

Rheological properties of bent-core liquid crystals

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We show that bent-core liquid crystalline materials exhibit non-Newtonian flow in their optically isotropic liquid phase. We conjecture that this behavior is due to the existence of nanostructured, fluctuating clusters composed of a few smectic-like layers. Shear alignment of these clusters explains the shear thinning observed in bent-core liquid crystals having either a nematic phase or non-modulated smectic phase. By contrast, smectogens having a modulated smectic phase do not shear thin at low shear rates, but even show a slight shear thickening which may be due to entanglements of wormlike and/or helical clusters.

1. Introduction

In complex or ordered fluids, the microscopic structure of the fluid may change under applied stress and therefore the viscous and/or elastic behavior of the material becomes rate dependent. Examples of this occur in foams, polymer melts, slurries, and liquid crystals,¹ and are all characterized by non-Newtonian fluid flow. Specifically, liquid crystals are fluids with orientational and/or some positional order and may have Newtonian behavior in 3 (nematic) or 2 (smectic) dimensions in well-aligned samples.² In other cases flow may cause director and/or layer realignment resulting in a decrease of the viscosity (shear thinning) at increasing shear rates.

Recently liquid crystals of bent-core molecules have attracted considerable interest due to their (anti)ferroelectric³ chiral structures in the absence of molecular chirality.⁴ In this class of materials, the nematic phase is uncommon due to a strong tendency for smectic layering generated by close packing of the kinked molecules. Nonetheless, a number of bent-core compounds exhibiting macroscopically nematic phases have been synthesized recently.⁵ Theoretical⁶ and experimental studies on bent-core nematogens (BCNs) show spontaneous and induced biaxiality⁷ and giant flexoelectric effects;⁸ moreover, these materials promise both novel physics and opportunities for new technical applications. In addition, dynamic light scattering,⁹ electrohydrodynamic instability,¹⁰ magnetic field induced birefringence,¹¹ and NMR measurements¹² on BCNs indicate that their properties are unconventional not only in the nematic, but also in the optically isotropic phase immediately above.

Previous viscosity measurements on bent-core liquid crystals focused entirely on the rotational viscosities of the B₂ phase (a polar, tilted smectic phase) and was obtained by measuring ferroelectric switching times.^{13–15} Rotational viscous behavior in bent core nematics related to director fluctuations, have been determined by using dynamic light scattering¹¹ or by observing relaxation times while magnetically switching an aligned

sample.¹⁰ All of these measurements provide estimates of the rotational viscosity which range over 0.1–3 Pa s depending on temperature and the particular compound.

Flow viscosity measurements for bent-core phases are almost nonexistent because conventional methods typically require ~1 g of material, which is very difficult to obtain. However, recent measurements used electro-rotation of cylindrical glass rods dispersed in thin samples (having volumes of ~10 μm × 5 mm × 5 mm) to measure the flow viscosity by balancing an applied electric torque parallel to the rod axis with the viscous drag exerted on the cylindrical surface by the liquid crystal.¹⁶ Measurements on a single bent-core mesogen (in both the isotropic and nematic phases) yielded viscosity values, which ranged from 20 to 250 Pa s. It is particularly noteworthy that these values are 10–100 times larger than the rotational viscosities. Although these electro-rotation experiments only require sub-milligram amounts of material, they probe the viscosity only at very low (<0.1 s⁻¹) shear rates.¹⁶ Shear-rate dependent viscosity measurements on this class of material have never (to our knowledge) been reported. For this we have developed a novel, homemade nanolitre rheometer¹⁷ that requires only 10 nl (~10 μg) of material and provides rheological properties over a wide range of shear rates (10–10,000 s⁻¹).

