Macromolecules **1989,** *22,* 4102–4105

Magnetooptic Investigation of Chain Conformation and Landau Coefficients in Oligomeric Liquid Crystals

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ABSTRACT: Magnetically induced birefringence measurements in the isotropic phase are reported for monomers containing a phenyl benzoate core, the associated dimer, and mixtures of the two. The coefficients in the Landau free energy expansion are obtained. On the basis of the results, we conclude that the dimer spacer exhibits a nearly completely random conformation in the isotropic phase and extends significantly in the nematic phase.

In recent years the liquid-crystalline states of bulk polymers have become the subject of intense scrutiny. Although much of the interesting behavior is associated with the rigid mesomorphic groups, the semiflexible spacers also pay a crucial role in determining such properties as the latent heat at the nematic–isotropic (NI) phase transition, the discontinuity in the nematic order parameters, and the accessibility of the supercooling temperature T^* of the isotropic phase.[1-3] Prior to recent theoretical[4-6] and experimental work in this area, it was generally assumed that the flexible spacers act as inert solvents, occupying volume but otherwise playing no active role in the phase transition. This picture, however, has been completely shattered by the work of Sigaud, Yoon, Griffin, and others, wherein magnetic susceptometry, calorimetry, and NMR have been used to show that the characteristics of the NI transition in the polymer can be quite different from those of the model monomer.[1-3,7-11] In many compounds it was found, for example, that an otherwise coiled, flexible spacer in the isotropic phase tends to extend and therefore rigidify in the nematic. The extension of the spacer would, of course, be reflected in the transition enthalpy[1] to the extent that both the available chain configurations and the pair-excluded volume would be altered.

In light of the significant differences between monomeric and polymeric liquid crystals, the issue of "crossover" must be addressed. In other words, as the molecule is lengthened by the addition of a mesogenic unit and spacer, at what point does the oligomer begin to exhibit properties more like a polymer than a monomer? To this end work has been performed on a number of systems. Blumstein et al. have investigated[12-14] the monomer *p*-azoxyanisole (PAA) and two related main-chain dimers, 9DDA9 and 9AZA9, which contain a decyl and a heptyl spacer, respectively. Since the monomer and dimers differ somewhat in their aromatic groups, however, direct comparison of physical data can be somewhat clouded. Griffin and Britt[15] have synthesized a model monomer consisting of a 4,4′-phenyl benzoate mesogenic core between a pair of pentyloxy groups ($C_5H_{11}OC_6H_4COOC_6H_4OC_5H_{11}$). The dimer, consisting of the two mesogenic cores separated by the spacer $OC_{10}H_{22}O$, corresponds to a pair of monomers (minus two hydrogens) attached end to end. The tetramer[16] and much longer polymer have also been synthesized. Thus, given the close similarity between the monomer and repeat unit of the oligomer, one would expect many physical properties, such as the optical and magnetic anisotropies, to scale simply as the number of repeat units.[1] As a consequence, one can directly compare quantities such as the transition enthalpy per repeat unit in the monomer and dimer, drawing conclusions about physical quantities such as spacer conformation. It is with this in mind that we have performed Cotton–Mouton measurements in the isotropic phase of the phenyl benzoate monomer and dimer, as well as in mixtures of the two materials. Drawing on our own data and that of others, we have obtained the coefficients up to fourth order in a Landau expansion for the various samples. Our central result is that the quadratic coefficient a increases slightly with dimer concentration, whereas the cubic and quartic coefficients increase substantially. From these results we make inferences about the dependence of the spacer conformation on the nematic order parameter.

The monomer and dimer were synthesized according to procedures described elsewhere.[17,18] Four concentrations were studied, expressed in terms of dimer weight fraction X: $X = 0, 0.352, 0.669$, and 1.000. Samples were contained in a 1-cm path-length cuvette, which in turn was housed in a brass oven temperature controlled to 25 mK. The oven was inserted in the bore of an 8.2-T superconducting magnet with transverse optical ports. Details of the oven and birefringence apparatus are given elsewhere.[19] The field H was swept from 0 to typically 2 or 3 T in approximately 6 min, and the field-induced optical birefringence Δn was computer recorded.

