

Large Flow Birefringence of Nematogenic Bent-Core Liquid Crystals

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We have found that bent-core liquid crystalline materials show exceptionally large intrinsic flow birefringence in their isotropic liquid phase. This effect is more than 100 times larger than typical values measured for low molecular weight liquid crystals. The specific flow birefringence (i.e., normalized by the flow viscosity) is an order of magnitude larger than in both side-chain polymeric as well as low molecular weight liquid crystals. We propose that this large enhancement for bent-core compounds may be attributed to nanoscale smecticlike clusters that persist above the nematic-isotropic transition temperature, and shear align under shear flow; however, this mechanism has not yet been definitively confirmed.

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Introduction.—Flow birefringence (shear flow induced optical anisotropy) is typically produced in liquids containing large asymmetric particles in the presence of a gradient in the flow field. The first example was provided by J. C. Maxwell in 1870, who described the phenomenon of double reflection using Canada balsam [1]. The most common examples for flow birefringence are solutions where the solutes are macromolecules that are geometrically and optically asymmetric, or become anisotropic under mechanical shear. Interesting results have been obtained for large flexible biological macromolecules, such as DNA and RNA [2,3], as well as for micellar structures, such as cetyltrimethyl-ammonium bromide (CTAB) in ionic (KBr) aqueous solution [4], polymer solutions [5], and side-chain liquid crystal polymers—the latter possessing the largest known flow birefringence [6].

The isotropic phase of liquid crystals formed by small molecular weight molecules also exhibits a readily detectable flow birefringence [7]. As discussed by de Gennes [8] and Chandrasekhar [9], the flow induced birefringence (δn) in the isotropic phase of liquid crystals can be related to the shear rate $\dot{\gamma} = \partial v_x / \partial z$ as $\delta n = -\frac{2\Delta n \mu}{3a(T-T^*)} \dot{\gamma}$, where μ is the flow viscosity, T is the temperature, T^* is the supercooling limit of the isotropic-nematic transition temperature, Δn is the birefringence in the nematic phase at $T = T^*$, a is the leading temperature-independent coefficient in a standard Landau expansion of the free energy, and the directions x and z lie parallel and perpendicular to the shear direction, respectively. The shear-rate independent, intrinsic flow birefringence $C\mu$, that is characteristic of the material, can be obtained from the derivative of the induced birefringence with respect to the shear rate: $|\frac{d(\delta n)}{d\dot{\gamma}}| = \frac{2\mu\Delta n}{3a(T-T^*)} \equiv C\mu$. In typical low molecular weight liquid crystals composed of rod-shaped molecules $C\mu \sim 10^{-8}$ s at $T - T^* = 1^\circ\text{C}$ [10], which is almost 4 orders of

magnitude smaller than in side-chain liquid crystal polymers, where the shear induces a transition to the nematic phase [6] at similar $T - T^*$.

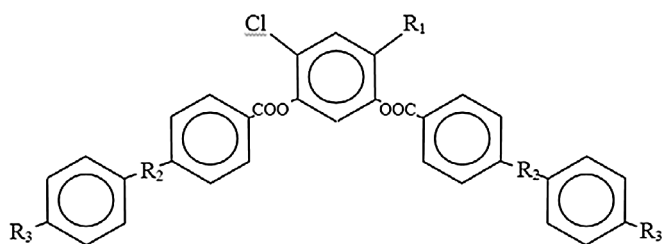
Recently, liquid crystals composed of bent-shaped molecules have attracted considerable interest due to their chiral, ferroelectric [11] symmetry even in the absence of chirality on molecular level [12]. Although they mainly form layered (smectic) liquid crystalline phases, a number of new bent-core compounds exhibiting nematic phases (BCNs) have recently been synthesized [13]. Theoretical [14] and experimental studies of BCN materials report spontaneous [15] and induced [16] biaxiality as well as giant flexoelectric response [17], which promise not only novel physics but also opportunities for new technological applications. In addition, dynamic light scattering [18], electro-hydrodynamic instabilities [19], magnetic field-induced birefringence [20], rheological [21–23], and NMR measurements [24] on BCNs show that bent-core materials are non-Newtonian fluids even in their isotropic phase. This behavior has been attributed to a nanostructure that contains temporary smectic clusters of a few layers size [23]. In this model the observed viscosities, decreasing from 100 to 0.1 Pa s as the shear rate increasing from 0.1 to 10^5 s⁻¹, can be explained by shear alignment of these smectic clusters—an effect that should also have optical consequences, such as a significant flow birefringence, which could reveal further details about (as well as confirm) the proposed nanostructure.