In this nanolitre rheometer¹⁷ (see Fig. 1) a tiny drop of the fluid under study is held *via* surface forces as a liquid bridge between two long, narrow glass rods. The key components consist of a drive system (speaker), a temperature controlled chamber, and a piezoelectric transducer to measure the force. One rod was attached to the speaker cone and the other to a piezoelectric sensor, and measurements were obtained by driving the speaker at a selected frequency and measuring the transferred force to the piezoelectric device *via* the connecting fluid element. Both the amplitude and the phase of the current are detected using a lock-in amplifier. From these values, the flow viscosity (η) and elastic modulus (G) of the material can be determined.^{17,18}

To get a general picture of the rheological properties of bent-core liquid crystals, we have studied a wide range of bent-core materials and a few typical rod-like compounds for comparison. The molecular structures and phase diagrams of the materials studied are shown in Table 1. The reference rod-like molecules are pentyl-cyano-biphenyl (5CB) and octyl-cyano-biphenyl

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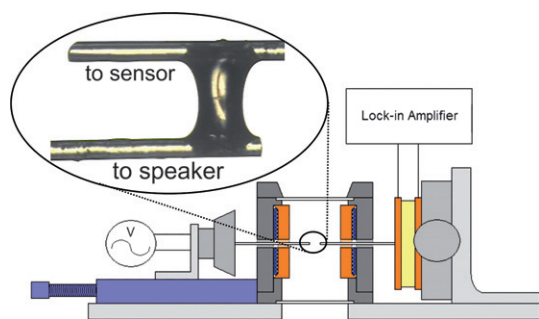


Fig. 1 Cross-section of the nL-rheometer consisting of three basic components: a drive system such as a small speaker (left), a temperature controlled chamber (center), and a piezoelectric crystal to measure the force (right). The magnified picture at top left shows the microscopic top view the fluid liquid crystal drop between the axially driven lower rod and the upper rod connected to the sensor.

(8CB). Among the nine bent-core compounds, five exhibit the nematic phase (BCN) at temperatures below the isotropic fluid phase and four exhibit a smectic phase (bent-core smectogen or BCS) below the isotropic fluid. BCS3 has an isotropic to B_2 (SmCP with C_2 symmetry)¹ transition, BCS1 and BCS4 have isotropic to B_7 (smectic with modulated layer structure probably due to double tilted layer structure with C_1 symmetry)¹, and BCS2 has an isotropic to B_7 to B_2 sequence of transitions.

2. Results and discussion

The rheological properties (*i.e.* shear-rate and temperature dependence of η and G) for the calamitics and bent core nematogens are shown in Fig. 2. We find that the calamitics behave as Newtonian fluids, in that their flow viscosities (η) have no observable shear rate dependence and their shear modulus G was found to be less than the sensitivity of the measurement, so basically $G = 0$.

The bent-core nematics have a strikingly different behavior both in the nematic and isotropic phases. First, they are

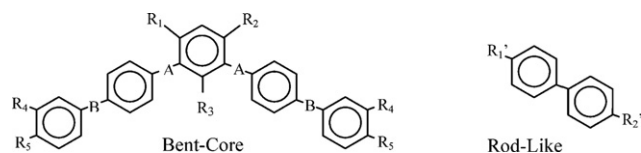
unequivocally non-Newtonian with large shear thinning behavior. Secondly, the magnitudes of the viscosities are remarkably larger—typically an order of magnitude at high shear rates—than the liquid crystals composed of rod-shaped molecules of similar size and chemical composition. The finite shear modulus decreases with increasing shear rate for all of the BCNs studied, and are adequately described with a power law relationship of the form $G = g/\dot{\gamma}^\beta$, where g and β are fitted parameters. While g is different for each sample, the values of β do not vary greatly and have an average value of 0.75. The viscosity for shear rates in the $\dot{\gamma} = 500\text{--}10000\text{ s}^{-1}$ range shows a relaxation type behavior similar to the viscosity dependence typically observed in fluids containing particulate suspensions.¹⁹ In such systems, the shear rate dependence is due to intrinsic timescales related to changes in the inter-particle spacing. Motivated by this, we have performed a trial fit of our data to a relaxation relationship of the form,

$$\eta(\dot{\gamma}) = \frac{\eta_o - \eta_\infty}{1 + (\dot{\gamma}/\dot{\gamma}_o)^m} + \eta_\infty \quad (1)$$