In all cases the birefringence was found to be linear in H^2 (Figure 1), and the Cotton–Mouton coefficient $C(X, T)$ $[\equiv \partial \Delta n / \partial H^2]$ was determined by a linear least-squares fit of the data. Data were typically taken over a temperature range $T_c \le T \le T_c + 5$ K, where T_c is the first-order phase-transition temperature. At all concentrations C^{-1} was found to be linear in T (Figure 2), indicating a mean-field susceptibility exponent $\gamma = 1$. Given the apparent mean-field behavior in the isotropic phase, the Cotton–Mouton coefficient C can be shown to be[20]

$$C(X, T) = \frac{\Delta n_o \Delta \chi_o}{3a(X)[T - T^*(X)]} \equiv \frac{\Phi(X)}{[T - T^*(X)]} \quad (1)$$

where $\Delta\chi_o$ and Δn_o are the volume magnetic susceptibility anisotropy and birefringence for fully saturated order and a is the quadratic coefficient in the Landau free energy expansion:

$$\mathcal{F} = \tfrac{1}{2}a(T - T^*)S^2 - \tfrac{1}{3}bS^3 + \tfrac{1}{4}cS^4 - \tfrac{1}{3}\Delta\chi_o H^2 S \quad (2)$$

S, of course, is the scalar nematic order parameter. The Cotton–Mouton constant was measured as a function of temperature for each concentration, and $T^*(X)$ and $\Phi(X)$ were obtained by a linear least-squares fit of C^{-1} vs T; the

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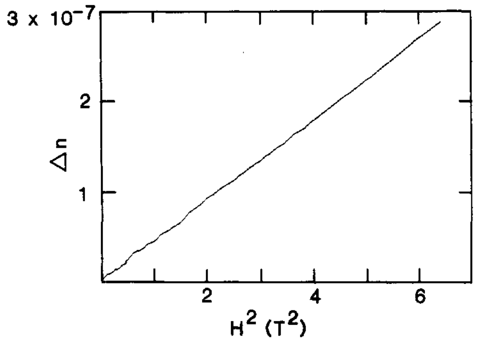

Figure 1. Typical computer trace of Δn vs H^2. For this sample $X = 0.669$ and $T = 129.50$ °C.

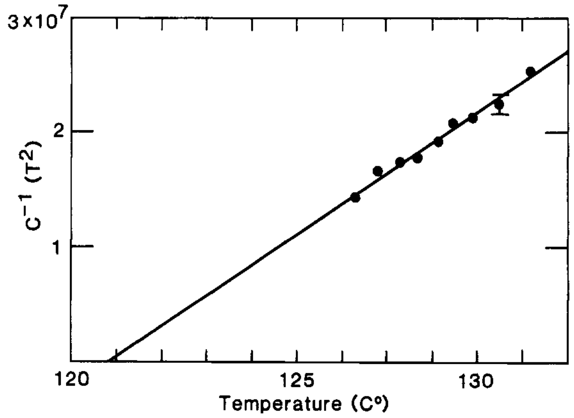

Figure 2. Typical plot of C^{-1} vs temperature, in this case for $X = 0.669$. The solid line is a linear least-squares fit whose slope is equal to $1/\Phi$ (cf. eq 1).

Table I
Measured Parameters vs Dimer Concentration *X*

dimer concn	$\Phi(K/T^2)$	T^*, °C	$T_c - T^*$
0	$(5.1 \pm 0.5) \times 10^{-7}$	78.3 ± 0.3	1.3 ± 0.3
0.352	4.5×10^{-7}	101.5	3.2
0.669	3.8×10^{-7}	120.8	5.2
1.000	4.1×10^{-7}	140.1	8.9

results are given in Table I as a function of dimer weight fraction X. Moreover, since the NI transition is by symmetry first order, the supercooling temperature T^* toward which the Cotton–Mouton coefficient appears to diverge is cut off by the actual transition temperature T_c. The difference $\delta T \equiv T_c - T^*$, which is a measure of the discontinuity of the first-order transition, is also given in Table I.

