar to that expressed by Eq. 3-1 to the effective solvated dimensions of the n-PVEs respectively perpendicular and parallel to the orientation of the nematic director (which is assumed likewise to be the alignment direction of the LCP mesogenic units) then it appears that the backbones of the 2-, 3-, 5-, 7- and 11-PVE LCPs in SCB are more highly extended perpendicular to the nematic director.
Figure III-3: Influence of methylene spacer length $n$ on the reduced twist and bend viscosity increments obtained for n-PVE-N in SCB at $T_{NI} - T = 5^\circ C$. 
Table III-3

<table>
<thead>
<tr>
<th>[γ₁]cc/g</th>
<th>[η_bend]cc/g</th>
<th>[η_bend]/[γ₁]</th>
<th>R_L, nm</th>
<th>R_H, nm</th>
<th>R_L/R_H</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% 2-PVE-22:</td>
<td>16</td>
<td>23</td>
<td>1.4</td>
<td>2.6</td>
<td>2.3</td>
</tr>
<tr>
<td>8% 3-PVE-30:</td>
<td>10</td>
<td>16</td>
<td>1.5</td>
<td>2.7</td>
<td>2.4</td>
</tr>
<tr>
<td>8% 5-PVE-30:</td>
<td>7.1</td>
<td>9.6</td>
<td>1.4</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td>8% 7-PVE-30:</td>
<td>7.0</td>
<td>8.5</td>
<td>1.2</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>8% 9-PVE-30:</td>
<td>6.4</td>
<td>4.3</td>
<td>0.68</td>
<td>2.0</td>
<td>2.3</td>
</tr>
<tr>
<td>8% 11-PVE-30:</td>
<td>7.7</td>
<td>17</td>
<td>2.3</td>
<td>3.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>
than parallel to it -- i.e., the global configuration of these LCPs is oblately anisotropic. By contrast, the backbone of the dissolved 9-spacer polymer evidences a slightly greater extension parallel to its mesogens; hence it is implied to have a somewhat prolately anisotropic global configuration.

Extending the logic of this analogy to an interpretation of the relative extent of configurational anisotropy among the n-PVEs, the ratios $[\eta_{\text{bend}}]/[\gamma_1]$ listed in Table III-3 imply that the trend through this series of LCPs on increasing the alkyl spacer length from two to nine methylene units is one of decreasing oblate anisotropic conformation in nematic solution. This behavior is qualitatively consistent with the prediction of the Warner-Wang theoretical model in regard to the effect one expects diminishing the perpendicular influence of the hinge coupling coefficient, $r_f$, by increasing n should have on the global conformation of a side-chain LCP. The divergence from the pattern exhibited by the 11-PVE polymer can once again be attributed to collective association among the particularly long spacer groups of this polymer, essentially augmenting the effective magnitude of $r_f$. (As mentioned in Chapter I, although the Warner-Wang model is formulated explicitly to predict polymorphic nematic phase transitions in side-chain LCPs in the bulk state, it is implicitly applicable to interpreting the configurational tendencies of side-chain LCPs dissolved in nematic solutions by appropriate modification of the parameters used.)

A physical argument can be made in support of the assumption on the relationships of $[\eta_{\text{bend}}]$ and $[\gamma_1]$ to anisotropic solvated dimensions of the side-chain LCPs stated above by considering that the backbones of the dissolved side-chain LCPs in the monodomain samples can accommodate a large scale twist deformation of the nematic director merely by rotational realignment. On a microscopic scale, some amount of torsional deformation of the backbone might also be involved, the extent of which would depend on the alignment coupling strength between the mesogens and
the backbone. In contrast, large scale bend deformations of the nematic director necessitate that the dissolved LCP molecules both internally rotate and translate relative to one another [73,74]. Consequently, if the LCP backbone has a larger projected length perpendicular to the nematic director than parallel to it, as would be the case in oblately anisotropic conformations of the molecules, one expects the relative increment of the bend distortion to exceed that of the twist distortion. The reverse relationship would be expected to be true if the LCP mesogens are preferably situated parallel to the polymer backbone, as in prolately anisotropic configurations of the polymer chains.

This interpretation has in fact been confirmed by the larger body of experimental results obtained in this group on studying the anisotropic viscous behavior of both side-chain and main-chain LCPs in dilute nematic solution [65,75-78]. Specifically, whereas the nematic solutions of the side-chain LCPs have in most instances been characterized by the inequality \( \eta_{\text{bend}} > [\gamma_1] \), dilute monodomain samples of the main-chain LCPs have unanimously been shown to display the opposite tendency, namely \( [\gamma_1] \gg [\eta_{\text{bend}}] \). In view of the seeming certainty that any preferred configurational anisotropy of main-chain LCPs in a nematic solution environment would favor the orientation paralleling its mesogenic units, identification of the above inequalities with oblate and prolate conformational anisotropy appears adequately warranted.

Lastly, it is of interest to numerically evaluate the anisotropic dimensions of the PVE polymers in 5CB. Rough estimates of these quantities obtain if one assumes that the LCPs behave as equivalent spheres with apparent dimensions that depend on the respective director distortion mode. Given this assumption, \( [\gamma_1] \) and \( [\eta_{\text{bend}}] \) may be independently substituted into Eq. 3.1, yielding the \( R_\perp \) and \( R_\parallel \) values reported in Table III-3. Not surprisingly, the trend through the ratios of these estimated
dimensions mirrors that of the $\eta_{\text{bend}}/\eta_{1}$ ratios, again reflecting a general tendency toward decreasing oblate configurational anisotropy as the spacer length of the polymers is increased. The decoupling influence of the spacer is as well again apparent in the trend toward decreasing apparent chain dimensions of the LCPs as $n$ increases.

One expects a priori that if the hydrodynamic volumes of the LCPs remain unchanged on traversing $T_{NI}$, the anisotropic radii of the polymers in a nematic environment should order as either

$$R_{\perp} > R_{\text{iso}} > R_{\parallel}$$

or

$$R_{\perp} < R_{\text{iso}} < R_{\parallel}$$

depending on whether they are oblately or prolately ellipsoidal in configuration. Referring to the estimated hydrodynamic radii of the polymers in CHCl$_3$ listed in Table III-1, it is noteworthy that the values of $R_{\perp}$ and $R_{\parallel}$ calculated for 5-PVE and 11-PVE do, in fact, obey the former relationship. Deviations from the appropriate inequality in the case of the other polymers can be attributed to 1) different solvency of the polymers by 5CB and CHCl$_3$, 2) incremental decoupling effects, and 3) the need to revise Eq. 3-1 to better theoretically model the incremental viscosity effects of anisotropically shaped particles in twist and bend distortion flow fields. In any case, the extent of configurational anisotropy among the n-PVEs at $\Delta T = -5^\circ C$ is evidently relatively modest.