Here η_o (η_∞) is the viscosity at low (high) shear rates $\dot{\gamma}$, and $\dot{\gamma}_o$ is the characteristic shear rate where the frequency dependence of the viscosity has an inflection. For spherical particle suspensions, the exponent m characterizes the rigidity of the suspended particles ($m = 1$ corresponds to rigid spheres and $m > 1$ represents compliant or “squishy” spheres).¹⁹ $\dot{\gamma}_o$ describes the rate at which the equilibrium particle distribution is regained; this rate is controlled by the particle diffusivity in dilute solutions: $D_o = k_B T / (6\pi\eta a)$, where a is the radius of the particle and T is the absolute temperature.

As shown by the solid lines in Fig. 2a, all viscosity measurements for the BCNs can be satisfactorily fit using Eq. (1), which already suggests that these materials, even though they are pure compounds, have similar rheology to dilute particle suspensions. Furthermore, we find $m = 2$, indicating that, whatever is the nature of the “particles”, they are not rigid. The characteristic shear rate, $\dot{\gamma}_o = D_o/a^2 = k_B T / (6\pi\eta a^3)$, provides us with an estimate of the size of the deformable particles as,

Table 1 Molecular structures of the bent-core and rod-like molecules used in this study and their phase transition temperatures



Name	R ₁ (R ₁ ')	R ₂ (R ₂ ')	R ₃	A	B	R ₄	R ₅	Phase Behavior (Cooling, °C)
5CB	(CN)	(C ₅ H ₁₁)						Cr 24 Nem 36 Iso
8CB	(CN)	(C ₈ H ₁₇)						Cr 22 SmA 34 Nem 41 Iso
BCN1	Cl	H	H	COO	COO	H	O(CH ₂) ₉ C ₂ H ₂	Cr 56 Nem 71 Iso
BCN2	Cl	H	H	COO	COO	H	OC ₁₁ H ₂₃	Cr 58 Nem 87 Iso
BCN3	Cl	Cl	H	COO	—	H	O(CH ₂) ₆ C ₂ H ₂	Cr 60 Nem 94 Iso
BCN4	Cl	Cl	H	COO	—	H	O(CH ₂) ₇ C ₂ H ₂	Cr 64 Nem 98 Iso
BCN5	Cl	Cl	H	COO	—	H	OC ₈ H ₁₇	Cr 75 Nem 115 Iso
BCS1	H	H	NO ₂	COO	NCH	H	OC ₈ H ₁₇	Cr 116 B ₇ 177 Iso
BCS2	H	H	H	COO	NCH	H	SC ₁₀ H ₂₁	Cr 99 SmCP 128 B ₇ 140 Iso
BCS3	H	Cl	H	COO	NCH	H	OC ₁₄ H ₂₉	Cr 68 B ₂ 127 Iso
BCS4	H	H	NO ₂	COO	—	H	O(CH ₂) ₉ C ₂ H ₂	Cr ₁ 34.3 Cr ₂ 109.7 B ₇ 118.0 Iso