In order to obtain the coefficient a we note that $\Delta\chi_o$ has been calculated[1] for the repeat segment for both the all-trans conformation of the alkyl groups ($\Delta\chi_o = 1.32 \times 10^{-7}$ cgs) and the coil conformation ($\Delta\chi_o = 1.19 \times 10^{-7}$ cgs). Given that the difference between these two extreme cases is small and that neither extreme is likely, we can reasonably take the value of $\Delta\chi_o$ to be 1.25×10^{-7} cgs, independent of temperature.[1] To obtain Δn_o, we constructed a thin sample cell with a measured optical path length of 9.66 ± 0.15 μm. The glass was coated with nylon 6/6 and rubbed to give parallel alignment. After filling the cell with monomer, the birefringence was measured in the nematic phase over the temperature region $T_c - 20\ \mathrm{K} \leq T \leq T_c$. Comparing the measured values of $\Delta n(T)$ with published results for $\Delta\chi(T)$,[1] we found that $\Delta n/\Delta\chi = (1.63 \pm 0.03) \times 10^6$ cgs, independent of temperature. Since $\Delta n(T)$ and $\Delta\chi(T)$ are both expected to approximately scale as the nematic order parameter,[20] we can take $\Delta\chi_o = 1.25 \times 10^{-7}$ cgs and find that $\Delta n_o = 0.204 \pm 0.004$. Finally, from eq 1 we see that $a(X) = (\Delta n_o \Delta\chi_o)/3\Phi(X)$; $a(X)$ is reported in Table II.

Table II
Derived Landau Coefficients (eq 2) vs Dimer Concentration *X*

dimer concn	a, erg/K/cm^3	b, erg/cm^3	c, erg/cm^3
0	$(1.7 \pm 0.2) \times 10^6$	$(1.8 \pm 0.2) \times 10^7$	$(3.4 \pm 0.5) \times 10^7$
0.352	$(1.9 \pm 0.2) \times 10^6$	$(5.1 \pm 0.6) \times 10^7$	$(9.4 \pm 1.1) \times 10^7$
0.669	$(2.3 \pm 0.3) \times 10^6$	$(9.0 \pm 1.1) \times 10^7$	$(15.1 \pm 1.8) \times 10^7$
1.000	$(2.1 \pm 0.4) \times 10^6$	$(11.5 \pm 2.0) \times 10^7$	$(16.3 \pm 2.6) \times 10^7$

The coefficients b and c in eq 2 can also be readily obtained. We use the two relationships[20]

$$\delta T = 2b^2/9ac \tag{3}$$

and

$$L = 2aT_cb^2/9c^2 \tag{4}$$

where L is the latent heat at the NI transition. The quantity δT is given in Table I, and the transition temperature T_c is, of course, equal to $T^* + \delta T$. The latent heats for the pure monomer and dimer are reported in ref 1; for the two intermediate concentrations we have linearly interpolated between $L(X = 0)$ and $L(X = 1.00)$. Thus, from eq 3 and 4 we can extract the Landau coefficients b and c, which are reported in Table II. Note that, for the monomer, at least, the values for the three coefficients are quite similar to those reported for other monomeric compounds.[21]

In the remainder of the paper we discuss the results, especially those for a, in terms of some current models of the NI phase transition. It should be noted that the ensuing discussion applies to rigid spherocylinders. Our goal is to treat the dimer as two rigid segments connected by a spacer of to be determined flexibility. To the extent that this group occupies volume and connects to the rigid segments, we cannot count on these models for reliable quantitative results. However, in light of the absence of appropriate theories, the discussion below provides a qualitative foundation for understanding the experimental results and hopefully will provide an impetus for further theoretical work.