Alternatively, estimates of $R_{\perp}/R_{\parallel}$ can be obtained by a trial-and-error procedure that are consistent via the expressions of the Brochard theoretical model with the experimentally measured solution twist and bend viscosity increments. Specifically, since the bend viscosity of each of the LCP mixtures is equivalently expressed as
\[ \eta_{\text{bend mix}} = (\gamma_1^0 + \Delta \gamma_1) - [(\alpha_2^0 + \Delta \alpha_2)^2/(\eta_c^0 + \Delta \eta_c)] \]

and in view of the fact that the Brochard expressions for \( \Delta \alpha_2 \) and \( \Delta \eta_c \) may be evaluated for any assumed value of \( R_\perp/R_\parallel \) in terms of \( \Delta \gamma_1 \), namely

\[ \Delta \alpha_2 = \frac{\Delta \gamma_1}{(R_\perp/R_\parallel)^2 - 1} \]
\[ \Delta \eta_c = \left[ \frac{\Delta \gamma_1}{(R_\perp/R_\parallel)^2 - 1} \right]^2 \]

one may identify unique values of \( R_\perp/R_\parallel \) leading to simultaneous consistency between calculated and measured values of the viscosity increments \( \Delta \gamma_1 \) and \( \Delta \eta_{\text{bend}} \) having knowledge of the solvent viscosity coefficients \( \gamma_1^0, \alpha_2^0, \) and \( \eta_c^0 \) alone. In principal, this method of assessing \( R_\perp/R_\parallel \) has the advantages that anisotropic flow field effects are explicitly taken into account, and that non-negligible concentration effects on the values one obtains cancel, since ratios of viscosity increments are taken. Unfortunately, as will be discussed at greater length in the subsequent section on the temperature dependence of \( \Delta \gamma_1 \) and \( \Delta \eta_{\text{bend}} \) in the 3-PVE and 9-PVE mixtures, the configurational anisotropies of the n-PVEs evaluated by this procedure are uniformly prolate, in disagreement with their assessment based on comparison of \( [\gamma_1] \) and \( [\eta_{\text{bend}}] \). As was stated earlier, the larger body of observation of the behavior of the side-chain LCP mixtures inclines us to believe that the latter criterion for assigning the configurational anisotropy of a particular polymer is more nearly accurate, and that the origin of the discrepancy between these two interpretive approaches derives at least in part from theoretical inadequacy of the Brochard model in the regime of nearly spherical LCP conformations.
Given the residual uncertainty that exists in unambiguously interpreting the configurational anisotropy of the PVEs, more definitive evidence of our assignments was sought by studying the polymer molecular weight dependence of the anisotropic viscosity increments in the LC/LCP mixtures. Measurements of $\gamma_1$ and $\eta_{\text{bend}}$ at $\Delta T = -5^\circ C$ were therefore made as previously discussed on 8%w/w solutions in 5CB of 3-PVE-N with nominal values of N = 6, 18, 23, and 30. The results obtained for the reduced values of these variables are plotted graphically in Figure III-4, from which it is apparent that the relationship $[\eta_{\text{bend}}] > [\gamma_1]$ is obeyed by the solutions of all four molecular weight fractions of the LCP. Furthermore, the ratios of the anisotropic chain dimensions of the 3-PVE fractions, estimated as before from $[\gamma_1]$ and $[\eta_{\text{bend}}]$ using Eq. 3-1 and summarized in Table III-4, are within measurable error molecular weight independent. This result confirms the expectation that the conformational anisotropy of a nematically solvated side-chain LCP is an intrinsic property of the particular polymer/solvent pair, dependent only on the absolute and reduced temperatures of the sample.

While the available range of molecular weights in this study was admittedly rather low, the double logarithmic plots of $R_\perp$ and $R_\parallel$ as functions of N illustrated in Figure III-5 yield essentially identical exponential molecular weight dependencies of

$$R_\perp, R_\parallel \propto N^{0.41}$$

A molecular weight exponent $\nu$ of this magnitude on the apparent hydrodynamic dimensions of 3-PVE is consistent with behavior intermediate between that of dense (i.e., non-draining or Zimm-like) and ideal statistical (i.e., free-draining or Rouse-like) coils, for which corresponding values of $\nu$ are 0.33 and 0.50, respectively. More typically, short chains such as these behave as free-draining coils. The closer
Figure III-4: Influence of LCP molecular weight on the reduced twist and bend viscosity increments obtained for n-PVE-N in SCB at $T_{NI} - T = 5^\circ C$. 
<table>
<thead>
<tr>
<th>8% 3-PVE-6</th>
<th>6.8</th>
<th>11</th>
<th>1.6</th>
<th>1.4</th>
<th>1.2</th>
<th>1.16</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% 3-PVE-18</td>
<td>7.8</td>
<td>12</td>
<td>1.6</td>
<td>2.2</td>
<td>1.8</td>
<td>1.16</td>
</tr>
<tr>
<td>8% 3-PVE-23</td>
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<td>2.3</td>
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<td>1.15</td>
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<tr>
<td>8% 3-PVE-30</td>
<td>10</td>
<td>16</td>
<td>1.5</td>
<td>2.7</td>
<td>2.4</td>
<td>1.15</td>
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Figure III-5: Logarithmic dependence of the apparent anisotropic chain dimensions $R_{\perp}$ and $R_{\parallel}$ on the degree of polymerization $N$ determined for 3-PVE-N in SCB at $T_{NI} - T = 5^\circ$C.
approximation to non-draining behavior in the present case is therefore taken as indication that there exist strong dipole-dipole associations between the mesogenic groups of the LCP and 5CB deriving from their structural similarity, especially in regard to their terminal cyano functionality.

The present results for 3-PVE-N may be compared with those obtained by Gu [75] for the methacrylate-backbone side-chain LCP MSHMA.

\[
\begin{align*}
&\text{CH}_3 \\
&(\text{CH}_2 - \text{C})_n \\
&\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
&\text{H} \\
&\text{C} \\
&\text{C} \\
&\text{C} \\
&\text{C} \\
&\text{C} \\
&\text{C} \\&
\end{align*}
\]

and by Pashkovsky et. al. [26] for the acrylate-backbone LCP PA-6.

\[
\begin{align*}
&\text{H} \\
&(\text{CH}_2 - \text{C})_n \\
&\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
&\text{C} \\
&\text{C} \\
&\text{C} \\
&\text{C} \\
&\text{C} \\
&\text{C} \\&
\end{align*}
\]

Using consistent calculational procedures adopted for analyzing the n-PVE-N data, one extracts from the data of the former study an estimated anisotropy ratio at $\Delta T = -5^\circ\text{C}$ of $R_\perp/R_\parallel = 1.27$, and molecular weight exponents of $\nu = 0.59$ and $\nu = 0.61$ for the parallel and perpendicular hydrodynamic dimensions of MSHMA in 5CB. On the other hand, based on measurement of $\Delta \gamma_1$ alone, values of $R_\perp/R_\parallel = 1.33$ at $\Delta T = -5^\circ\text{C}$ and of a configurationally averaged molecular weight exponent $\nu = 0.37$ emerge from the latter study of PA-6 in 5CB. It thus appears that, compared at equal temperature decrement and molecular weight, both MSHMA and PA-6 are more configurationally anisotropic than 3-PVE, whereas these polymers have respectively less and slightly
greater hydrodynamic association with SCB than does 3-PVE. Attempting to simultaneously rationalize these observations in terms of LCP molecular structure, one could cite appropriate differences among the three polymers in the relative conformational rigidity of their backbones, in their extent of solvent/mesogen chemical similarity, and in the lengths of their connecting spacer linkages.

