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## Liquid Crystals

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Gregory A. Dilisi<sup>a</sup>; Charles Rosenblatt<sup>a</sup>; Anselm C. Griffin<sup>b</sup>; Uma Hari<sup>b</sup>

<sup>a</sup> Department of Physics, Case Western Reserve University, Cleveland, Ohio, U.S.A. <sup>b</sup> Department of Chemistry, University of Southern Mississippi, Hattiesburg, Mississippi, U.S.A.

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## Splay elasticity in an oligomeric liquid crystal

by GREGORY A. DiLISI and CHARLES ROSENBLATT

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106,  
U.S.A.

ANSELM C. GRIFFIN and UMA HARI

Department of Chemistry, University of Southern Mississippi, Hattiesburg,  
Mississippi 39401, U.S.A.

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A magnetically-induced Freedericksz transition was used in conjunction with capacitance techniques to determine the splay elastic constant of the 4,4'-dialkoxyphenylbenzoate monomer '5005' [ $C_6H_{11}OC_6H_4COOC_6H_4OC_6H_{11}$ ] and its dimer. As a function of reduced temperature in the nematic phase, it was found that  $K_{11}$  of the dimer is only about 20 per cent larger than that of the monomer. Moreover, the values of  $K_{11}/S^2$  versus reduced temperature, where  $S$  is the scalar order parameter, are equal to within experimental noise. These results suggest that for short oligomers Meyer's entropic model for splay elasticity in polymer liquid crystals is not applicable. A lowest order correction to the entropic model is suggested, which partially accounts for excluded volume and dispersive effects.

With recent advances in the synthesis of polymer liquid crystals, attention is now focusing on the viscoelastic properties of these materials. In the late 1970s DeGennes realized that splay deformations are difficult to achieve in long main chain nematics [1]. For the case of semiflexible molecules, both bend and twist can be accommodated by having the molecule adjust to the contour of the deformation, as long as the molecular persistence length is much smaller than  $|q|^{-1}$ , where  $|q|$  is the magnitude of the wave vector of the deformation. For splay, however, this mechanism is not possible, since constant density requires the creation of gaps between molecules. As noted by Meyer [2], these gaps can still be filled by the ends of adjacent molecules, although at a significant cost in entropy. Thus, for long main chain polymers, the splay elastic constant  $K_{11}$  is expected to diverge as the molecular length to diameter ratio  $L/D$  diverges;  $K_{33}$ , on the other hand, may show some initial increase with chain length, consistent with a number of molecular theories of the 1970s [3-8], but eventually saturate as molecular curvature takes over. The crossover region, of course, is determined by the flexibility of the spacer groups, and thus the molecular persistence length.

Experimental results for  $K_{11}$  in liquid-crystalline polymers has to date been sparse. The Brandeis group has measured both the elastic constants and viscosities of tobacco mosaic virus (TMV) and poly benzyl- $\gamma$ -glutamate (PBG) in suspension. In one study of long chain molecules [9, 10] they found both  $K_{11}$  and  $K_{33}$  to be linear in concentration, consistent with the semiflexible chain theory, but inconsistent with theories of rigid rods. As a function of molecular length, they found in another study [11] that  $K_{11}$  scales approximately as  $L/D$ , but that  $K_{33}$  saturates in the region where the chain

length is equal to the persistence length. Parthasarthy *et al.* performed viscoelastic measurements on various molecular weights of PBG in a variety of solvents [12]. Although the solvent-dependent data for splay and bend are somewhat ambiguous, all data clearly show a significant enhancement of  $K_{11}$ , qualitatively consistent with the theory of Meyer. Both sets of measurements, however, are for lyotropic nematic polymers. Since much of the current interest, both pure and applied, concerns thermotropic materials, it is important to understand polymer elasticity in dense systems as well. Along these lines Tsvetkov and Kolomiets measured  $K_{33}$  in both a main chain aromatic polyester and its monomer [13], finding little difference between the two values. Sun and Kleman measured all three elastic constants for a semiflexible polymer with an average of 24 repeat units [14], finding that the splay elastic constant is approximately ten times larger than either twist or bend. Again, both results are consistent with the semiflexible model of elasticity.