Photinos and Saupe have recently derived the Cotton–Mouton coefficient C for rigid particles in a general potential.[22] For a fixed molecular concentration

$$1/C \propto \rho T[1 - 5\sum_{\kappa\geq1} \kappa B_\kappa \rho^\kappa] \tag{5}$$

where

$$B_\kappa = (1/4\pi)^{\kappa+1} \int P_2(\cos\theta_1)P_2(\cos\theta_2)\beta_\kappa(\Omega_1, \Omega_2, ..., \Omega_{\kappa+1})\, d\Omega_1\, d\Omega_2 \ldots d\Omega_{\kappa+1} \tag{6}$$

and ρ is the number density of rigid (persistence) lengths. Note that, for a fixed number of molecules, ρ decreases as the molecule stiffens and the characteristic persistence length increases. In eq 6 β_κ represents volume integrals of the products formed by the function $f_{ij} = \exp(-u_{ij}/k_BT) - 1$, where u_{ij} is the pair potential and k_B is Boltzmann's constant. In the subsequent discussion we retain only the first correction term $\kappa = 1$; this approximation is consistent with the theories discussed below and has no substantive effect on the qualitative results. The integral can be qualitatively treated[23] by noting that, for separations less than or equal to the largest of the rod dimensions and for certain orientations, $u_{ij} \gg k_BT$ and $f_{ij} \simeq -1$. The integral of f_{ij} over this distance contains two terms: an orientationally isotropic part arising from the integral over distances less than or equal to the *smaller* rod dimension and an anisotropic part arising from the remainder of the integral. This integral thus represents the negative of the effective excluded covolume β_1^{ex}. At larger separations where $u_{ij} \leq k_BT$, f_{ij} can be expanded in a series in $1/T$: $f_{ij} = -u_{ij}/k_BT + u_{ij}^2/2k_B^2T^2 - ...$, resulting in an additional contribution to β_1, which goes as $-(1/T)\beta_1' + \mathcal{O}(1/T^2)$. Thus $\beta_1 = -\beta_1^{ex} - (1/T)\beta_1' + \mathcal{O}(1/T^2)$ and, from eq 6, we obtain an analogous form for B_1. Substituting these results into eq 5, we find that

$$1/C \propto \rho T[1 - 5\rho(-B_1^{ex} - B_1'/T + \mathcal{O}(1/T^2))] = \rho T(1 + 5\rho B_1^{ex}) + 5\rho^2 B_1' + \mathcal{O}(1/T) \qquad (7)$$

Comparing eq 7 with eq 1, we immediately see that the parameter a is proportional to $\rho(1 + 5\rho B_1^{ex})$, where $B_1^{ex} < 0$ and $|B_1^{ex}|$ increases rapidly as the persistence length increases. T^* is related to the long-range anisotropic interactions through B_1'. Thus, to the lowest order approximation, a involves both the orientational entropy (the constant term) and the anisotropic part of the steric interactions (B_1^{ex}); in principle, a can be calculated for a strictly hard rod athermal system. In an early attempt to predict an NI transition for just such a system, Onsager obtained the pair-excluded volume for spherocylinders to the level of the second virial coefficient,[24] as developed above. Although his model is satisfactory for very long rods at low densities, the predictions become unrealistic at high densities owing to poor convergence of his truncated ($\kappa = 1$) free energy expansion. In that sense eq 7 is only an approximation, although it shows that a arises primarily from the direct orientational entropy and steric terms in the free energy.

In order to better understand a we need to investigate more sophisticated theories of nematic ordering of hard rods appropriate to high density and small aspect ratio. Lee, for example, used functional scaling to develop[25] a spherocylindrical particle generalization of the Carnahan–Starling equation for the free energy of hard spheres.[26] His model, which reduces to the Onsager theory in the low-density long-rod limit, is in good agreement with Monte Carlo simulations for short, high-density rods at the NI phase transition.[27-29] Moreover, his results are in reasonable agreement with elasticity and viscosity data for tobacco mosaic virus in suspension.[30-32] Lee's free energy density contains a number of terms, only two of which are functions of the nematic order parameter S

$$\mathcal{F}_S = \rho k_BT[\sigma(f) + 3\pi\alpha\eta(4 - 3\eta)\tau(f)/8(1 - \eta)^2] \qquad (8)$$

