Rheological Properties of Bent-Core Liquid Crystals

C. Bailey
K. Fodor-Csorba
J. T. Gleeson
Samuel N. Sprunt
Antal Jákli

Available at: http://works.bepress.com/antal_jakli/23/
Rheological properties of bent-core liquid crystals

C. Bailey, a K. Fodor-Csorba, a,c J. T. Gleeson, ab S. N. Sprunt ab and A. Jáklis a

Received 14th April 2009, Accepted 23rd June 2009
First published as an Advance Article on the web 24th July 2009
DOI: 10.1039/b907261f

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, 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. 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)ferroelectric chiral structures in the absence of molecular chirality. 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. Theoretical and experimental studies on bent-core nematogens (BCNs) show spontaneous and induced biaxiality and giant flexoelectric effects, moreover, these materials promise both novel physics and opportunities for new technical applications. In addition, dynamic light scattering, electrolyrodynamic instability, magnetic field induced birefringence, and NMR measurements 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. Rotational viscous behavior in bent core nematics related to director fluctuations, have been determined by using dynamic light scattering or by observing relaxation times while magnetically switching an aligned sample. 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 x 5 mm x 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. 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. 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 rheometer 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 rheometer (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.

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.

---

L. C. Institute and Chemical Physics Interdisciplinary Program, Kent State University, Kent, OH 44242, USA
Department of Physics, Kent State University, Kent, OH 44242, USA
Research Institute for Solid State Physics and Optics, Budapest, Hungary

3618 | Soft Matter, 2009, 5, 3618–3622
(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 B2 (SmCP with C2 symmetry)\(^1\) transition, BCS1 and BCS4 have isotropic to B7 (smectic with modulated layer structure probably due to double tilted layer structure with C\(_1\) symmetry)\(^3\), and BCS2 has an isotropic to B\(_2\) to B\(_7\) sequence of transitions.

### 2. Results and discussion

The rheological properties (i.e., shear-rate and temperature dependence of \(\eta\) and \(G\)) for the calamitics and bent core nematics are shown in Fig. 2. We find that the calamitics behave as Newtonian fluids, in that their flow viscosities (\(\eta\)) 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 \(G = g\gamma^\beta\), where \(g\) and \(\beta\) are fitted parameters. While \(g\) is different for each sample, the values of \(\beta\) do not vary greatly and have an average value of 0.75. The viscosity for shear rates in the \(\gamma = 500–10000 \text{ s}^{-1}\) 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,

\[
\eta(\gamma) = \frac{\eta_o - \eta_{\infty}}{1 + (\gamma/\gamma_o)^m} + \eta_{\infty}
\]

Here \(\eta_o\) (\(\eta_{\infty}\)) is the viscosity at low (high) shear rates \(\gamma\), and \(\gamma_o\) 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).\(^19\) \(\gamma_o\) describes the rate at which the equilibrium particle distribution is regained; this rate is controlled by the particle diffusivity in dilute solutions: \(D_o = k_BT/(6\pi\eta a),\) 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, \(\gamma_o = D_o/a^2 = k_BT/(6\pi\eta a^3),\) provides us with an estimate of the size of the deformable particles as,

![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.](Image 44x197 to 279x249)

![Image 67x610 to 266x725](Image 44x197 to 279x249)