In this Letter we describe oscillatory flow birefringence measurements on a series of bent-core materials and show that their specific flow birefringence C (the flow birefringence divided by the viscosity) is more than 10 times larger than in either side-chain polymeric or low molecular weight liquid crystals. The observed effect may also hold promise for practical applications such as ultrasensitive flow indicator devices.

Experimental results.—The molecular structures and phase diagrams of the materials studied are shown in Fig. 1.

The four bent-core compounds labeled BCN1-4 exhibit a nematic phase below the isotropic phase. BCN1 and BCN2 have one chlorine atom in their central benzene ring, and they differ from each other only in their hydrocarbon chains, which are unsaturated in BCN1 and saturated in BCN2. BCN3-4 are dichloro substituted molecules, having unsaturated chains with slightly different lengths.

To detect optical birefringence during shear, we placed our previously developed nanoliter rheometer [22] in an Olympus CX40 inverted polarizing microscope, where the crossed polarizers could be aligned at various directions with respect to a periodic shear applied at frequency ω . The setup is shown schematically in the bottom of Fig. 2. A film of bent-core material is suspended between parallel support rods separated by distance d ; the top rod is free to undergo oscillatory motion (along the rod), while the bottom rod is held fixed. This arrangement produces a variable shear rate given by $\dot{\gamma} = (v_0/d) \cos \omega t$, where v_0 is the maximum velocity of the top rod. In our experiments, the oscillation frequency ($f = \omega/2\pi = 130$ Hz) and the spacing d were fixed, and the shear rates were set by varying the amplitude s of the oscillation. The uniformity of the shear rates within a sample can be deduced from the uniformity of the intensity of light transmitted through the sample, placed between crossed polarizers. As seen in the upper right picture of Fig. 2, there is some intensity variation at the edges, so in our analysis we always used the intensity of the uniform area. The dc and 2ω components of the depolarized transmitted light intensity were measured with an HP34401A multimeter and a DSP lock-in amplifier (EG&G Instruments, model 7265), respectively. The bire-



Name	R ₁	R ₂	R ₃	Phase sequence in cooling (°C)
BCN1	H	COO/OOC	-O(CH ₂) ₅ CH=CH ₂	Cr 56 N 74 Iso
BCN2	H	COO/OOC	-OC ₁₁ H ₂₃	Cr 58 N 87 Iso
BCN3	Cl	-	-O(CH ₂) ₅ CH=CH ₂	Cr 60 N 94 Iso
BCN4	Cl	-	-O(CH ₂) ₅ CH=CH ₂	Cr 64 N 98 Iso

FIG. 1. Names, molecular structures, and phase sequences of the studied bent-core materials.

fringence δn was calculated from the transmitted light intensity I , using $I = \frac{1}{2} \sin^2 2\phi \sin^2(\frac{\pi}{\lambda} \delta n b)$, which is valid for uniaxial materials illuminated by a linearly polarized plane wave as in the case of our experiment. In this expression, $b \sim 125 \mu\text{m}$ is the thickness of the sample film, λ is the wavelength of illuminating light, and ϕ is the angle of the induced optical axis (or shear direction) with respect to the polarization direction of the incoming light. As we used white light for illumination, we obtained an effective induced birefringence by taking an average value for the wavelength, $\langle \lambda \rangle = 550$ nm.

An example of quantitative data and fit curves (solid lines) in $d = 75 \mu\text{m}$ wide film of BCN1 are plotted in the upper left part of Fig. 2 where we show the dc birefringence as a function of shear-rate. It is seen that the induced birefringence is basically a linear function of the shear rate, and is increasing as the material is approaching the isotropic to nematic transition. Both of these observations are in accordance with standard theory [8,9] for low molecular weight calamitic liquid crystals. As we see in Fig. 2, the induced birefringence is in the range of $\delta n \sim 3 \times 10^{-3}$, which is about 3% of the birefringence of BCN1 in the nematic phase.