3. TEMPERATURE AND SOLVENT DEPENDENCE

Having qualitatively examined the structure-derived influences of methylene spacer length and polymer molecular weight on the configurational anisotropy and hydrodynamic behavior of the n-PVE side-chain LCPs, it remained to determine the dependence of these properties on the solution variables of reduced temperature and nematic solvent type. Complementary measurements of the viscoelastic coefficients of SCB solutions of 3-PVE-30 and 9-PVE-30 and of an 8CB solution of 3-PVE-30 were therefore made at various temperature decrements within the nematic phase regions of these mixtures. Selection in studying the temperature-dependent behavior in SCB of the 3- and 9-spacer PVEs was based on their seeming opposite configurational anisotropy in this solvent at $\Delta T = -5^\circ C$. On the other hand, the decision to compare the behavior of 3-PVE-30 in SCB and in 8CB was motivated by the fact that 8CB exhibits distinctive pre-smectic character within its nematic temperature range, which it was thought might be manifested through the induction of a higher degree of configurational anisotropy in the dissolved LCP.

Summary is given in Table III-5 of the results obtained from the combined Fredericksz transition, field-dependent, and zero-field DLS decay rate measurements for the splay, twist, and bend elastic constants and of the twist and bend viscosity
coefficients for 5CB and its 8% w/w solutions of 3-PVE-30 and 9-PVE-30 at temperature decrements of \( \Delta T = -2, -5, \) and \(-10^\circ C\). Table III-6 compiles these same values of the viscoelastic constants for 8CB and its 3% w/w solution of 3-PVE-30 at temperature decrements of \( \Delta T = -1, -3, \) and \(-5^\circ C\). This particular choice of temperature decrements for the 5CB and 8CB mixtures facilitates comparison of the equilibrium and dynamical behavior of 3-PVE between the two solvents since, based on results reported by Madhusudana and Pratibha [57], each successive pair of \( \Delta T \) values corresponds to approximately equal values of the solvent order parameter, \( S \).

One observes among the values of the elastic constants reported in Tables III-5 and III-6 continuity with their previously discussed trend as a function of PVE spacer length. Moreover, it is evident from the present set of results that the tendency of the dissolved polymers to reduce the distortion elasticity of the solvent increases in proportion to the relative magnitude of \( \Delta T \) in either solvent. This is again attributed to progressive disruption of nematic order in the solvent due to the disordering influence of the non-mesogenic LCP constituents. The effect was visually evidenced in the 3-PVE-30/8CB planar monodomain sample by a \(~2^\circ C\) suppression of the nematic-to-smectic transition temperature, \( T_{AN} \). On the other hand, comparison of the various twist and bend viscosity increments of the mixtures with their corresponding elasticity decrements supports generalization of the assertion made earlier, that it is the former increments which account predominantly for the measured retardation of the nematic director distortion relaxation rates in the mixtures relative to the pure solvent.

The reduced temperature dependence of the apparent anisotropic dimensions of 3-PVE-30 and 9-PVE-30 in their respective mixtures is summarized in Tables III-7 and III-8. The estimated values of \( R_L \) and \( R_H \) were computed as before from the corresponding bend and twist reduced viscosity increments. Specific comparisons of
### Table III-5

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<td>SCB 3-PVE 9-PVE</td>
<td>SCB 3-PVE 9-PVE</td>
</tr>
<tr>
<td>$K_{11} \times 10^{-8}$ dyn cm$^{-5}$%</td>
<td>35 30 31</td>
<td>46 35 39</td>
<td>57 42 48</td>
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<tr>
<td>$K_{22} \times 10^{-8}$ dyn cm$^{-5}$%</td>
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<td>31 26 26</td>
<td>42 30 33</td>
</tr>
<tr>
<td>$K_{33} \times 10^{-8}$ dyn cm$^{-5}$%</td>
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<td>56 46 45</td>
<td>80 65 67</td>
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<tr>
<td>$\gamma_1$ poise$^{-5}$%</td>
<td>.30 .70 .47</td>
<td>.50 .91 .76</td>
<td>.80 1.3 1.2</td>
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<tr>
<td>$\eta_{bend}$ poise$^{-5}$%</td>
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<td>.15 .35 .20</td>
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### Table III-6

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<td>8CB 3-PVE</td>
<td>8CB 3-PVE</td>
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<td>$K_{11} \times 10^{-8}$ dyn cm$^{-5}$%</td>
<td>35 32</td>
<td>50 43</td>
<td>61 51</td>
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<tr>
<td>$K_{33} \times 10^{-8}$ dyn cm$^{-5}$%</td>
<td>35 30</td>
<td>52 45</td>
<td>67 59</td>
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<td>.48 .67</td>
<td>.65 .88</td>
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### Table III-7

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<th>$S_{SCB}$</th>
<th>[\gamma_1], cc/g</th>
<th>$\gamma_{bend}$, cc/g</th>
<th>$R_{L}$, nm</th>
<th>$R_{L}/R_{\parallel}$</th>
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<td>13</td>
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<td>0.415</td>
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<td>16</td>
<td>2.7</td>
<td>1.2</td>
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<tr>
<td>-10</td>
<td>0.465</td>
<td>7.2</td>
<td>17</td>
<td>2.8</td>
<td>1.3</td>
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### Table III-8

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<th>[\gamma_1], cc/g</th>
<th>$\gamma_{bend}$, cc/g</th>
<th>$R_{L}$, nm</th>
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<td>14</td>
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<tr>
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<tr>
<td>-5</td>
<td>0.445</td>
<td>12</td>
<td>15</td>
<td>2.7</td>
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Figure III-6: Variation with temperature of the estimated anisotropic hydrodynamic ratios $R_{\perp}/R_{\parallel}$ for 3-PVE-30 and 9-PVE-30 in S5CB.
Figure III-7: Variation with solvent nematic order parameter, S, of the estimated anisotropic hydrodynamic ratios $R_L / R_\parallel$ for 3-PVE-30 in 5CB and in 8CB.
the temperature variation in the anisotropy ratios of 3-PVE-30 and 9-PVE-30 in 5CB and of 3-PVE-30 in 5CB and in 8CB are illustrated graphically in Figures III-6 and III-7. The latter figure makes use of the surrogate parameter \(S\) as the temperature scale abscissa in order to normalize comparison of the behavior of 3-PVE-30 in the two solvents.