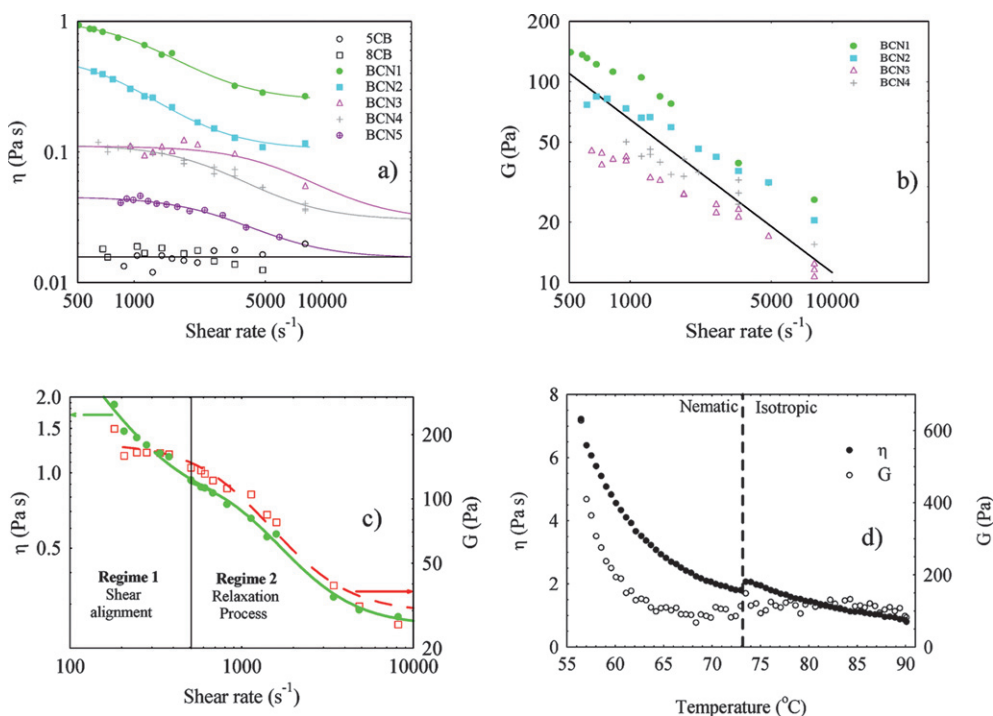


Fig. 2 The shear rate dependences of the (a) viscosity and (b) shear modulus in the isotropic phases at a temperature $\sim 10^\circ\text{C}$ above the isotropic-nematic transition for the various liquid crystals in Table 1. The shear moduli for the calamitics (5CB and 8CB) are not shown because they were within the experimental error ($\sim 5\text{ Pa}$) of our measurement. (c) The viscosity and shear modulus of BCN1 in the $10^2\text{--}10^4\text{ s}^{-1}$ shear rate range, showing an additional shear thinning at low shear rates. (d) The temperature dependence of the viscosity, and elastic constant of BCN1 at a shear rate of 517 s^{-1} .

$$a \approx \left(\frac{k_B T}{6\pi\eta\dot{\gamma}_0} \right)^{1/3} \quad (2)$$

resulting in $a \approx 8, 11, 10, 13, 16\text{ nm}$ for BCN1-5, respectively.

We believe these “particles” most probably are due to the kinked shape of the molecules, which tend to lock them into layered (or smectic-like) clusters, as illustrated in Fig. 3.

We note that such tendency for layering, known as “cybotactic groups”,²⁰ is often observed even in rod-like molecules such as 8CB²¹ in the nematic phase, but only in a narrow temperature range above a smectic phase. For this reason in the isotropic phase the calamitic materials essentially behave as Newtonian fluids with viscosities in the lower range of our measurement errors. The striking feature of the bent-core nematics we studied is that they preserve the cybotactic smectic clusters even in their isotropic phase, resulting in the observed shear thinning even in

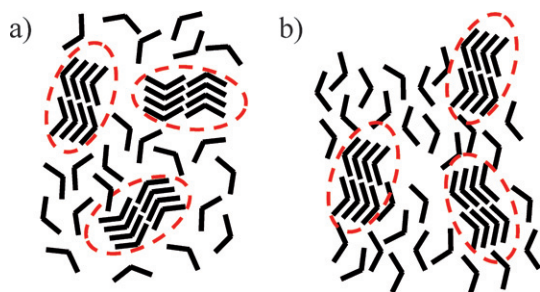


Fig. 3 Proposed nanostructure of bent core nematogens in (a) the isotropic and (b) the nematic phase.