where $\sigma(f)$ is the usual orientational entropy for the distribution function f, i.e., $\sigma(f) = \int f(\Omega)\ln[4\pi f(\Omega)]d\Omega$, α is an increasing function of the aspect ratio, and η is the packing fraction. The function $\tau(f)$ describes the angle-dependent excluded volume effects and is given by

$$\tau(f) = (4/\pi)\int\int|\sin\gamma(\Omega_1, \Omega_2)|\, f(\Omega_1)\, f(\Omega_2)\, d\Omega_1\, d\Omega_2 \qquad (9)$$

where γ is the angle between the two rods. For very weak magnetically induced order we can always write $f \simeq [1 - 5SP_2(\cos\theta)]/4\pi$, and thus eq 8 and 9 can be easily evaluated. We find after performing the integrals that

$$\mathcal{F}_S = \rho k_BTS^2[5 - 0.763\alpha\eta(4 - 3\eta)/(1 - \eta)^2] \qquad (10)$$

Comparing eq 10 with eq 2, we immediately see that

$$a = 2\rho k_B[5 - 0.763\alpha\eta(4 - 3\eta)/(1 - \eta)^2] \qquad (11)$$

The result in eq 11 is quite similar to the coefficient a obtained by Collot et al.,[33] using a density functional theory in which thermodynamic quantities such as pressure and free energy are functionals of the *local* density $\rho(x)$. They performed a truncated expansion of $\mathcal{F}$ in powers of S for hard ellipsoids, finding that a is composed of two terms, one linear in ρ (and equal to the first term in eq 11) and another that is a somewhat complicated function of the aspect ratio. In both models this second term appears with a minus sign, is an increasing function of the packing fraction, and increases approximately linearly with the aspect ratio.

We now apply these models, qualitatively at least, to the results in Table II. If we assume that both the monomer and dimer are perfectly rigid in the isotropic phase, then both models[25,33] (and that of Onsager as well[24]) would predict a sharp decrease in a on increasing the dimer concentration. We can understand this as follows: for equal mass densities in the isotropic phase, the number density ρ for pure dimer is half that for pure monomer. Moreover, the packing fractions η for monomer and dimer are equal, but the aspect ratio parameter α (cf. eq 11) for the dimer is slightly more than twice that of the monomer. As a result, we would expect that a for pure dimer would be only 0.2–0.4 times that for pure monomer. In fact, we experimentally find that a *increases* with X, a result qualitatively consistent with those that obtained on PAA and 9DDA9.[11] If instead we now assume that the spacer in the dimer is completely flexible, permitting almost free rotation of one mesogenic core with respect to the other, the mesogenic units would nearly mimic free monomers; both the aspect ratio parameter α and the number density associated with the dimer would then be the same as those of the monomer. Consequently, the parameter a would be approximately equal for both monomer and dimer. The small but real *increase* observed in a with dimer concentration can be understood from eq 9. Unlike two free monomers, the two segments of the dimer are constrained by the linkage (spacer) group. The result of the constraint is a reduction in the excluded volume integral (eq 9), resulting in a change of the constant 0.763 in eq 11 to a smaller value. Qualitatively similar results are obtained for the density functional theory. Thus, a dimer consisting of a flexible spacer that translationally constrains the two mesogenic units would, according to these models, exhibit a Landau coefficient a, which is slightly larger than the corresponding value for the monomer. This is precisely the behavior observed. We note in passing that de Gennes has proposed a model[34] for the isotropic phase in which *the persistence length increases as the square of the nematic correlation length*. The consequences of this pretransitional stiffening would, according to the above discussion, be a decrease in a, which is not observed. We thus feel that de Gennes' model is not directly applicable to our system.

