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Flexoelectricity of a calamitic liquid crystal elastomer swollen with a bent-core liquid crystal

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We have measured the electric current induced by mechanical distortion of a calamitic liquid crystal elastomer (LCE) swollen with a low molecular weight bent-core nematic (BCN) liquid crystal, and have determined, for the first time, the bend flexoelectric coefficient \( e_3 \) of such a BCN-LCE composite. In one method, we utilise air-pressure to induce a mechanical bend deformation and flexoelectric polarization in a BCN-LCE film, and then measure the polarization current as a function of time. An alternative technique uses a rotary-motor driven scotch yoke to periodically flex the BCN-LCE; in this case, the magnitude and phase of the induced current are recorded via a lock-in amplifier. The flexoelectric coefficient, \( e_3 \), was found to be \( \sim 20 \, \text{nC/cm}^2 \), and is stable in magnitude from room temperature to \( -65 \, ^\circ\text{C} \). It is about one third the value measured in samples of the pure BCN; this fraction corresponds closely to the molar concentration of BCN in the LCE. The flexoelectric current increases linearly with the magnitude of the bend deformation and decays with frequency. These observations indicate a promising way forward towards producing very low-cost, self-standing, rugged electromechanical energy conversion devices.

Introduction

Flexoelectricity (electric polarization induced by mechanical flexure) is a well known property of the liquid crystalline (LC) state of matter. The effect was first predicted and observed almost 40 years ago, and it arises when a material comprised of orientationally ordered anisotropic molecules (nematic LC) undergoes a distortion in the direction of average molecular orientation, and the combination of molecular asymmetry and broken orientational symmetry produces a non-zero electric polarization. In traditional, rod-shaped (or calamitic) LCs, flexoelectric coupling is invariably small. The effect was therefore only of academic interest until a new class of nematic liquid crystals, based on molecules with a bent-core or “banana” shape, was synthesized. Recent studies have shown that many properties of bent-core nematics (BCNs) are unusual. It has been proposed that this is because of an underlying super-molecular nanostructure consisting of temporary smectic, so called “cybotactic”, clusters, with the layer normal tilted with respect to the molecular orientation direction. This mechanism can explain the exceptionally large flexoelectric response exhibited by certain BCNs - e.g., values of \( e_3 \) more than 100 times larger than would be expected based solely upon molecular properties. Such a remarkable enhancement makes possible a new generation of mechanical-to-electrical energy conversion technologies. However, this technology would be severely limited in environmental ruggedness due to the fluidity of the underlying liquid crystal. To realize practical materials, one then needs a method of encapsulating the BCN in a mechanically robust but flexible matrix that stabilizes the BCN’s orientational order against variations in environmental conditions, yet still carries over the flexoelectric properties of the fluid.

To achieve such a stabilizing matrix, we chose to swell extant liquid crystal elastomer (LCE) networks with a suitable BCN. This is an attractive approach because (1) a well-known property of common isotropic elastomeric systems is their ability to swell in suitable solvents, and (2) it requires no additional synthesis, but rather uses two available materials. LCE’s combine the anisotropic physical properties of liquid crystals together with the elasticity of rubbery polymers. Bulk samples of LCE are unique in their ability to change their shape spontaneously as a consequence of their global orientational (nematic) or combined orientational/axial (smectic) order. Our recent results showed that calamitic LCE networks are capable of swelling bent-core compounds uniformly (i.e., without micro-phase separation) to an equilibrium saturation value of about 40–50% of BCN solvent. In this paper we report studies of the direct flexoelectric properties of these BCN-LCEs and show that they preserve the strong flexoelectricity of the pure BCN but in a mechanically robust, self-supporting film. Thus BCN-LCEs may hold the realistic promise for a new generation of cheap and highly processible mechanical energy conversion devices.

Experimental

There are several established techniques to measure the flexoelectric effect and its coefficients (\( e_1, e_3 \)). Almost all of these methods measure converse flexoelectricity, i.e., specific director distortions induced by an applied electric field. Some of these involve surface torques, however, unknown details about the surface anchoring of the molecules complicate the interpretation...
of such measurements. Measurements of bulk distortions are more accurate and reliable. Here the most common method is to apply an AC electric field across a hybrid aligned cell,\textsuperscript{19} and measure the polar component of the distortion by optical methods. Other techniques include electric field induced periodic domain structure,\textsuperscript{20} use of inhomogeneous electric fields,\textsuperscript{21} and applying an electric field across a wedge cell.\textsuperscript{22} Direct measurements (flexing induced electric current) have been previously performed by applying pressure waves,\textsuperscript{23} short pulses of laser heating,\textsuperscript{24} or recently by the direct mechanical flexing of a flexible sandwich cell.\textsuperscript{12}

For LCEs, most optical-based measurements of converse flexoelectricity are not feasible. Electric-field induced distortion in LCEs is highly suppressed due to the anchoring of mesogens to the polymeric component of the elastomer.\textsuperscript{25} On the other hand, LCEs are more responsive to mechanical distortion without flow. For this reason we employed two separate direct flexing measurement techniques. One is a mechanical flexing technique using a motor-driven scotch yoke, where the induced current is measured with a lock-in amplifier synchronized to the motor frequency. This has the advantage of ease of accurate measurement of harmonics of the periodic signal, but does not fully show the time dependence of the flexoelectric signal. The second technique uses excess air pressure to induce the mechanical deformation during which we measure the induced current as a function of time.