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

<table>
<thead>
<tr>
<th>Name</th>
<th>R(_1) (R(_1^\prime))</th>
<th>R(_2) (R(_2^\prime))</th>
<th>R(_3)</th>
<th>A</th>
<th>B</th>
<th>R(_4)</th>
<th>R(_5)</th>
<th>Phase Behavior (Cooling, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5CB</td>
<td>(CN) (C(_1)H(_2)_1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 24 Nem 36 Iso</td>
</tr>
<tr>
<td>8CB</td>
<td>(CN) (C(_1)H(_2)_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cr 22 SmA 34 Nem 41 Iso</td>
</tr>
<tr>
<td>BCN1</td>
<td>Cl</td>
<td>H</td>
<td>COO</td>
<td>COO</td>
<td>H</td>
<td>O(CH(_2))(_2)_C(_3)H(_2)</td>
<td></td>
<td>Cr 56 Nem 71 Iso</td>
</tr>
<tr>
<td>BCN2</td>
<td>Cl</td>
<td>H</td>
<td>COO</td>
<td>COO</td>
<td>H</td>
<td>O(C(_3)H(_2))(_2)</td>
<td></td>
<td>Cr 58 Nem 87 Iso</td>
</tr>
<tr>
<td>BCN3</td>
<td>Cl</td>
<td>Cl</td>
<td>H</td>
<td>COO</td>
<td></td>
<td>H</td>
<td>O(CH(_3))(_2)_C(_3)H(_2)</td>
<td></td>
</tr>
<tr>
<td>BCN4</td>
<td>Cl</td>
<td>Cl</td>
<td>H</td>
<td>COO</td>
<td></td>
<td>H</td>
<td>O(CH(_2))(_2)_C(_3)H(_2)</td>
<td></td>
</tr>
<tr>
<td>BCN5</td>
<td>Cl</td>
<td>Cl</td>
<td>H</td>
<td>COO</td>
<td></td>
<td>H</td>
<td>O(C(_3)H(_1))(_2)</td>
<td></td>
</tr>
<tr>
<td>BCS1</td>
<td>H</td>
<td>H</td>
<td>NO(_2)</td>
<td>COO</td>
<td>NCH</td>
<td>H</td>
<td>O(C(_3)H(_1))(_2)</td>
<td></td>
</tr>
<tr>
<td>BCS2</td>
<td>H</td>
<td>H</td>
<td>COO</td>
<td>NCH</td>
<td>H</td>
<td>SC(_10)_H(_2)</td>
<td></td>
<td>Cr 93 SmCP 128 B(_7) 140 Iso</td>
</tr>
<tr>
<td>BCS3</td>
<td>H</td>
<td>Cl</td>
<td>H</td>
<td>COO</td>
<td>NCH</td>
<td>H</td>
<td>OC(_3)H(_2)(_2)</td>
<td>Cr 68 B(_2) 127 Iso</td>
</tr>
<tr>
<td>BCS4</td>
<td>H</td>
<td>H</td>
<td>NO(_2)</td>
<td>COO</td>
<td></td>
<td>H</td>
<td>O(CH(_2))(_2)_C(_3)H(_2)</td>
<td>Cr 34.3 C(_3)_2 109.7 B(_7) 118.0 Iso</td>
</tr>
</tbody>
</table>
resulting in $a \approx 8, 11, 10, 13, 16$ 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 $8CB$21 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 their isotropic range as far as $15 \, ^\circ C$ above the clearing point. This behavior can be clearly attributed to the bent molecular shape. We note that previous papers10,22 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 $\sim 22$ nm.26

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

\[
\alpha = \left( \frac{k_B T}{6\pi \eta \gamma_0} \right)^{1/3} \tag{2}
\]

Fig. 3 Proposed nanostructure of bent core nematogens in (a) the isotropic and (b) the nematic phase.
the increase in \( \eta \) to the 0.05 s\(^{-1}\) shear rate measured by electro-
rotation\(^{16}\) 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 \(T\)\(\cdot T_{Ls} \) (\(T_{Ls}\) 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\(_7\)\(_0\)) 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 growth\(^{27}\) 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 calamities 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\(_2\) phase there is a threshold shear rate (100 s\(^{-1}\) < \(\gamma_{th}\) < 500 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 \( \eta \) 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 \( \eta \) for BCN1 and BCN5, the BCS series, and 8CB. c) The temperature dependence of \( \eta \) 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.

Acknowledgements

The work was supported by NSF-DMR-0606160. We are grateful to Prof. W. Weissflog for kindly providing BCS1 compound and to Dr H. Sawade for synthesis of the BCS2 and BCS3 compounds.

References

17 C. Bailey, A. Jakli, Broad range nanoliter rheometer, U.S. Patent pending.
21 A. J. Leadbetter, R. M. Richardson and C. N. Colling, J. Physique Col., C1, 1975, 36, 37.