We now turn to the nematic phase, where NMR and X-ray results indicate that the spacer of the associated polymer becomes highly extended.[2,3,35] From arguments in the preceding paragraph, we would expect that for dimers the coefficient a would sharply decrease in the nematic phase. In order to better understand the manifestations of this behavior, we assume that a is analytic and, because of the elongation of the spacer, can be expanded in a power series in S

$$a = a_0 - a_2S^2 + \mathcal{O}(S^3) \qquad (12)$$

where a_0 is the quadratic coefficient for the dimer in the isotropic phase, as given in Table II. (Note that because the order parameter is actually a second rank tensor $\mathbf{Q}$, no term linear in the order parameter is permitted in eq 12[36].) Since the spacer becomes on average stiffer with increasing nematic order, the coefficient a_2 as defined in eq 12 is expected to be positive. Upon substituting the expression for a into eq 2, we find that the measured quadratic coefficient in the nematic phase remains a_0, unchanged from the isotropic phase. This *must* be the case, since the *coefficients* in the Landau expansion cannot be functions of the order parameter. The second term in eq 12, however, does renormalize the quartic coefficient in eq 2 by contributing a term $-{}^1/_2 a_2(T - T^*)$.

In order to understand why the coefficient b is so much larger for the dimer than it is for the monomer, we note that b is related to the biaxiality of the nematic phase. If b were to change sign as some function of, for example, molecular length, the point $b = 0$ on a temperature–molecular length phase diagram would correspond to a crossover from a prolate to biaxial to an oblate nematic phase. Right at the nematic–isotropic phase transition, the isotropic phase would be in equilibrium with a prolate, an oblate, and a biaxial nematic phase.[37,38] For dimers, however, which become elongated and more prolate in the nematic phase, one would expect the biaxial character to be considerably weaker than in the monomer. Thus is is easy to see qualitatively, at least, that the coefficient b for the dimer should be considerably larger than b for the monomer.

The foregoing discussion is consistent with a number of experimental investigations that indicate that extended conformers are preferred in the nematic phase. Latent heat measurements, for example, indicate a 5-fold increase in L per repeat unit in going from monomer to dimer.[1] Nevertheless, L increases by an additional factor of 2 for the polymer, perhaps indicating that the spacer in the dimer is not as fully extended in the nematic phase as it is in the polymer. This conclusion, moreover, is consistent with ^{2}H NMR data on the polymer and dimer,[17] which show discrete splittings (corresponding to the C–D bond order parameters) well into the nematic phase for the dimer, but coalescing into a single splitting for the polymer. Such a result would indicate that, in the polymer, averaging of the C–D bond orientation becomes independent of the position of the bond along the spacer; this is not the case for the dimer. One might thus expect an even further increase in the coefficient b for longer oligomers as any biaxial characteristics are even further reduced.

To summarize, we have performed Cotton–Mouton measurements in the isotropic phases of a phenyl benzoate monomer, dimer, and mixtures of the two. The results indicate that the spacer in the dimer is extremely flexible in the isotropic phase, but owing to large differences in the latent heats and in $T_c - T^*$ between monomer and dimer, we conclude that the spacer extends significantly in the nematic phase.

Note added in proof: We thank Prof. Geoffrey Luckhurst for bringing to our attention his theoretical work on pretransitional behavior of dimers (Heaton, N. J.; Luckhurst, G. *Mol. Phys.* **1989**, *66*, 65) and related experimental work (Dunmur, D. A.; Wilson, M. R. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1109).

Acknowledgment. We thank Drs. R. G. Petschek, A. Jamieson, and K. Devanand for useful discussions, and Uma Hari for synthesis of the monomeric and dimeric mesogens. This work was supported by the National Science Foundation Division of Materials Research under Grants DMR-8614093 and DMR-8796354 (C.R.) and DMR-8417834 (A.C.G.).

Registry No. Phenyl benzoate, 93-99-2; phenyl benzoate dimer, 121525-21-1.