So as to understand better the limitations of various models of elasticity as applied to the *crossover* from monomer to polymer, we have begun to investigate the nearly symmetric 4,4'-dialkoxyphenylbenzoate monomer '5005' [ $C_5H_{11}OC_6H_4COOC_6H_4OC_5H_{11}$ ] and its oligomers [15, 16]. In this paper we report on dielectric-based Fredericksz measurements of the splay elastic constant for the monomer and dimer as a function of temperature in the nematic phase. A simple application of the entropic theory [2] suggests that, in the absence of intermolecular interactions, calculated values of  $K_{11}$  for the dimer should be approximately a factor of two larger than for the monomer. Instead, we find experimentally that  $K_{11}$  of the dimer is only slightly ( $\sim 20$  per cent) larger than that of the monomer as a function of reduced temperature and, when scaled by  $S^2$ , where  $S$  is the scalar nematic order parameter, the two elastic constants are identical to within experimental noise. The purpose of this paper then, is to report on elastic constant measurements for both monomer and dimer, as well as to examine a possible correction to Meyer's model for which excluded volume and certain dispersive effects are important in the short chain limit, but become small as  $L/D \rightarrow \infty$ .

The monomer and dimer were synthesized according to procedures described elsewhere [15, 17]. A pair of glass slides, coated with a well defined area ( $0.273 \pm 0.002 \text{ cm}^2$ ) of indium tin oxide, was first treated with Nylon 6/6, then rubbed unidirectionally. The slides were separated by kepton spacers, adjusted for optimum parallelism, and placed in an oven temperature controlled to 5 mK for the monomer and 50 mK at considerably higher temperatures for the dimer. The entire assembly was then inserted into the bore of a superconducting magnet, such that the field  $\mathbf{H}$  was oriented normal to the glass, and the sample connected to an Andeen-Hagerling Model 2500 A capacitance bridge operating at 125 millivolts (rms) at 1 kHz. The capacitance was first measured for the empty cell. Since the area of the cell is known, the cell spacing  $t$  was obtained, and found to be  $96.5 \pm 0.5 \mu\text{m}$  for the cell eventually filled with monomer and  $62 \pm 1 \mu\text{m}$  for the cell filled with dimer. The cell was then filled with either monomer or dimer and brought deep into the nematic phase. At a fixed temperature the field was swept slowly upward at 0.6 G/s and the capacitance recorded. Since the capacitance of the empty cell is known, the effective dielectric constant  $\epsilon_{\text{eff}}$  was obtained. A typical experimental run is shown in figure 1.

The samples were made sufficiently thick so as to avoid difficulties arising from a finite surface anchoring energy [18, 19]. Then, using the usual expression for the Fredericks transition [20], we obtain  $K_{11} = H_{\text{th}}^2 t^2 \chi_a / \pi^2$ , where  $H_{\text{th}}$  is the threshold field for the Fredericksz transition and the magnetic susceptibility anisotropy  $\chi_a$  is

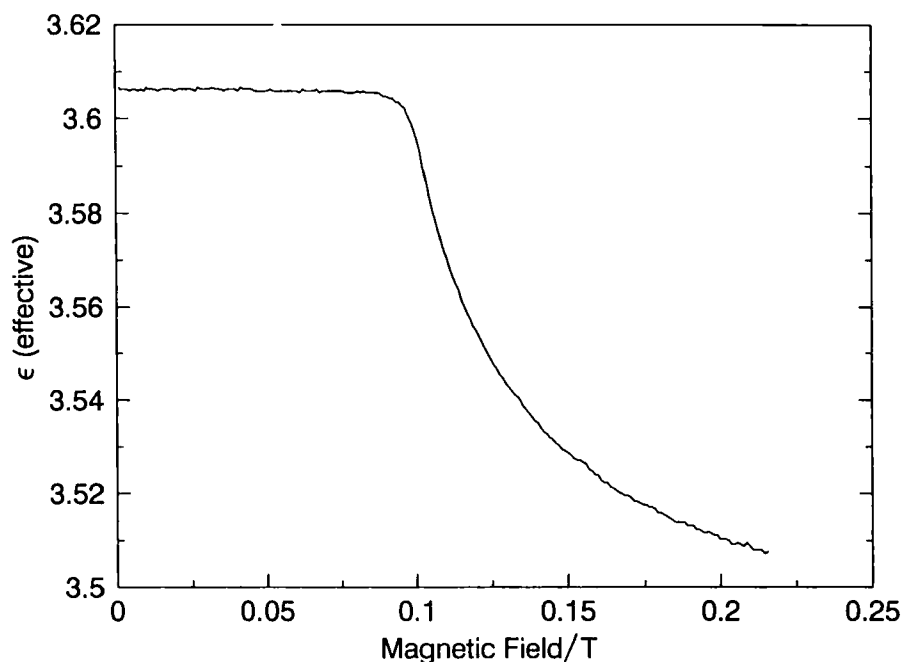


Figure 1. Typical experimental trace of effective dielectric constant  $\epsilon_{\text{eff}}$  versus magnetic field. This example is for the monomer at  $T = 77.67^\circ\text{C}$ , corresponding to  $T_{\text{NI}} - T = 3.86^\circ\text{C}$ .