their isotropic range as far as 15°C above the clearing point. This behavior can be clearly attributed to the bent molecular shape. We note that previous papers^{10,22} already suggested clusters based on electrohydrodynamic instability studies and NMR studies, respectively. According to ref. 22 the clusters consist of “entanglements”, whereas in ref. 10 cybotactic smectic clusters are proposed. Recently translational self-diffusion NMR measurements²³ were performed on one of the bent-core materials (BCN1) that we studied here by rheological measurements. While ^1H diffusion and ^2H relaxation times reveal a peculiar slow dynamic behavior, in accordance with prior DLS measurements,¹¹ ^1H relaxation times seem to be affected only by fast dynamics. To explain these, both of our smectic cluster model and Domenici’s entanglement model²² were considered, but the data could not conclusively distinguish between these two. Our rheological results presented here not only favor the cybotactic cluster model, but also explains how the shear-rate dependence of the rheological behavior can be used to calculate the cluster size. Preliminary small angle X-ray scattering studies also seem to verify the presence of smectic aggregates with layer correlation lengths in the range of 4–5 nm in the isotropic and 8–10 nm in the nematic phases.²⁴ This is comparable with the estimated size of the aggregates determined from our rheological measurements, especially considering that the clusters are not necessarily spherical.^{20,25} We note that prior X-ray scattering studies in the nematic phase of BCN5 show a smectic correlation length of $\sim 22\text{ nm}$.²⁶

Fig. 2c shows the shear rate dependence of η and G for BCN1 over a wider ($10^2\text{--}10^4\text{ s}^{-1}$) shear-rate range where we find an additional shear-thinning regime below 500 s^{-1} . Extrapolation of

the increase in η to the 0.05 s^{-1} shear rate measured by electro-rotation¹⁶ provides comparable ($\sim 100 \text{ Pa s}$) values. This huge value can be explained by the presence of smectic clusters with random layer orientation at very low shear rate; and the observed shear thinning at higher shear rates (but still below $\sim 500 \text{ s}^{-1}$) can then be explained as the result of a shear alignment of the smectic clusters. The temperature dependences of the viscosity and shear modulus are shown in Fig. 2d for the isotropic and nematic phases of BCN1. We see only a small change (decrease due to flow alignment of the nematic phase) at the transition to the nematic phase, indicating that the structure of the aggregates does not change considerably during the transition. This behavior is in sharp contrast with the temperature dependences measured in the bent-core smectogens (see Fig. 4a), where we have plotted the data with respect to $T-T_{I-S}$ (T_{I-S} denotes the isotropic to smectic transition temperature). We first see that BCS1, which has a classical B_7 structure composed of smectic ribbons, has more than an order of magnitude larger viscosity and shear modulus than those with B_2 and modulated SmCP (B_7') phases. While this may be partly related to the different shear rates used with these samples, it cannot explain the differences between BCS1 and BCS2, where similar shear rates were utilized. In all of the B_7 samples (BCS1, 2 and 4), we see that there exists a peak (or hump) in viscoelastic response approximately 4°C below the transition to the B_7 phase. This behavior does not exist in the BCS3 (B_2 phase) sample. It is likely that this feature is related to the helical filamentary growth²⁷ which forms in the B_7 phase, creating an unorganized smectic structure with many defects, and it is only after some time (or at lower

temperature), when these filaments join to form larger smectic domains, so that the viscoelastic values decrease. Fig. 4b shows the viscosity for some of our smectogens (BCSs) and compares them to the calamitics and bent-core nematogens in their isotropic phase. The viscosity for the smectogens is smaller than the BCNs, partially because their temperatures are higher. To compare the viscosity values, in Fig. 4c we show the temperature dependences for several bent core materials for the same shear rate of 401 s^{-1} . We see that BCN1, which had the largest viscosity among the BCNs studied, follows roughly the temperature dependence of the viscosity of BCS3 in the B_2 phase and the peak value in BCS2 in the B_7 phase. Although the viscosities of the BCSs in their isotropic phase clearly fall below the extrapolated isotropic value of BCN1, all the smectogens also show shear thinning similar to the nematogens, suggesting the presence of nanoscopic smectic aggregates in their isotropic phase, as we surmised for the BCN materials although to a much weaker extent.