It is evident from the results reported in these two figures and tables that, in both PVE polymers, there is a general qualitative trend for \(R_\perp\) to increase relative to \(R_{\parallel}\) with increasing nematic order in the solutions. Quantitatively, it appears that the 3-spacer polymer adopts an increasingly oblate configuration in both 5CB and 8CB, the effect being more pronounced in the former solvent, whereas the 9-spacer LCP becomes increasingly less prolate in 5CB as temperature is decreased. These observations augment the previous comparison of 3-PVE-30 and 9-PVE-30 in 5CB at a single reduced temperature, and imply that increasing the orienting influence of the nematic field generally favors the tendency toward lateral packing of the PVE mesogenic groups. Compared at any particular reduced temperature, the inverted configurations of 3-PVE-30 and 9-PVE-30 in 5CB again reflect the spacer length dependence of the relative backbone/mesogen orientational coupling strength. The observed difference in the behavior of 3-PVE-30 in 5CB and 8CB, on the other hand, can be interpreted as manifestation of greater LCP excluded volume effects in the higher temperature nematic solvent.

As alluded to earlier, Brochard model analysis of the experimental data leads to an interpretation that is both quantitatively and, in most respects, qualitatively divergent with that given above. The inverse anisotropy ratios \(R_{\parallel}/R_\perp\) for the three LCP/LC mixtures leading to consistency with the Brochard expressions are presented as functions of the pure solvent order parameter in Figure III-8. It is seen from this plot that the configurational anisotropies of the polymers in all three mixtures are
Figure III-8: Variation with solvent order parameter of the inverse configurational anisotropy ratios of 3-PVE-30 in 5CB and 8CB, and of 9-PVE-30 in 5CB, as estimated from the experimental twist and bend viscosity increments using the Brochard theoretical expressions.
Figure III-9: Variation with solvent order parameter of the rotational relaxation times of 3-PVE-30 in 5CB and 8CB, and of 9-PVE-30 in 5CB, as estimated from the experimental twist and bend viscosity increments using the Brochard theoretical expressions.
decreased, precisely opposite to the trend suggested by the interpretation based on data analysis via Eq. 3-1. On the other hand, compared at equal reduced temperature, the relative ordering of the ratios \( R_1/R_0 \) among the three systems is preserved.

While the Brochard model interpretation of the data cannot be dismissed \textit{a priori} on grounds that it fundamentally contradicts expectations deriving from Warner-Wang theory, reason to doubt the numerical accuracy of the results presented in Figure III-8 emerges on back-calculating self-consistent values of the polymer chain relaxation time \( \tau_R \). As Figure III-9 illustrates, a physically unacceptable inverted trend is apparent in the temperature variation of this parameter, particularly in regard to the relaxation times computed for the 3-PVE-30/5CB solution. It may be conjectured that the origin of such anomalous implied behavior resides in the failure of the Brochard model to properly account for incremental viscosity effects in nematic mixtures of LCPs whose conformations approach spherical symmetry. In particular, it seems plausible to suggest that the anisotropic solution viscosity increments \( \Delta \gamma_1, \Delta \alpha_2, \text{and } \Delta \alpha_3 \) should not in fact uniformly vanish as predicted in this case. Further experimental evidence questioning the quantitative theoretical adequacy of the Brochard model will be presented in the following section of this chapter.

C. DLS AND RHEOLOGICAL CHARACTERIZATION OF Me-Si-6-CN AND MA-6-OCH\(_3\)

Using the combination of DLS and rheological characterization techniques discussed in Chapter II, the anisotropic viscoelastic coefficients of dilute 5CB mixtures of two additional side-chain LCPs were determined. Both polymers were
was its methyl siloxane polymeric mainchain. Manifesting the greater thermal lability of the backbone of this LCP compared with that of the vinyl ether series of polymers, undiluted MeSi-6-CN exhibits only smectic A thermotropic behavior over a temperature interval that extends from sub-ambient to 156°C. In regard to mesogen type, spacer length, and molecular weight as determined by GPC, this LCP is otherwise structurally comparable to the PVE polymers. On the other hand, the second of the two LCPs characterized in this study, MA-6-OCH₃, was chemically distinct from the preceding materials in regard to its methacrylate backbone, its methoxy-terminal mesogenic groups and, most conspicuously, its high molecular weight. The less polar nature of the mesogens of this LCP is indicated by the fact that MA-6-OCH₃ displays both nematic and smectic A mesophases as a neat material, with respective transition temperatures of $T_{NI} = 69°C$ and $T_{AN} = 104°C$.

Figure III-10 provides a composite illustration of the transient-stress rheological profiles obtained for homeotropically-aligned monodomain films of a
comparable results obtained for 5CB mixtures of MA-6-OCH₃ at weight concentrations of 2.55%, 0.89%, and 0.46% are presented in Figure III-11. Each of the mixtures was characterized using an applied steady shear rate of 16 sec⁻¹. It is apparent from Figure III-10 that an oscillatory viscous response develops in the 5CB solution of MeSi-6-CN below a characteristic reduced temperature. Moreover, Figure III-11 indicates that this trend is additionally concentration-dependent. In view of the fact that pure 5CB has been shown to exhibit shear-aligning behavior over its entire nematic range [66], the pattern of behavior displayed in these figures provides direct evidence that the hydrodynamic character of the dissolved polymers is such that they positively increment the Leslie coefficient α₃ of the solvent, thereby inducing director-tumbling behavior. Neglecting further analysis, this result is qualitatively consistent with the Brochard model interpretation that the LCPs have oblate anisotropic configurations in 5CB.

In order to more quantitatively test this apparent implication of the rheological behavior of the samples, both sets of rheograms were numerically modelled as previously indicated in Chapter II, making use of the corresponding values of γ₁ obtained by DLS characterization of the mixtures. Examples of the fits of the experimental data to the predictions of the 2-D ELP model for shear-aligning and shear-tumbling responses of the sample solutions are provided in Figures III-12. Comparison between the modelled and observed response of the sample is seen to be excellent in the shear-aligning case depicted in Figure III-12A. Despite progressive damping of the apparent viscosity with successive oscillations in the shear-tumbling case, Figure III-12B demonstrates the ability of the model to accurately reproduce the strain periodicity of the oscillations in addition to the initial stress overshoot behavior of the sample in this temperature regime.
Figure III-10: Rheograms illustrating the temperature dependence of the transient shear stress response of an initially homeotropically aligned film of the 2%w/w MeSi-6-CN/5CB mixture.
Figure III-11: Rheograms illustrating the temperature dependence of the transient shear stress response of initially homeotropically aligned films of MA-6-OCH₃ in SCB. The concentrations of LCP in each case are (a) 2.55% w/w, (b) 0.89% w/w, and (c) 0.46% w/w.
Figure III-12: Comparisons between the modelled and observed strain dependence of the transient shear stress response of MA-6-OCH₃ in SCB. The data in (a) were obtained from the 0.46%w/w LCP mixture at a temperature decrement of ΔT = -2.6°C, in the regime where the mixture retains the flow-aligning character of the pure nematic solvent. The rheogram in (b) was obtained from the 0.89%w/w mixture of the same polymer at ΔT = -1.4°C. The strain-dependent periodicity of the oscillatory stress response of the fluid in this case is clearly evident.
Summary of the results obtained from model interpretation of the rheological data along with those obtained from Mode 2 DLS characterization of the MeSi-6-CN and MA-6-OCH3/5CB mixtures is given in Tables III-9 and III-10, respectively. The tabulated results for $\eta_c$ were back-calculated from the experimental $\eta_{bend}$ values, and are seen to conform within measurable error in each case to the equality