From the fits we have inferred the induced birefringence per unit shear rate—i.e, the quantity $C\mu$ —in the materials BCN1-4. As demonstrated in Fig. 3(a), $C\mu$ shows the expected linear behavior when plotted versus $(T - T^*)^{-1}$. Here we note that, within the error, for the studied materials $T^* \approx T_{\text{NI}} - 0.5^\circ\text{C}$, where T_{NI} is the isotropic to nematic transition. We also extract values for $C\mu$ at $T - T^* = 1^\circ\text{C}$, and then, using independent measurements of the viscosity μ [23], we obtained values for the specific flow birefringence C . These results are tabulated in

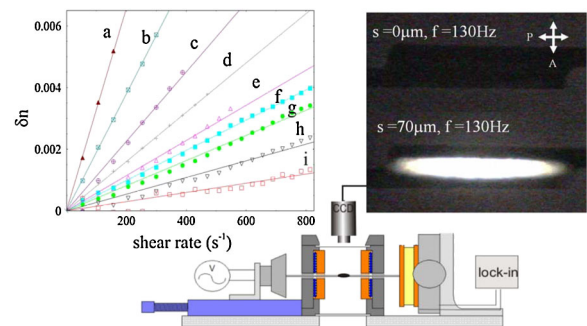


FIG. 2 (color online). Illustration of the shear-induced birefringence of BCN1 measured between crossed polarizers in the isotropic phase. Lower part: Schematics of the experimental setup; Upper left: Graph of the birefringence versus shear rate at (a) 74.7 °C, (b) 75.2 °C, (c) 76.2 °C, (d) 77.2 °C, (e) 78.2 °C, (f) 79.2 °C, (g) 80.2 °C, (h) 82.2 °C, and (i) 87.5 °C above the nematic phase as calculated from the transmitted light intensities. Upper right: Polarizing microscope pictures of the material at 76.3° between the actuating and sensing rods of the nl rheometer without shear (top) and with shear with $\dot{\gamma} \sim 570 \text{ s}^{-1}$ (bottom).

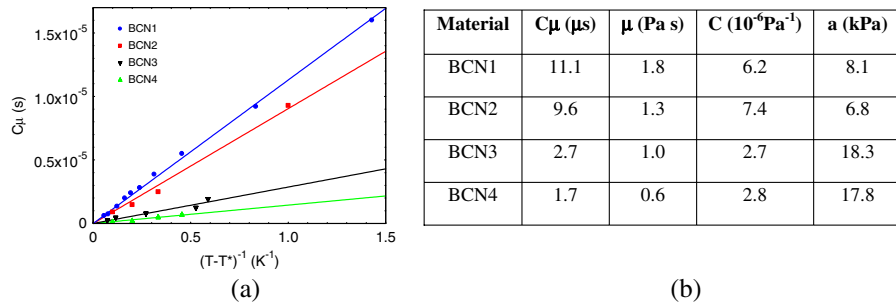


FIG. 3 (color online). (a) Temperature dependence of the shear induced birefringence parameter $C\mu$ on approach to the nematic transition temperature for the studied bent-core nematogens shown in Fig. 1. (b) Tabulated values of the induced birefringence per unit shear rate ($C\mu$), the viscosity values, the values of C deduced at $T - T^* = 1^\circ\text{C}$, and the Landau coefficient a .

Fig. 3(b) in units of microsecond (μs) and MPa^{-1} , respectively. We can see that $C\mu$ for the bent-core nematogens is in the range of 1–10 μs , which is 2–3 orders of magnitude larger than typical for liquid crystals based on rod-shaped molecules, such as pentyl cyano biphenyl (5CB), for which $C\mu \sim 20$ ns [10]. Actually, even when we compare the specific birefringence C to typical results for 5CB, where $\mu \sim 0.03$ Pa s, C for BCN1 is about 9 times larger at comparable values of $T - T^*$. In addition, since Δn of 5CB is about twice as large as in BCN1, we deduce that the Landau coefficient a of BCN1 is about 18 times smaller than in 5CB. Within the measurement errors this is comparable to the 25-fold decrease reported by Wiant *et al.* [20] for the same bent-core compound.

