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Short Communication

Viscoelastic properties of a bent and straight dimeric liquid crystal

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Abstract. — Absolute values for the elastic constants and viscosities are reported in the nematic phase for two dimers based upon the monomer 4,4'-dipentylbenzyloxyphenylbenzoate. One dimer has an even number of methylene units in the spacer and, in consequence, is approximately straight in the all-trans conformation. The other dimer has one less methylene unit, and is therefore bent. We find that the ratio $K_{33}/K_{11}$ for the odd dimer is reduced relative to that for the even member of the series. Moreover, we find that the absolute elastic constants for the odd dimer are of order one-half that of the even dimer. The system is analyzed in terms of recent theories by Terentjev, Rosenblatt, and Petschek, and by Terentjev and Petschek, with results in reasonable agreement with experiment.

Oligomeric liquid crystals are useful for the insight they provide about crossover behavior from the monomer to the liquid crystalline polymer regime. In recent years we have performed a number of experiments on a system of oligomers based upon the monomer 4,4'-dipentylbenzyloxyphenylbenzoate ("5005") to elucidate its viscoelastic, critical, and interfacial properties [1-6]. Recently we reported on a light scattering measurement of the Frank elastic constants $K_{11}$, $K_{22}$ and $K_{33}$ for two dimers [5]. One dimer consists of two monomers attached end-to-end (minus a pair of terminal hydrogens), thus having ten methylene units in the spacer group; in consequence, the molecule is approximately straight in the all-trans conformation. We refer to this dimer as the "even" dimer. In the other molecule a CH$_2$ unit is removed from the spacer, leaving nine methylene units. This "odd" dimer exhibits a kink between the mesogenic groups in the all-trans conformation. We found that although the ratios of the twist to splay elastic modulus $K_{22}/K_{11}$ are about the same for the two species, the ratio of the bend to splay modulus $K_{33}/K_{11}$ is considerably smaller for the odd dimer than it is for the even member of the series. Such behavior was predicted by Gruler [7] and Helfrich [8], who suggested that a kinked molecule might exhibit a reduced bend elasticity by reorienting so as
to partially relieve the elastic strain. Since publication of the elasticity ratios we have added a Faraday magnetic susceptometer to our laboratory. This now allows us to extract the absolute values of the three elastic constants and associated viscosities, which is the central result of this communication. These results, moreover, are examined in light of the recent models of Terentjev, Rosenblatt, and Petschek [9] and Terentjev and Petschek [10], which were developed specifically for dimers with a semiflexible spacer.