taken from [21]. As seen in figure 1,  $H_{\text{th}}$  is somewhat ambiguous owing to rounding of the data. This problem has been discussed in detail elsewhere [22], but in this case can generally be ascribed to variations in cell thickness across the active region of the sample, as well as a small contribution arising from sample orientation with respect to  $\mathbf{H}$ . Overall, then, an uncertainty of approximately  $\pm 5$  per cent is attached to the extracted values of  $K_{11}$ , which are plotted versus  $T - T_{\text{NI}}$  in figure 2. As is readily apparent,  $K_{11}$  of the dimer is only about 20 per cent larger than that of the monomer at comparable reduced temperatures. Since  $K_{11}$  depends on the orientational distribution function, we can make the comparison more meaningful by scaling  $K_{11}$  by  $S^2$  [ $\equiv \langle P_2 \rangle^2$ ], the square of the scalar part of the usual nematic order parameter  $\mathbf{Q}$ . The ratio  $\kappa \equiv K_{11}/S^2$  should then be *nearly* independent of temperature and depend solely on the (weakly temperature dependent) details of the molecules. In order to obtain  $S$  we note that  $S$  very closely approximates  $\chi_a/\chi_a^0$ , where  $\chi_a^0$  is the susceptibility anisotropy for fully saturated order.  $\chi_a^0$  has been calculated [19] and is taken to be  $(1.25 \pm 0.06) \times 10^{-7}$  cgs for both monomer and dimer, an excellent approximation since the magnetic susceptibility is a local quantity [23] and the dimer is just two monomers attached end-to-end with a pair of hydrogens removed.  $\kappa$  is thus plotted in figure 3, where we find that  $K_{11}/S^2$  is much less sensitive to temperature than is  $K_{11}$ . Moreover, within the uncertainty of this derived quantity, we find that  $\kappa$  is approximately the same for both the monomer and dimer. Even considering experimental error we suspect that  $\kappa$  versus reduced temperature for the two species would not differ by more than 15 per cent.

In order to understand this result we first turn to the entropic model of Meyer [2], which is applicable in the long chain limit and for  $S = 1$ . In the absence of splay the

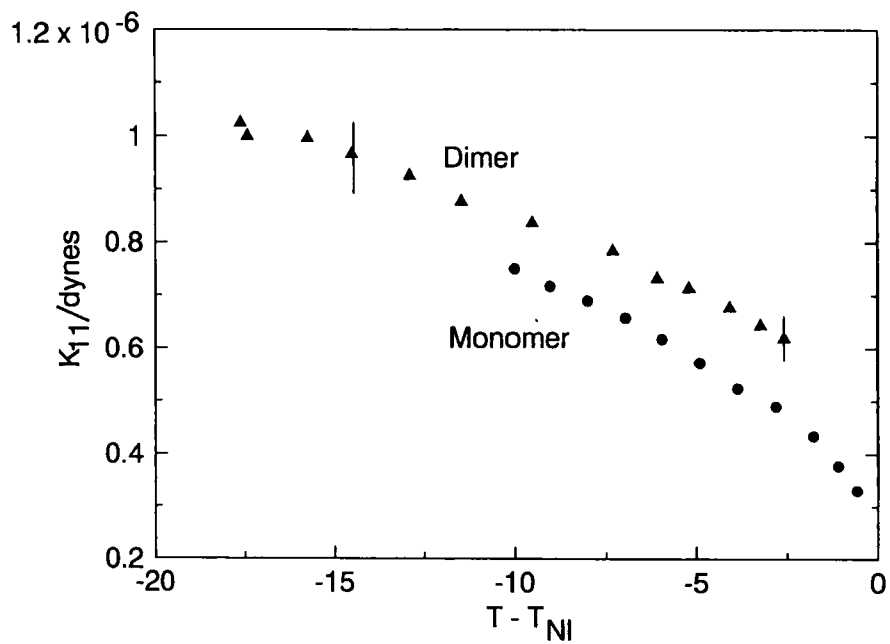


Figure 2. Splay elastic constant versus reduced temperature for the monomer (●) and dimer (▲).