$$\eta_b - \eta_c = \alpha_2 + \alpha_3 \quad 3-7$$

which obtains on applying Parodi's relationship to the Leslie coefficient expressions for $\eta_b$ and $\eta_c$ (Eqs. 1-19 and 1-20). In the case of the MeSi-6-CN mixture, the reported $K_{33}$ values were confirmed by magnetic Frederickse transition measurements. Inspection of these tables reveals that the nematic solutions of both LCPs display common patterns of behavior.

Among the measured elastic constants, for instance, one observes a consistent trend toward enhancement of $K_{33}$ and of the ratio $K_{33}/K_{22}$ in the LCP solutions relative to 5CB, the effect increasing both with increasing nematic order and with increasing LCP concentration. Curiously, $K_{22}$ decreases in the LC/LCP mixtures in comparison with the pure solvent. An intuitively straightforward rationalization of this effect is not obvious. It might instead have been anticipated that the solution increments of both elastic constants would demonstrate the same tendency as a function of reduced temperature, either uniformly increasing with order parameter, indicative of pre-smectic-like behavior, or uniformly decreasing, in consequence of a disordering influence of the coil-like dissolved polymers. The plausibility of the present results is nevertheless supported phenomenologically by similar reported findings in the literature. Specifically, the effect of dissolved side-chain LCPs separately to enhance the bend elasticity [26] and to diminish the twist elasticity [65,79] of nematic solvents has been experimentally confirmed. There has
Table III-9

MeSi-6-CN, 2.00% w/w

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<td>SCB</td>
<td>SCB/LCP</td>
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<tr>
<td>$K_{22}\times 10^{-8}\text{dyne}\pm 5%$</td>
<td>22</td>
<td>22</td>
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<tr>
<td>$K_{33}\times 10^{-8}\text{dyne}\pm 5%$</td>
<td>41</td>
<td>57</td>
<td>56</td>
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<tr>
<td>$\gamma_1 \text{ poise} \pm 5%$</td>
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<td>.57</td>
<td>.50</td>
</tr>
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<td>$\eta_c \text{ poise} \pm 5%$</td>
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### MA-6-OCH₃, 2.55%w/w

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<td>.72</td>
<td>.53</td>
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### MA-6-OCH₃, 0.89%w/w

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<td>K₃₃x10⁻⁸dyne±5%:</td>
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<tr>
<td>γ₁ poise±5%:</td>
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<td>-.034</td>
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<tr>
<td>ηb poise±5%:</td>
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<td>.19</td>
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<td>ηc poise±5%:</td>
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Table III-10, continued

MA-6-CH₃, 0.46% w/w

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<td>SCB</td>
<td>SCB/LCP</td>
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<td>25</td>
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<td>32</td>
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<tr>
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<td>53</td>
<td>58</td>
<td>72</td>
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<td>.80</td>
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<td>ηbend poise ±5%:</td>
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<td>-.034</td>
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<td>.63</td>
<td>.78</td>
<td>.79</td>
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additionally been at least one reported demonstration of the tendency exhibited by a series of structurally related side-chain LCPs simultaneously to increase $K_{33}$ and to decrease $K_{11}$ relative to their respective values in the pure solvent [80]. The results in this instance were argued to have been a consistent manifestation of the implied oblate anisotropy of the dissolved coils.

Of greater immediate interest from the standpoint of interpreting the configurational tendencies of MeSi-6-CN and MA-6-OCH$_3$ in 5CB, however, are the results obtained for the anisotropic viscosity increments induced in the solvent. In this regard as well, it is seen that the solutions of both polymers display common patterns of behavior. These may be summarized as follows:

1) The LCP solution increments to $\alpha_3$ are uniformly positive, and increase in magnitude both with increasing nematic order and, as shown by the MA-6-OCH$_3$ results, with increasing LCP concentration. The concentration dependence of $\Delta\alpha_3$ appears within experimental error to be linear in the range of concentrations studied.

2) The solution increments to $\alpha_2$ on the other hand are all negative. However, whereas the absolute magnitude of $\Delta\alpha_2$ increases with LCP concentration, this quantity consistently decreases with temperature in both polymer mixtures. The direction of change in $\Delta\alpha_2$ as a function of increasing nematic order in the two LCP mixtures is thus positive, qualitatively similar to the reduced temperature variation observed for $\Delta\alpha_3$.

3) Paralleling the patterns seen in $\Delta\alpha_3$ and $\Delta\alpha_2$, both $\Delta\eta_b$ and $\Delta\eta_c$ are increasing functions of LCP concentration, whereas the trends for these two viscosity increments with increasing nematic order are opposite, i.e., the magnitude of $\Delta\eta_b$ increases while that of $\Delta\eta_c$ decreases as temperature is decreased. Thus, the ratio $\Delta\eta_b/\Delta\eta_c$ is in all cases an increasing function both of LCP concentration and of the
nematic order of the solutions, in analogy with the behavior of the ratio $\Delta \alpha_3 / \Delta \alpha_2$.

4) As was observed in the study of the n-PVE-N LC/LCP mixtures, the solution increments to $\gamma_1$ generally exceed those to $\eta_{\text{bend}}$ in the SCB mixtures of both MeSi-6-CN and MA-6-OCH$_3$. However, like the ratios $\Delta \alpha_3 / \Delta \alpha_2$ and $\Delta \eta_b / \Delta \eta_c$, the ratio $\Delta \eta_{\text{bend}} / \Delta \gamma_1$ is seen to be an increasing function both of LCP concentration and of nematic order.

5) Lastly, the measured increments $\Delta \alpha_1$ are uniformly positive, and increase both with LCP concentration and with increasing nematic order.