Data from our earlier measurements [5] yielded the ratios \( K_{22}/K_{11} \) and \( K_{33}/K_{11} \), as well as the relaxation rates for splay (\( \Gamma_1 = K_{11}q^2/\eta_{\text{play}} \)), bend (\( \Gamma_3 = K_{33}q^2/\eta_{\text{bend}} \)), and twist (\( \Gamma_2 = K_{22}q^2/\gamma_1 \)) where \( \eta_{\text{play}}, \eta_{\text{bend}}, \) and \( \gamma_1 \) are the viscosities and \( q \) the scattering wavevector. In addition, we had previously obtained the ratio \( K_{11}/\Delta_{X^v} \) using a magnetically-induced Fredericksz technique [2], where \( \Delta_{X^v} \) is the volumetric susceptibility anisotropy. Thus, in order to absolutely determine \( K_{11} \), as well as the other viscoelastic constants, we have separately measured the mass susceptibility anisotropy \( \Delta \chi \). A 10 kG electromagnet equipped with Faraday pole pieces was used in conjunction with a Cahn model 2000 microbalance, sensitive to 1 \( \mu \)g. An empty quartz bucket with a capacity of approximately 0.1 cm\(^3\) was situated between the pole pieces at a point where \( \nabla \times \chi \) is maximum, where \( \chi \) is the magnetic field. The bucket was first weighed in zero magnetic field, then at maximum field; the difference between the two weights corresponds to the magnetic force on the empty bucket. The bucket was then filled with KCl for calibration purposes and weighed in zero field to determine the mass \( m_{\text{KCl}} \) of the KCl. It was then weighed at maximum field, allowing us to extract the magnetic component of force \( F_{\text{mag}}(\chi) \) on the salt alone. Since \( F_{\text{mag}}(\chi) = \chi_{\text{KCl}} m_{\text{KCl}} \chi \), \( \chi_{\text{KCl}} \) is the susceptibility per unit mass of the salt (which can be obtained from standard tables), we were able to empirically determine \( \chi = 1.35 \times 10^7 \text{ G}^2/\text{cm} \) at the location of the bucket. As a check, this procedure was repeated with NaCl, with completely consistent results. The bucket was then filled with either odd or even dimer (approximately 70 mg), which was synthesized according to procedures described elsewhere [11-13]. The weight of the bucket + liquid crystals was then determined in the absence and in the presence of the magnetic field at several temperatures in the isotropic phase. From these measurements we extracted \( m_{\text{dimer}} \) and \( F_{\text{mag}}(\chi) \) and, since \( \nabla \times \chi \) is known, we were able to obtain \( \chi_{\text{iso}} \), the magnetic susceptibility in the isotropic phase. Measurements were made at approximately five temperatures in the isotropic phase near the nematic transition, and the value of \( \chi_{\text{iso}} \) was taken to be the average of these values. Scatter was less than 2 \%. The sample was then brought into the nematic phase and weighed with and without the magnetic field. Since the field is sufficient to align the bulk of the nematic in the bucket (except for a region of thickness \( \xi \approx \text{few microns near the walls, where } \xi \text{ is the magnetic coherence length} \), we extracted \( \chi_{\text{n}} \) as a function of temperature, where \( \chi_{\text{n}} \) is the component of mass susceptibility parallel to the nematic director. Finally, the mass susceptibility anisotropy (per gram) \( \Delta \chi \) is given by \( \frac{3}{2} (\chi_{\text{n}} - \chi_{\text{iso}}) \), and is shown for both species in figure 1. Note that the scatter comes about because \( \Delta \chi \) corresponds to a small difference between similar values of susceptibility. A smooth curve is drawn through the data and is used for obtaining \( K_{11} \). Then, assuming the density of the dimer is approximately 1 g/cm\(^3\), we obtain the volumetric susceptibility \( \Delta \chi \) vs. temperature. Along with the threshold fields \( H_{\text{th}} \), we are thus able to obtain \( K_{11} \) absolutely from the \( K_{11}/\Delta \chi \) data in reference [2]. Also, since elastic constant ratios have been obtained [5], \( K_{22} \) and \( K_{33} \) can be extracted as well. Finally, since the viscosities depend on absolute values of the elastic constants, \( \eta_{\text{play}}, \gamma_1 \), and \( \eta_{\text{bend}} \) can also be obtained. Elastic moduli are shown in figures 2 and 3, and viscosities are shown in figures 4 and 5. Liberal error bars for \( K_{11} \) have an upper limit of 12 \%, for \( K_{22} \) 20 \%, and for \( K_{33} \) 25 \%, about 10 \% (half) of which come from systematic error in \( \Delta \chi \). If \( \Delta \chi \) were different, all values would change systematically by the same relative amount. Error bars for the respective viscosities are slightly larger. Note that a complete error analysis is
Fig. 1. — Mass susceptibility anisotropy vs. reduced $T - T_{NI}$ for the even dimer (●) and for the odd dimer (▲). Solid lines represent smoothing of the data for calculational purposes. Note that $T_{NI}$ for the odd dimer is 134.6 °C, and for the even dimer is 149.0 °C.

Presented in detail in reference [4].

Given the absence of appropriate theoretical models, we will dispense with the viscosities by simply noting that the odd and even dimers exhibit similar values and, as expected, the twist viscosity $\gamma_1$ is the largest of the three. Turning now to the elastic moduli, we find as we did before that the bend modulus of the odd dimer is suppressed relative to $K_{11}$ and $K_{22}$. Additionally, we find that the absolute elastic constants for the even dimer tend to be approximately twice those of the odd dimer. These sorts of issues have been dealt with by Terentjev, Rosenblatt, and Petschek [9], who addressed flexibility, and by Terentjev and Petschek [10], who addressed the elastic behavior of monomers and semiflexible dimers. In addition to an interaction potential involving hard core repulsive as well as isotropic and anisotropic attractive parts, the models contain a stiffness parameter $\Omega$. This parameter is determined by an effective bending energy of the spacer, which connects the two adjacent mesogens comprising the dimer. Since $\Omega \sim E_B/k_B T$, where $E_B$ is the effective bending energy, $\Omega$ essentially incorporates into one parameter all mechanisms of chain flexibility. In the case where the spacer chain imposes a non-zero equilibrium bend angle $\theta_0$ between the two mesogens, the width of the distribution around $\theta_0$ is still determined by the bare rigidity parameter $\Omega$. A particularly important result of the model [10] is that for $\theta_0 = 0$ (even dimer) the elasticities as functions of the nematic order parameter $S$ are virtually independent of spacer rigidity $\Omega$. For odd dimers, on the other hand, the bent equilibrium shape brings dramatic changes to the magnitude and behavior of all three elastic constants of the corresponding uniaxial phase. Taking $\Omega = 8$, which is the value expected for typical dimers with nine to ten methylene units in the spacer [9], one finds for small bend angles ($\theta_0 = 10^\circ$) only slight changes in the elastic constants. For larger angles ($\theta_0 \approx 40^\circ$), $K_{33}$ is substantially reduced relative to $K_{11}$ over the entire temperature (i.e., order parameter) range.