References and Notes

(1) Sigaud, G.; Yoon, D. Y.; Griffin, A. C. *Macromolecules* **1983**, *16*, 875.
(2) Yoon, D. Y.; Bruckner, S.; Volksen, W.; Scott, J. C.; Griffin, A. C. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 41.
(3) Yoon, D. Y.; Bruckner, S. *Macromolecules* **1985**, *18*, 651.
(4) Ronca, G.; Yoon, D. Y. *J. Chem. Phys.* **1982**, *76*, 3295.
(5) Abe, A. *Macromolecules* **1984**, *17*, 2280.
(6) Yoon, D. Y.; Baumgartner, A. *Macromolecules* **1984**, *17*, 2864.
(7) Esnault, D.; Galland, D.; Volino, F.; Blumstein, R. B. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 409.
(8) Martins, A.; Ferreira, J. B.; Volino, F.; Blumstein, A.; Blumstein, R. B. *Macromolecules* **1983**, *16*, 279.
(9) Blumstein, A.; Maret, G.; Vilasager, S. *Macromolecules* **1981**, *14*, 1543.
(10) Samulski, E. T.; Gathier, M. M.; Blumstein, R. B.; Blumstein, A. *Macromolecules* **1984**, *17*, 479.
(11) Maret, G. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1983**, *24*, 249.
(12) Blumstein, R. B.; Poliks, M. D.; Stickles, E. M.; Blumstein, A.; Volino, F. *Mol. Cryst. Liq. Cryst.* **1985**, *129*, 375.
(13) Blumstein, R. B.; Stickles, E. M.; Blumstein, A. *Mol. Cryst. Liq. Cryst.* **1982**, *82*, 205.
(14) Blumstein, R. B.; Stickles, E. M. *Mol. Cryst. Liq. Cryst.* **1982**, *82*, 151.
(15) Griffin, A. C.; Britt, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 4957.
(16) Griffin, A. C.; Sullivan, S. L.; Hughes, W. E. *Liquid Crystals*, in press.
(17) Griffin, A. C.; Samulski, E. T. *J. Am. Chem. Soc.* **1985**, *107*, 2975.
(18) Griffin, A. C.; Havens, S. J. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 969.
(19) Rosenblatt, C. *J. Phys.* (*Les Ulis, Fr.*) **1984**, *45*, 1087.
(20) Poggi, Y.; Filippini, J. C.; Aleonard, R. *Phys. Lett. A* **1976**, *57*, 53.
(21) Coles, H. J. *Mol. Cryst. Liq. Cryst.* **1978**, *49*, 67.
(22) Photinos, P.; Saupe, A. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 217.
(23) Rosenblatt, C. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 107.
(24) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
(25) Lee, S.-D. *J. Chem. Phys.* **1987**, *87*, 4972.
(26) Carnahan, N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, *51*, 635.
(27) Frenkel, D.; Mulder, B. M.; McTague, J. P. *Phys. Rev. Lett.* **1982**, *52*, 287.
(28) Frenkel, D.; Mulder, B. M.; McTague, J. P. *Mol. Cryst. Liq. Cryst.* **1985**, *123*, 119.
(29) Frenkel, D.; Mulder, B. M. *Mol. Phys.* **1985**, *55*, 1171.
(30) Lee, S.-D.; Meyer, R. B. *J. Chem. Phys.* **1986**, *84*, 3443.
(31) Hurd, A. J.; Fraden, S.; Lonberg, F.; Meyer, R. B. *J. Phys.* (*Les Ulis, Fr.*) **1985**, *46*, 905.
(32) Fraden, S.; Hurd, A. J.; Meyer, R. B.; Cahoon, M.; Casper, D. L. D. *J. Phys. Colloq.* **1985**, *46*, C3-85.
(33) Collot, J.-L.; Wu, X.-G.; Xu, H.; Baus, M. *Phys. Rev. A* **1988**, *38*, 2022.
(34) de Gennes, P.-G. *Mol. Cryst. Liq. Cryst.* **1984**, *102*, 95.
(35) Chin, H. H.; Azaroff, L. V.; Griffin, A. C. *Mol. Cryst. Liq. Cryst.* **1988**, *157*, 443.
(36) de Gennes, P.-G. *The Physics of Liquid Crystals*; Clarendon: Oxford, 1975.
(37) Yu, L. J.; Saupe, A. *Phys. Rev. Lett.* **1980**, *45*, 1000.
(38) Melnik, G.; Photinos, P.; Saupe, A. *Phys. Rev. A* **1989**, *39*, 1597.