Note from Fig. 4b that, while the B_2 material (BCS3) shows a monotonic shear thinning, the B_7 materials (BCS2 and BCS4) show a peak in their viscosities at a particular shear rate similar to the behavior observed in surfactant solutions which form wormlike micelles.^{28–30} Finally, in Fig. 4d the temperature dependence at different shear rates of the viscoelastic response in the smectic phases can be seen for BCS2, which has a B_7 – B_2 phase transition under cooling. We observe that shear thinning occurs in each of the phases, but in B_7 phase there is a threshold shear rate ($100 \text{ s}^{-1} < \gamma_{\text{th}} < 500 \text{ s}^{-1}$), which does not appear in the B_2 phase. This indicates that the shear is not effective in

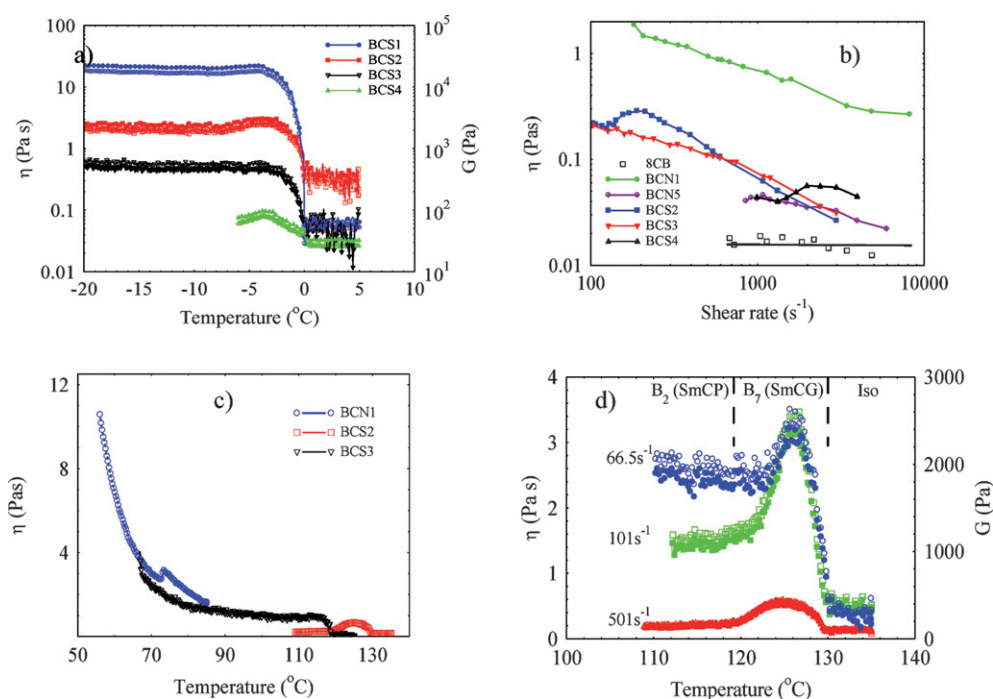


Fig. 4 (a) The temperature dependence of the flow viscosity η and of the shear modulus G , which trends closely with the viscosity, for the bent-core smectogens in Table 1. The temperatures have been adjusted to the isotropic-smectic transition. The shear rates used are 71.2 s^{-1} (BCS1), 66.5 s^{-1} (BCS2), 231 s^{-1} (BCS3), and 401 s^{-1} (BCS4). (b) A comparison of the shear rate dependence of η for BCN1 and BCN5, the BCS series, and 8CB. (c) The temperature dependence of η for several samples at a shear rate of 401 s^{-1} . (d) The temperature dependence of the viscoelastic response for BCS2 at various shear rates. We see that the shear thinning is much more prominent in the B_2 phase and less so in the B_7 phase.

realigning the B₇ layers below some threshold, most probably due to the modulated layer structure of the B₇ phase.

3. Summary

In summary, we have shown that a variety of bent-core mesogens are non-Newtonian fluids in their isotropic phase. This behavior is attributed to an underlying nanostructure containing smectic-like clusters of a few smectic layers, which may associate/dissociate in some metastable fashion at random positions. These smectic clusters appear to shear-align, explaining the shear thinning behavior exhibited by the nematogens and those smectogens that have a SmCP phase. In contrast, the smectogens having a B₇ phase do not shear align at low shear rates, and in fact show a slight shear thickening that might be caused by entanglements of modulated (wormlike or helical) clusters.

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