The bent-core solvent employed in our study is 4,6-dichloro-1,3-phenylene-bis 4-[(40-(9-octenyloxy))biphenyl] carboxylate with one terminal chain unsaturated and the other saturated; we denote this compound BCb-us (see Ref. 1)). It has a nematic phase between 97.6 °C and 48 °C. The preparation of the calamitic nematic LCE was described in Ref. 26, and swelling of this LCE with BCb-us was performed using the process described in Ref. 17. The LCE swells by a factor of roughly 2 in volume by absorbing bent-core liquid crystal; this indicates the swollen LCE contains around 30 mol% BCN. The swollen LCE has the phase sequence, isotropic (87.0 °C) nematic (−3.6 °C) glass. The structure of the material is shown in Fig. 1.

### Air blow flexing

This setup is illustrated in the top of Fig. 2. A film of BCN-LCE is placed between two flexible electrodes (30 μm aluminium foil). The flexible LCE sandwich cell (5 × 5 × 0.5 mm\textsuperscript{3}) is placed on a horizontal heating plate. One end of the sandwich cell is fixed to a hot plate and the other is allowed to move freely. A burst of excess air pressure is then applied through the heating plate, perpendicular to the LCE sandwich cell, forcing the sandwich to flex upwards. Gravitational and elastic restoring forces return the LCE to the original position. The applied pressure amplitude is varied by an electronically controlled valve. An electronic pressure modulator allows an “on” or “off” square wave signal to be applied with variable duty cycle (10–90%) and frequency (f < 10 Hz). The signal (polarization current) arising from the BCN-LCE sandwich cell is first amplified by a current sensitive pre-amplifier (1 V/nA); subsequently most of the 60 Hz noise was removed from the signal via a low-pass filter.

### Mechanical flexing

This method is the same as previously used in measuring the flexoelectricity of fluid BCNs\textsuperscript{12} and is illustrated in the bottom of
A 0.5 mm thick BCN-LCE film is placed between two flexible electrodes which are in turn sandwiched between two brass sheets; these transfer the mechanical bending motion to the LCE. A spacer, which is slightly larger than the LCE prevents the brass sheets from compressing the LCE and shorting the circuit. A DC motor with adjustable gearing is used with a scotch yoke to translate rotation into a sinusoidal linear motion. A photogate monitors the frequency of the motion, and provides the reference signal to the lock-in amplifier. The apparatus is enclosed within a heated box, with temperature sensors placed both at the bottom of the box and in the air near the sample.

As previously shown for this technique, the magnitude of the flexoelectric coefficient $e_3$ can be calculated from the measured RMS current ($I_{\text{RMS}}$) across the electrodes of area $A$ of the cell with length $L$ flexed along an axis perpendicular to the director with amplitude $S_0$ and angular frequency $\omega$, as

$$|e_3| = \frac{\sqrt{2}I_{\text{RMS}}L^2}{8A\omega S_0}$$

(1)

**Results**

The time dependence of the low-pass filtered electric current, measured across the 30 mol% BCN-LCE at 70 °C under a 2 Hz, 20% duty cycle square-wave applied air-pressure variation (20 kPa), is shown in Fig. 3. When the BCN-LCE sample is flexed by the application of the air pulse, a peak is observed after a small delay of around 5 ms. After a rise over ~30 ms, the signal from the sample decays away within 0.1 s. This slow decay is most likely due to screening out the induced polarization by impurity ions. When the air-pulse is withdrawn a peak with opposite sign (as expected for a flexoelectric signal) is observed with similar characteristic rise and decay times. When the sample is restricted in movement with an applied layer of adhesive tape and the same air-pressure is applied, the response is observed to reduce significantly as seen in Fig. 3, although the non-zero signal indicates that there is still some residual movement. These observations indicate that a linear flexo-electric effect is observed and the signal is not an artefact.

The amplitude of the current pulse was also measured at a fixed frequency of 5 Hz, as a function of air pressure. We observe (see Fig. 4) that the amplitude of the flexing is proportional to the air pressure. The same Fig. 4 also shows the frequency dependence of the induced current at 50 kPa. We see that the current decreasing to about third from 2 Hz to 10 Hz.