Referring to the Brochard model expressions for $\Delta \alpha_2$, $\Delta \alpha_3$, $\Delta \eta_b$, and $\Delta \eta_c$ given in Chapter I, it is clear that this model is incapable of resolving the various experimental viscosity results to a single, self-consistent interpretation for the behavior of the anisotropy ratios of these two LCPs. In particular, there is an inherent theoretical contradiction implied by the results obtained for $\Delta \alpha_2$ and $\Delta \alpha_3$, inasmuch as the opposite signs of these two increments infer qualitatively divergent interpretations for the sense of the configurational anisotropy of the polymers. Similar contradictory interpretations obtain on comparing $R_\perp / R_\parallel$ values computed from the ratios $\Delta \gamma / \Delta \eta_c$, $\Delta \gamma / \Delta \eta_b$, and $\Delta \eta_b / \Delta \eta_c$. Presumably, these same antagonistic tendencies underlie the physically unacceptable trend in the $\tau_R$ results extracted from the n-PVE-N/SCB data.

On the other hand, if one assumes that the evolution of configurational anisotropy in MeSi-6-CN and MA-6-OCH$_3$ is such that the LCPs monotonically depart from spherical coil dimensions with increasing nematic order, then the temperature and concentration variations seen in the ratios $\Delta \alpha_3 / \Delta \alpha_2$ and $\Delta \eta_b / \Delta \eta_c$ qualitatively support the notion that both LCPs distort oblately in response to the nematic mean field. As seen in Figures III-13 and III-14, this interpretation is
additionally fostered by the trends observed in pairwise comparison of the quantities \([\eta_{\text{bend}}]/[\gamma_1]\), or \([\eta_b]/[\eta_c]\) obtained from the experimental data. The influence of the molecular weight difference between these two LCPs is clearly apparent in comparing the relative magnitudes of corresponding values of the different reduced viscosities. In the case of the higher molecular-weight methacrylate polymer, Figures III-14A and B furthermore indicate a measurable concentration dependence of the various \([\eta_i]\).

Nominal estimates for the anisotropy ratios of MeSi-6-CN and MA-6-OCH\(_3\) computed from the ratios \([\eta_{\text{bend}}]/[\gamma_1]\) and \([\eta_b]/[\eta_c]\) according to Eq. 3-1 are displayed as functions of reduced temperature in Figures III-15 and III-16, respectively. The results shown for MA-6-OCH\(_3\) were computed from concentration-corrected intrinsic viscosities, \([\eta_i]^*\), obtained on extraction of the corresponding reduced viscosities to infinite dilution as suggested by the Huggins equation, i.e.,

\[
[\eta_i] = [\eta_i]^* + k[\eta_i]^*c^2
\]

The former figure indicates that \(R_\perp/R_\parallel\) values variously estimated from \([\eta_{\text{bend}}]/[\gamma_1]\) and \([\eta_b]/[\eta_c]\) agree quite well with one another in the case of MeSi-6-CN. In Figure III-16, the divergence in the anisotropy of MA-6-OCH\(_3\) implied by the ratio \([\eta_b]/[\eta_c]\) is regarded as artifactual, since it numerically results from the smallness of \(\Delta\eta_c\) at the lowest temperature rather than a true divergence in \(\eta_b\).

Cross-comparison of anisotropy ratio estimates for the two different LCPs suggests that the methacrylate polymer exhibits more pronounced oblate character in SCB than the siloxane-backbone material throughout the entire nematic temperature range of the solutions. This result is somewhat surprising in view of the respective melt mesophasic behaviors of the two LCPs. It must be borne in mind, however, that intramolecular excluded volume and solvation effects play a significant role in
Figure III-13: Comparison of the temperature variation of the anisotropic reduced viscosities obtained for 2% w/w MeSi-6-CN in SCB.
Figure III-14: Comparison of the temperature variation of the anisotropic reduced viscosities obtained for three different concentrations of MA-6-OCH₃ in SCB.
Figure III-15: Reduced temperature variation in the anisotropy ratio of MeSi-6-CN in 5CB, as estimated from the ratios of the indicated reduced viscosities.
Figure III-16: Reduced temperature variation in the anisotropy ratio of MA-6-OCH₃ in 5CB, as estimated from the ratios of the indicated intrinsic viscosities.
determining the hydrodynamic dimensions of a polymer in solution. From this standpoint, both the more flexible backbone and the greater chemical similarity to 5CB of the mesogens of MeSi-6-CN favor this polymer's exhibiting stronger polymer-solvent interactions with 5CB than does MA-6-OCH$_3$, in consequence of which it appears that anisotropic distortion of the former LCP is relatively less favored.

A final remark is in order regarding the results found for the Leslie increments $\Delta \alpha_1$. Physically interpreted, these represent LCP solution changes in the extensional viscosity of 5CB [34]. As previously stated, their trend with increasing LCP concentration and nematic order is increasingly positive. Based on the results reported by Kneedle et al. in reference [60], this behavior is qualitatively analogous to the differences observed in comparing $\alpha_1$ between 5CB and 8CB at successively increasing equal values of the solvent order parameter. Specifically, whereas $\alpha_1$ is negative and decreases as a function of $S$ in 5CB, this coefficient is uniformly positive in 8CB, and diverges on approaching $T_{AN}$. The positive increments to $\alpha_1$ observed in the LCP solutions are therefore suggestive of the induction of pre-smectic-like enhancement of lateral mesogenic order in 5CB by the dissolved polymers, and seem additionally to confirm the oblate anisotropic character of the coils in solution.
It has been the intent of this work to compare and contrast the influences of side-chain LCP structure and molecular weight in relation to the nematic character of the LC solvent in determining the anisotropic conformation adopted by a side-chain LCP in dilute nematic mixtures with LC solvents. In this regard, a variety of behaviors has been observed. An inherently related goal of the work has been to experimentally test the accuracy of the predictions of the Brochard and the Warner-Wang models. Conclusions drawn in the previous chapter with regard to both issues may now be summarized, and indications given of those areas that deserve further experimental scrutiny.

In restatement of the significant results obtained from the n-PVE-N studies, depolarized dynamic light-scattering characterization of dilute mixtures of the polymers with SCB shows directly that the relaxation rates for splay, twist, and bend distortions of the nematic director decrease on the addition of polymer. Independent measurement of the elastic constants of the mixtures indicates that these changes are accounted for by small decreases in the various $K_{ii}$ and comparatively larger increases in the corresponding viscosity coefficients of the solutions relative to their values in the pure solvent. The results obtained for both sets of viscoelastic constants demonstrate that the static and hydrodynamic influence of the dissolved LCPs on the anisotropic behavior of SCB generally diminishes with successive increases in the length of the methylene spacer groups of the polymers.

Furthermore, the patterns that emerge in comparing the ratio $[\gamma_1]/[\eta_{\text{bend}}]$ as a function of spacer length and temperature suggest that, for $n = 2, 3, 5$, and 7, the solvated LCPs have anisotropically oblate configurations in the nematic SCB.
mixtures. The extent of this anisotropy evidently increases modestly with increasing nematic order in the solution, whereas it decreases with increasing spacer length, such that an inversion to prolate conformations is implied in the case of the 9-spacer LCP. This observation in regard to the spacer length dependence of the configurational anisotropy of the polymers is consistent with the predictions of the Warner-Wang model. The apparent reversion to oblate character observed in the SCB solution of 11-PVE-30 represents an exception to this rule, and presumably reflects smectic-like lateral association of the methylene spacer moities when these exceed a critical length.