In order to compare our results with the predictions of this model, which describes $K_{ii}$ as a function of order parameter, it is first necessary to calculate the dependence of the elasticities on temperature. For the even dimer we choose a theoretical saturated mass susceptibility anisotropy $\Delta\chi_{\text{sat}} = 1.25 \times 10^{-7} \text{erg G}^{-2}\text{g}^{-1}$ [14]. The order parameter $S(T)$ was then taken as $\Delta \chi(T)/\Delta \chi_{\text{sat}}$, and thus predictions for $K_{ii}(S)$ are convertible to $K_{ii}(T)$. In addition, we note that all three elastic constants for the even dimer depend approximately on only a single dimensional prefactor $W$ in the interaction potential. Adjusting $W$ to give the most reasonable
Fig. 2.

Elastic constants for even dimer vs. $T-T_{NI}$. (●) represents $K_{11}$, (■) represents $K_{22}$, and (▲) represents $K_{33}$. Solid lines are theoretical fits for (from top to bottom) bend, splay, and twist. Error bars are discussed in reference [4].

Fig. 3.

Same as figure 2, except for odd dimer.

Fig. 4.

Viscosities for the even dimer vs. $T-T_{NI}$. (●) represents $\eta_{\text{splay}}$, (■) represents $\gamma_1$, and (▲) represents $\eta_{\text{bend}}$. Error bars are discussed in reference [4].

Fig. 5.

Same as figure 4, except for odd dimer.

fit for all three elastic constants over the entire temperature range, we obtain the theoretical values shown in figure 2. Although the theoretical values for splay and twist are reasonable, they appear to exhibit a slightly steeper slope with temperature than do the experimental points. Some of this discrepancy may be due to experimental error in the order parameter dependence $S(T)$ deduced from figure 1. (Note that the values for the susceptibility measured herein differ from reference [14] by about 10%, which affects the conversion from $K_{ii}(S)$ to $K_{ii}(T)$). Additionally, we note that the conversion from order parameter to temperature through the susceptibility data is likely flawed since we have assumed a constant $\Delta \chi_{\text{sat}}$, corresponding to the fully extended even dimer. However, the saturated susceptibility anisotropy is likely increasing
with decreasing temperature, owing to changes in the distribution of spacer conformations with temperature. Thus, $S(T)$ is in actuality less steep than that obtained from the magnetic data, and in consequence the predicted elasticities should actually be less steep than shown in figure 2. The large $K_{33}/K_{11}$ ratio predicted for the even dimer is also qualitatively consistent with the experimental data, although it is somewhat disturbing that the theoretical second derivative of $K_{33}$ with respect to temperature is negative. It is obvious that factors beyond mean field which influence the bend elasticity would have to be considered to achieve better agreement with experiment.

In order to construct a plot of $K_{ii}(T)$ for the odd dimer, the experimental data for the corresponding order parameter $S(T)$ should be employed. The nematic order parameter for the odd dimer is calculated as above, where we have chosen $\Delta \chi_{\text{sat}} = 0.94 \times 10^{-7}$ erg G$^2$g$^{-1}$, based on the molecular bend angle. For the case of odd dimers, both $S(T)$ and $K_{ii}(T)$ strongly depend on the given combination of the rigidity and equilibrium bend $(\Omega, \theta_0)$ of the spacer. Here we have chosen $\Omega = 8$ and $\theta_0 = 37^\circ$ based upon previous results for an aliphatic spacer with nine methylene units [9]. Given these parameters and the same prefactor $W$ as used for the even dimer, figure 4 shows the calculated elastic constants for the odd dimer. As for the even dimer, there is quantitative agreement with experiment for the splay and twist constants, which indicates that the chosen values of $\Omega = 8$ and $\theta_0 \approx 37^\circ$ for a dimer with nine carbons in the spacer are quite appropriate. (We note, moreover, that these parameters also predict the nematic-isotropic phase transition temperature $T_{NI}$, the supercooling temperature, and $S(T)$ well below $T_{NI}$). The quantitative agreement is particularly satisfying given that the magnitudes of the odd elasticities are about a factor of two smaller than those of the even dimer. In fact, such differences in the elasticities are not predicted even qualitatively in references [7] and [8]. However, as with the even dimer, the predictions of the shape of $K_{33}$ are inconsistent with the experimental data. This arises from factors not described by the mean-field calculation, which affect the bend elasticity of the uniaxial nematic phase of semiflexible dimers, and are beyond the scope of the current model. Nevertheless, it is clear that the trend to reduce the bend constant relative to splay is well described by the mean-field calculation (consistent with experiment), especially given the qualitative arguments and experimental errors of at least 10% throughout.

Viscoelastic properties of rigid rods interacting via dispersive forces are sufficiently difficult to predict; when the molecule consists of two or more mesogens with a semiflexible spacer, predictions become even more problematical. In this communication we have reported on absolute viscoelastic measurements of a dimer consisting of an even and odd number of methylene units in the spacer, and have attempted to compare these results with those of a model designed specifically for this purpose. The important points which come about from this work are that experimentally, we find that $K_{33}/K_{11}$ is substantially reduced for a bent dimer and that the elasticities of the odd dimer are considerably smaller than for the even dimer, and that theoretically, the model does a reasonable job of predicting the elastic constants.

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