The mechanical parameters (sample size and flexing amplitude) and the induced electric current values as seen in Fig. 3 are of the same magnitude as those obtained in pure, fluid BCN’s, indicating comparable flexoelectric coefficients. However, some caution is warranted for this comparison because Eq. (1) refers to a sample with both ends clamped and flexed in the center, and the BCN-LCE data applies to a sample with one end free. To obtain a quantitative comparison between the flexoelectric coefficient of the pure BCNs and those of the BCN-LCE, we have measured the temperature dependence for both materials in the same mechanical flexing device; the results are displayed in Fig. 5. We see that the maximum signal of the 30 mol% BCN-LCE is about 1/3 that of the pure BCN. This is roughly the mole fraction of the BCN in the elastomer indicating, as expected, that the signal is coming from the BCN content. The response in the pure BCN begins a sharp decrease near the nematic to isotropic transition, whereas for the swollen elastomer the decrease is much more gradual. Importantly, the flexoelectric effect in the swollen elastomer exists over a significantly wider temperature range (over 60 °C). Fig. 5 also shows the signals (scaled to the mechanical flexing value below the transition) measured by the air blow technique. We find that although the temperature dependence agrees with that of the mechanical flexing data, the scatter in the air-blow signal is higher due to the less precise temperature control.
Discussion

We have shown that a calamitic LCE swollen with substantial fraction of a bent-core nematic LC (BCN) preserves the high value of the flexoelectric coefficient \( e_3 \) found in the pure BCN. Thus, even though the mechanism responsible for giant flexoelectricity in BCNs is not yet fully established, it clearly is not rendered ineffective by an elastomer network. A candidate explanation for the large flexoelectric effect is the presence of polar, cybotactic smectic clusters, which can become aligned via a bend deformation. Significant evidence for this scenario is provided by small angle X-ray scattering (SAXS) images, examples of which are presented in Fig. 6. While in the pure elastomer, no SAXS is observed, in the BCN there is a strong low angle diffuse peak corresponding to a spatial periodicity of 32 Å, which suggests short-range correlated molecular layering characteristic of smectic cybotactic groups. Since this periodicity is smaller than of the molecular length of 41 Å, these clusters likely possess a SmC structure with tilt angle of \( \sim 40^\circ \). A corresponding diffuse peak can be seen in the swollen elastomer, but now with significantly more correlated layers that are partially oriented normal to the direction along which the sample was slightly stretched. Some recent results on similar bent-core materials show that these clusters are polar,\(^{27}\) which may contribute to the measured large flexoelectricity as already noted in.\(^{12}\)

The fact that the swollen BCN-LCE is self standing, and the temperature range of its flexoelectric response is substantially increased by the presence of the elastomer matrix, makes these materials viable for lightweight, easily processible energy conversion devices. In this context it is useful to compare the BCN-LCE with some inorganic materials, which also posses flexoelectric-type behavior due to special sample design. For example, in barium strontium titanate one can induce a polarization of about \( 1 \mu C/m^2 \) of a 1.8 mm thick slab with a strain gradient of \( 0.01/m \);\(^{28}\) while with the BCN-LCE composite we generated a 2 nA/cm\(^2\) current density at 3 Hz with a 0.1 m\(^-1\) strain gradient, which corresponds to \( 1 \mu C/m^2 \) polarization, i.e. the same charge per area at 10 times larger strain gradient but 4 times smaller film thickness. Thinner flexoelectric ceramic composites have been also fabricated, but they are both fragile and difficult to stress,\(^{29}\) whereas in principle one can make elastomer films as thin as 20–50 μm, which would increase the induced current per

![Fig. 4](image-url)  
**Fig. 4** Scaled pressure and frequency dependence of the induced current. The pressure dependence (■) was measured at 5 Hz. The scaled frequency response was measured at 25 kPa (●) in the air blow device, and independently by the mechanical flexing method (□).

![Fig. 5](image-url)  
**Fig. 5** The calculated flexoelectric coefficient \( e_3 \) vs. temperature (relative to the nematic-isotropic transition) measured by the direct flexing method for the pure bent-core liquid crystal (red open square) and for the elastomer swollen by 30 mole % of bent-core liquid crystal (solid circles). Data in open squares are the results obtained from the air-pressure technique normalized to the values of the direct flexing at \( T - T_{NI} = -30^\circ C \).

![Fig. 6](image-url)  
**Fig. 6** Small angle X-ray results on (a): pure liquid crystal elastomer; (b): on the pure bent-core liquid crystal at 85 °C; (c) and (d): LCE swollen by the bent-core liquid crystal BCb-us at 88 °C and 40 °C, respectively. These images were obtained on beam line X6B at the National Synchrotron Light Source at Brookhaven National Laboratory. The X-ray energy was 16 keV.
unit volume by another factor of 10. Furthermore, flexoelectric crystals must have a suitable shape, which makes the fabrication process for crystalline or ceramic solid materials much more difficult and expensive compared to BCN-LCE materials.

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References

25 Application of an electric field across a LCE.