The nature and extent of anisotropic configurational coupling of a side-chain LCP to the nematic field moreover appears to be an intrinsic property of the monomeric structure of the polymer, as evidenced by the insensitivity of the anisotropy ratio of 3-PVE-N dissolved in SCB to the degree of polymerization of the material. On the other hand, the molecular weight dependence of the anisotropic hydrodynamic dimensions of this polymer, estimated as equivalent sphere radii parallel and perpendicular to the nematic director from $[\gamma_1]$ and $[\eta_{\text{bend}}]$, respectively, implies that there exists strong hydrodynamic association between the solvent and the mesogens of the LCP, presumably in consequence of the chemical similarity of these two groups. Equivalently stated, the hydrodynamic behavior of the dissolved coils appears to be more nearly non-draining than free-draining.

DLS studies of MeSi-6-CN and MA-6-OCH$_3$ in SCB have shown that these two LCPs behave qualitatively similar to 3-PVE-30 in respect to the relative magnitude and temperature variation of their ratio $[\gamma_1]/[\eta_{\text{bend}}]$. By implication, the configurational anisotropies of these two LCPs in SCB are likewise taken to be oblate, to an extent that increases with the nematic order of the solution. Supporting
this interpretation are the reduced temperature trends observed in the ratios \( \eta_b/ \eta_L \)
and \( K_{33}/K_{22} \), as well as in the anisotropic viscosity increments \( \Delta \alpha_1 \) and \( \Delta \alpha_3 \) obtained
by electric field-dependent DLS, magnetic Fredericksz transition, and rheological
characterizations of these mixtures.

A final illustration of the combined influences of mesogen type, backbone
type, and flexible spacer length in determining the configurational response of a side-
chain LCP to the orientationally anisotropic environment of a nematic solvent is
given in Figure IV-1, which replots as a function of reduced temperature the
\( [\gamma_1]/[\eta_{\text{bend}}] \) estimates for the anisotropy ratios of 3-PVE-30, 9-PVE-30, MeSi-6-CN,
and MA-6-OCH\(_3\) in 5CB. Assessed in terms of their relative tendencies toward
oblate character, the results displayed in this figure imply the ranking

\[
\text{MA-6-OCH}_3 > 3\text{-PVE-30} > \text{MeSi-6-CN} > 9\text{-PVE-30}
\]

Referring to Eqs. 1-1 and 1-7, rationalization of this behavior in the context of the
Warner-Wang model suggests that the inequality \( \chi v_c < \nu_f/n \) characterizes the former
three LCPs, whereas in 9-PVE-30 this relationship is reversed. Since the frequency
distribution of side-chains along the backbone is the same in all four polymers, and
there is no obvious structural basis for assuming there to be any significant amount of
variation in the extent of side-chain/main-chain nematic coupling among them, it
would appear that the parameter \( \nu_f \) exerts a predominant role in determining the sense
of the configurational anisotropy that develops in each case. This argument
intuitively accords with what one expects in considering the different spacer lengths
and chemical functionalities of the various "hinge" elements in this particular group
of side-chain materials.

A secondary influence of backbone flexibility is evident in the relative ranking
of the three oblate LCPs, emphasizing the role of the parameter \( \varepsilon \). Neglecting a
Figure IV-1: Reduced temperature variation in the anisotropy ratios in SCB of the various side-chain LCPs investigated in this work in SCB, as estimated from their respective $[\eta_{bend}]/[\eta_1]$ ratios.
possible molecular weight influence, the distinctly higher degree of oblate anisotropy inferred for MA-6-OCH₃ could as well derive in part from the polarity difference between its methoxy-terminal mesogens and the highly polar cyanobiphenyl moieties of 5CB. Thus, there might exist some amount of solution enhancement of lateral ordering of the mesogens within this polymer due to their marginal miscibility in 5CB, reminiscent of induced-smectic phase separation phenomena frequently seen in binary mixtures of polar and non-polar low-molecular-weight LCs [81,82]. This same non-ideal solution behavioral influence of mesogen polarity differences has been observed in a variety of side-chain LCP/LC mixtures [83]. An effect of this type could be accounted for within the formalism of the Warner-Wang model as a reduction in the effective value of χ in the methacrylate polymer compared with the cyanobiphenyl mesogen LCPs, whose nematic interactions with 5CB undoubtedly involve mesogen-solvent dipole pairing.

Aside from the fairly small degrees of configurational anisotropy observed among the polymers, the non-mesogenic coil-like character of the LCPs is evidenced by the uniformly opposite temperature variation of their estimated anisotropy ratios and their hydrodynamic volumes, calculated as \( \frac{4}{3} \pi R^3 \). As Table IV-1 demonstrates, all three of the polymers 3-PVE-30, MeSi-6-CN, and MA-6-OCH₃ hydrodynamically expand with increasing temperature, analogous to the behavior of conventional linear-chain polymers in isotropic solvents in which the temperature variation of the Flory polymer-solvent interaction parameter, χ, is negative. An extension of this behavior is seen in comparing the estimated anisotropy ratios and hydrodynamic volumes of 3-PVE-30 at equal values of the solvent order parameter between 5CB and 8CB. Thus, at higher absolute temperatures in the latter solvent, this LCP appears to be more highly expanded, in consequence of which its anisotropy at comparable nematic solvent strength is reduced. The analogous contrast in the
<table>
<thead>
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<th>V_{h} \times 10^{-19} \text{cc/chain}</th>
<th>\Delta T = -2</th>
<th>\Delta T = -5</th>
<th>\Delta T = -10</th>
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<td>3-PVE-30/5CB:</td>
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<td>9-PVE-30/5CB:</td>
<td>0.33</td>
<td>0.38</td>
<td>0.38</td>
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<td>MeSi-6-CN:</td>
<td>3.7</td>
<td>3.1</td>
<td>2.7</td>
</tr>
<tr>
<td>MA-6-OCH_{3}/5CB:</td>
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<td>32</td>
<td>28</td>
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<tr>
<td>3-PVE-30/8CB:</td>
<td>0.75</td>
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</table>
anisotropies of MeSi-6-CN and MA-6-OCH$_3$ compared at equal reduced temperatures in SCB has been argued to reflect greater intramolecular excluded volume effects in the former LCP, deriving from its higher backbone flexibility and higher solvency in this solvent.