The optical axis of the induced birefringent state was determined by lock-in measurements of the 2ω component of the transmitted I when we rotated the direction of the crossed polarizers with respect to the oscillatory shear direction. We found that the 2ω component is minimized when the polarized or crossed analyzer axes make $\pm 45^\circ$ angles with respect to the shear direction, indicating that the optical axis is at 45° with respect to the flow velocity. The same observation was confirmed for all shear rates studied.

Discussion.—Recent rheological [23] and x-ray [25] measurements on our materials [see Fig. 4(a)], together with published x-ray data on similar compounds [26], all show the existence of smecticlike clusters over a very wide temperature range (which extends over 10°C into the isotropic phase). This strongly suggests that the exceptionally large flow birefringence of BCNs can be attributed to a nanostructure of the isotropic phases of bent-core materials that contains temporary smectic clusters of a few layers in typical size. The unusually large flow birefringence then can be explained by the shear-aligning of such clusters by direct shear alignment of the layers, and by the alignment of the director to 45° with respect to the flow by the Zvetkov mechanism [7]. Note that these two alignment mechanisms enforce each other, since the director in the smectic clusters is tilted by about 45° as well, as was found from our x-ray measurements [25]. This mechanism is

portrayed in Figs. 4(a)–4(c). Comparing the induced birefringence to that of the nematic phase of $\Delta n = 0.11$, we can estimate the volume fraction of the smectic clusters. For example at 2.3°C above the isotropic-nematic transition of BCN1, the maximum δn is about 3% of Δn of the nematic phase, indicating that almost 3% of the molecules could be involved in smectic clusters.

The nanoscale temporary clusters have positional order, so they are smectic instead of nematic. This can be seen in Fig. 4(a), where the maximum intensity corresponds to a periodicity of 32 \AA , which indicates either a tilted structure with about 45° tilt angle, or a partially bilayer smectic configuration. The latter structures are very rare in bent-core liquid crystals and limited only to those with very short terminal chains. The four lobed alignments of the diffused peaks in magnetic fields [25] also exclude this option. The shear, which aligns the layers of the clusters, therefore will explain the induced optical axis by about 45° with respect the flow. This shows that the flow alignment mechanism of nematic clusters [7,8] works also for our smectic clusters. Importantly, the smectic ordering is not unstable under shear, as was observed for shear induced nematic-SmA transitions [27]. Although our model is consistent with the experimental results, we cannot rule out other models, such as some type entanglements of the bent-

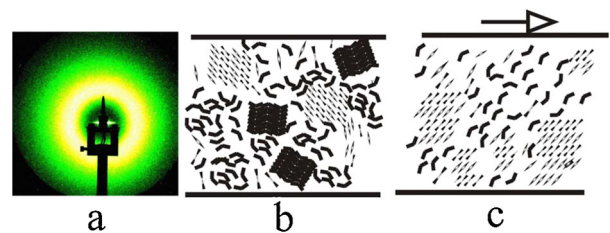


FIG. 4 (color online). (a) Small angle x-ray pattern of BCN at 80°C in the isotropic phase. The x-ray image was obtained on beam line X6B at the National Synchrotron Light Source at Brookhaven National Laboratory. The x-ray energy was 16 keV. (b) Proposed model of the nanostructure of bent-core nematogens (BCNs) in the isotropic phase at rest; (c) the model under shear flow.

core molecules induced by shear. For unambiguous confirmation for our model, x-ray measurements under shear would likely be definitive.

Finally, it is tempting to compare the specific flow birefringence, C , of the BCN materials, to other complex fluids, such as strongly flow birefringent micellar structures [4], polymer solutions [5], and side-chain liquid crystal polymers, although in those cases the relation between the induced birefringence and the shear rate is not linear, but rather resembles the relation associated with a field-induced phase transition [28]. Because of this non-linearity in large molecular weight systems, the flow birefringence may even depend on the film thickness [29], light wavelength, and shear rate, so we shall make only a qualitative comparison at similar temperature differences $T - T^*$ and film thicknesses, and at relatively low shear rates. We find that the specific flow birefringence $C \sim 6 \times 10^{-6} \text{ Pa}^{-1}$ of the monochloro compounds, BCN1 and BCN2, are comparable to or even larger than in micellar structures, where $C \leq 10^{-7} \text{ Pa}^{-1}$ [30], and in side-chain liquid crystal polymers, where $C \sim 10^{-6} \text{ Pa}^{-1}$ [6].

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