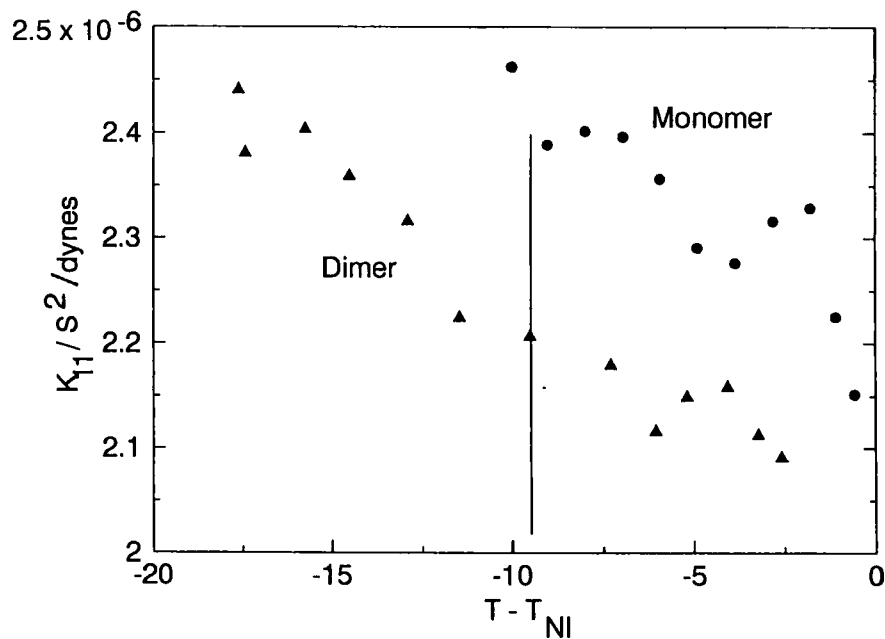


Figure 3.  $K_{11}/S^2$ , where  $S$  is the scalar part of the nematic order parameter, versus reduced temperature.

number of densities of molecular tops (t) and bottoms (b) would be the same, having a value  $\rho_t = \rho_b = \rho_0 = \rho_m/M$ . Here  $\rho_0$  is the undisturbed number density,  $\rho_m$  the mass density of monomers, and  $M$  the molecular weight. In the presence of splay, and assuming no 'hairpin turns', the density of bottoms is given by  $\rho_b = \rho_0 + \Delta\rho$  and of tops  $\rho_t = \rho_0 - \Delta\rho$  where

$$\Delta\rho = (L/2)\rho_0\nabla \cdot \mathbf{n}. \quad (1)$$

$L$  is the molecular length projected along the director. Meyer then assumed that the chain ends can be considered an ideal gas, and that tops and bottoms must be correlated so as to maintain constant density for uniform splay. The resulting change in the free energy  $\mathcal{F}$  is given by

$$\Delta\mathcal{F} = (k_B T/8d)(L/d)(\nabla \cdot \mathbf{n})^2, \quad (2)$$

where  $d = (L\rho_m/M)^{-1/2}$  is a typical lateral size of the molecule. The splay elastic constant  $K_{11}$  can be extracted from equation (2) and is given by

$$K_{11} = (k_B T/4d)(L/d). \quad (3)$$

According to the simple interpretation of this model, one expects to find a linear increase in the entropic contribution to  $K_{11}$  with molecular length. Such behaviour is not too different from what is observed in longer molecules [13]. For shorter molecules, however, it's clear from the results of figures 2 and 3 that the model is not applicable, and that a simple doubling of molecular length does not result in a doubling of  $K_{11}$ . Part of this breakdown is undoubtedly due to the increased relative importance of intermolecular interactions in shorter molecules. (Since the dimer is essentially two monomers attached end-to-end, one would expect these interactions to be nearly the same independent of chain length.) However, it must be noted that the *magnitudes* predicted by equation (3) are quite substantial, and are of the same order (or larger) as the measured values of  $\kappa$  (cf. figure 3). Thus, the lack of an observed  $L/d$  dependence in the data *cannot* be explained by a small contribution from equation (3), in conjunction with a large dispersive contribution, to the total elastic constant  $K_{11}$ . Part of the difficulty, then, must arise from treating the ends as an ideal gas. This approximation is, of course, quite reasonable in the long chain (dilute end) limit for which Meyer intended the model. As the molecules shorten, however, ends will begin to interact. A complete theory for these interactions is beyond the scope of this paper, although we have calculated a simple correction to Meyer's model which partially accounts for excluded volume and dispersive interactions associated with molecular ends.