A theoretical basis for rationalizing the antagonistic influences of absolute and reduced temperature on the anisotropic distortion of a nematically solvated LCP is provided by Brochard's adaptation of Flory-Huggins theory to thermotropic nematic mixtures [52.84]. In order to account for the solubility coupling influence of the orientationally ordered nematic matrix, Brochard proposes the following revised expression for the Flory solvent-solute interaction parameter $\chi_{nem}$ in the nematic phase

$$\chi_{nem} = \chi_{iso} + \frac{\tau S^2}{T}$$

where $\chi_{iso}$ represents a virtual value for the interaction parameter in a hypothetical isotropic phase at the same temperature, $S$ is the order parameter, $T$ is the absolute temperature, and the sign of the coupling coefficient $\tau$ determines whether the existence of nematic order contributes positively ($\tau < 0$) or negatively ($\tau > 0$) to the solubility of a particular polymer solute.

In the case of a nematic LC/LCP mixture, it is expected that the value of $\tau$ will sensitively reflect the balance of competing mesogenic and non-mesogenic influences exerted by each of the various structural elements of the molecule. Assuming the polymeric nature of the material dictates $\chi_{iso} > 0$, a positive value of $\tau$ implies that the solubility of the LCP, hence its thermodynamic and hydrodynamic volumes, will increase with increasing temperature in the nematic solution phase. This appears to be the case for 3-PVE-30, MeSi-6-CN, and MA-6-OCH$_3$. The inversion in the temperature dependence of the anisotropy and hydrodynamic volume observed for 9-
PVE-30 in SCB, on the other hand, suggests \( \tau < 0 \) in this case. The plausibility of a negative value for \( \tau \) in the 9-PVE-30/SCB mixture can be argued on the basis of the nearly complete decoupling influence of the long spacer in this LCP.

Assuming the present estimates of the anisotropies of the various LCPs to be at least qualitatively accurate, there remains the problem of explaining the discrepancies with the Brochard model implied by certain key relationships among the various experimentally measured solution viscosity increments. The inherently contradictory implication of the observation \( \Delta \alpha_3 > 0 \) and \( \Delta \alpha_2 < 0 \) in particular deserves further attention. It would appear that the physical basis for this theoretically anomalous effect of the dissolved polymers also serves to explain the divergence between Brochard model predictions and experimental observations in regard to the relative magnitudes of \( \Delta \eta_b \) and \( \Delta \eta_c \), and of \( \Delta \gamma_1 \) and \( \Delta \eta_{\text{bend}} \).

Consistency with the results obtained from the MeSi-6-CN and MA-6-OCH\(_3\) SCB mixtures obtains if the Brochard expressions for \( \Delta \alpha_2 \) and \( \Delta \alpha_3 \) are empirically modified according to

\[
\delta \alpha_2 = \left( \frac{c_b T}{N} \right)_{\text{TR}} \left( 1 - \frac{\kappa R_1^2}{R_2^2} \right) \tag{4.2}
\]

and

\[
\delta \alpha_3 = \left( \frac{c_b T}{N} \right)_{\text{TR}} \left( \frac{R_1^2}{\kappa R_1^2} - 1 \right) \tag{4.3}
\]

where the parameter \( \kappa \) is assumed to be an implicitly temperature- and solvent-dependent positive function having a value greater than one. Equations 4.2 and 4.3 in turn require that Brochard's expressions for \( \Delta \gamma_1 \), \( \Delta \eta_b \), and \( \Delta \eta_c \) be correspondingly revised according to

\[
\delta \gamma_1 = \left( \frac{c_b T}{N} \right)_{\text{TR}} \frac{(R_1^2 - \kappa R_1^2)^2}{\kappa R_1^2 R_2^2} \tag{4.4}
\]
\[ \delta \eta_b = \left( \frac{c_k B T}{N} \right) \kappa_R \left( \frac{R_1^2}{\kappa R_1^2} \right) \]  

and

\[ \delta \eta_c = \left( \frac{c_k B T}{N} \right) \kappa_R \left( \frac{\kappa R_1^2}{R_1^2} \right) \]

It will be noted that, within a certain range of values for \( \kappa > 1 \), it is possible to account in a qualitatively self-consistent manner for all of the trends in the experimental data cited in the previous chapter.

The particular form of the above modifications implies that there is an intrinsic contribution to viscous energy dissipation in the LCP mixtures associated with nematic extension of the mesogenic side-chains parallel to the director, whatever the configuration of the polymeric backbone. On the same physical grounds that the inequalities \( |\alpha_2| > |\alpha_3|, \eta_c > \eta_b \), and \( \gamma_1 > \eta_{\text{bend}} \) typify the behavior of low-molecular-weight rod-like nematics, it is entirely reasonable to expect that the rod-like pendant moieties of a dissolved LCP independently contribute to the various anisotropic viscosity coefficients of an LC/LCP mixture. One need only bear in mind that it is the mesogenic attributes of these portions of a side-chain LCP which overwhelmingly account for its miscibility in the nematic phase of an LC solvent to see the justification in this argument. The magnitude of this contribution is accordingly greatest in the case of the larger of these pairs of coefficients, and becomes increasingly masked as the LCP backbone anisotropy increases.

An interesting difference in the prediction of Eq. 4-4 compared to that of Eq. 1-54 is that \( \Delta \gamma_1 \) remains finite even if the polymer assumes a globally spherical conformation. This aspect of the Brochard model has been investigated experimentally by Jakli [85], whose measurements of \( \Delta \gamma_1 \) in nematic solutions of a
low-molecular-weight polystyrene sample demonstrated a negligible influence of the
dissolved polymer, seemingly concurring its isotropic conformation. The prediction
of a finite increment to $\gamma_1$ by an isotropically configured side-chain LCP does not in
any case conflict with these results, since the effect is specifically associated with the
extended mesogenic side-groups of the polymer.

A valid question in regard to the quantitative integrity of the anisotropy
assignments made in this work is whether the hydrodynamically equivalent sphere
estimates of $R_{11}$ and $R_{\perp}$ from [$\gamma_1$] and [$\eta_{\text{bend}}$] accurately reflect these dimensions of
the polymers. In fact, theoretical analogues to Eq. 3-1 expressing the dependence of
any of the various nematic intrinsic (reduced) viscosities on the hydrodynamic
dimensions of a dissolved polymeric solute, whether isotropic or anisotropic, have yet
to emerge. Neither do there yet exist appropriate theoretical relationships that would
allow one to infer the unperturbed thermodynamic dimensions of a nematically
dissolved polymer from its measured hydrodynamic dimensions.

It would therefore seem that rigorous confirmation of the results reported in
this work will require the employment of absolute size determination techniques such
as SAXS and/or SANS. Surprisingly in this regard, despite the wide use of these
methods to elucidate the mesophase conformational behavior of side-chain LCPs as
pure melts, comparable studies performed on dilute nematic solutions of the materials
appear at present to be restricted to Mattoussi's work [8] cited in Chapter I. Given the
potential for future implementation of side-chain LCPs in LC electro-optical device
applications, further investigations of this sort are clearly warranted.
Chapter I.

Chapter II.

Chapter III.


Chapter IV.