In the spirit of the van der Waals model for fluids, we add an excluded volume  $V_e$  associated with the tops and bottoms of the molecules. Moreover, we add mean field energetic terms which account for the differences between top-bottom and top-top (or bottom-bottom) interactions. The relevant part of the free energy per volume can be written as

$$\begin{aligned} \mathcal{F} = & -\frac{1}{2}k_B T\{\rho_t \log(\rho_t/(1 - \rho_t V_e)) + \rho_b \log(\rho_b/(1 - \rho_b V_e))\} \\ & -\frac{1}{2}a\rho_b^2 - \frac{1}{2}a\rho_t^2 - b\rho_b\rho_t. \end{aligned} \quad (4)$$

The coefficients  $a$  and  $b$  are appropriate volume integrals of the top-top and top-bottom pair potentials. In the presence of a splay-induced  $\Delta\rho$ ,  $\mathcal{F}$  can be expanded in powers of  $\Delta\rho$ . The lowest surviving terms are given by

$$\Delta\mathcal{F} = \{(k_B T L/8d^2)[1 - \rho_0 V_e]^{-2} + (b - a)/4d^4\}(\nabla \cdot \mathbf{n})^2. \quad (5)$$

The corresponding contribution to the elastic constants is

$$K_{11} = \{(k_B TL/4d^2)[1 - \rho_0 V_c]^{-2} + (b - a)/2d^4\}. \quad (6)$$

For the case at hand  $L_{\text{monomer}} = 27.6 \text{ \AA}$ ,  $L_{\text{dimer}} = 53.7 \text{ \AA}$ , and the corresponding  $d$  is approximately  $4.6 \text{ \AA}$ . From the bare entropic model of equations (3) we find the splay elastic constants of  $1.6 \times 10^{-6}$  and  $3.8 \times 10^{-6}$  dynes for the monomer and dimer, respectively. If  $V_c$  is of order one or two times  $d^3$ , however (cf. equation (6)), the excluded volume correction will cause both elastic constants to increase, although the monomer increases by a far larger percentage than the dimer; both entropic terms would then be more nearly equal, although still a factor of two or so larger than the measured values in figure 3. There is no reason, however, for the coefficients  $a$  and  $b$  to be equal (both of whose magnitudes are expected to be of the same order as the entropic terms). It is thus possible that the interaction terms partially offset the large entropic terms, such that the total splay elastic constants for monomer and dimer are nearly equal both to each other and to the measured values. This scenario, of course, requires  $a > b$ , which is likely in the presence of short range smectic correlations. In that sense, then,  $a$  and  $b$  reflect dispersive forces for the entire molecules. In the other limit, when  $L/d$  is large, both the excluded volume correction and the interaction term are, of course, unimportant, and  $K_{11}$  in equation (6) reduces to the Meyer's form in equation (3). It must be emphasized that the description above is only a zeroth order correction to Meyer's model: this model does not correctly account for correlations of molecular ends, and thus still overcounts the volume of phase space available to tops and bottoms.

For long, semiflexible, molecules, Meyer's entropic model represents a reasonable description of the splay elastic constant; in the short-chain regime (for which it was not intended), his model results in a contribution to  $K_{11}$  which is much too large. In this limit the splay elastic constant must include a large dispersive component, as well as an important contribution from excluded volume effects. We have attempted to modify Meyer's model to introduce these effects. In essence the ends can no longer be considered an ideal gas, but rather interact via hard repulsions and a longer range attraction. The result of these corrections is to substantially change the monomer's splay elastic constant, but to leave Meyer's result unchanged in the large  $L/d$  limit. Although only an approximation to a correct statistical theory, the modified model indicates that both the entropic and dispersive contributions are important for short oligomers, crossing over into a purely dilute entropic regime for polymers where  $K_{11}$  is proportional to  $L/d$ .

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