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Giant flexoelectricity in bent-core nematic liquid crystal elastomers

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Recently ferroelectric ceramic and bent-core nematic liquid crystals have demonstrated flexoelectricity (coupling between curvature strains to electric polarization) up to 104 times larger than the previous standards. This may allow for usable electromechanical devices. However, ceramics are too rigid to withstand large bending and bent-core nematic fluids must be physically supported—their technological applicability is still limited. In this paper, we show that novel side-chain bent-core nematic elastomers not only produce giant flexoelectricity but are also robust and flexible enough for microscale parasitic power generation. © 2010 American Institute of Physics. [doi:10.1063/1.3358391]

Flexoelectricity that couples elastic curvature strains to electric polarization has been simultaneously and independently studied both in crystals and in liquid crystals since the 1960s.1,2 In liquid crystals it arises when a material comprised of orientationally ordered molecules with anisometric shape (pear or banana shape) undergoes a distortion in the direction of average molecular orientation (or director), and the combination of molecular asymmetry and broken orientational symmetry produces a nonzero electric polarization that couples to either bend or splay by the flexoelectric constants e1 and e3, respectively.2 In calamitic liquid crystals that consist of rod-shape molecules, the flexoelectric coupling is small; on the order of 10 pC/m. Bent-core (banana-shaped) nematic liquid crystals (BCN), that were theoretically used to illustrate the dipole mechanism of the bending induced flexoelectricity,2 were experimentally studied only recently.3,4 These studies showed that many properties of BCNs are quite unusual.3–8 The flexoelectric effect with bent-core molecules was expected, based on single molecule properties (shape and dipole moment) and theoretical models,9,10 to be only ~10 times larger than that for calamitics. It is both surprising and exciting that the flexoelectric response of bent-core nematics was found to be more than three orders of magnitude larger (e3 ~ 50 nC/m).11,12 Interestingly this enhancement is similar to those found recently in ferroelectric ceramics.13,14 This spectacular enhancement—combined with developments in the synthesis and processing of LCEs—finally allows the harnessing LC flexoelectricity for practical applications, though the fluid nature of BCNs require bulky elastic support or encapsulation. Liquid crystal elastomers (LCEs) are intriguing materials that combine liquid crystalline order (orientational and/or translational) and rubber elasticity.15 Recently we found that conventional liquid crystal elastomers swollen by bent-core fluids also show giant flexoelectricity,12 albeit still not robust enough for long term operation. LCEs studied to date have been composed exclusively of rod shaped (calamitic) mesogens. Bent-core liquid crystal elastomers (BCLCEs) were synthesized only very recently.17 In this letter, we show that aligned side-chain BCLCEs not only produce giant flexoelectricity but are also robust and flexible enough for microscale parasitic power generation.

The synthesis of the bent-core liquid crystalline material used to create the side chains of the elastomer, and the preparation of the aligned side-chain bent-core liquid crystalline elastomer (BCLCE) are described in the supplementary information (SI) (see Fig. S1).18 The measurement of the flexoelectric effect was done by periodic flexing of the elastomer and lock-in detection of the induced electric current. This method is the same as described previously for measuring the flexoelectricity of fluid BCNs (Ref. 11) and LCEs swollen with a BCN.15 For details, see the SI. For periodic flexing of the film with amplitude S0 at an angular frequency ω, and assuming an arc shape of the flexed film with a distance between inflection points L1, (Fig. S2 of the SI), the magnitude of the bend flexoelectric coefficient e3 can be calculated from the measured RMS current (I RMS) across electrodes of area A, placed on either side of the sample film, as e3 = (2/I RMS) (L2/8S0). (Here the factor L2/8S0 is an approximation for the radius of curvature of the flexing.)

Figure 1 shows e3 measured as a function of temperature on our BCLCE film and compares it with data measured in the fluid low molecular weight BCN, and in the calamitic elastomer swollen by the same BCN (Ref. 12) for a consistent set of parameters (f = ω2π = 2.9 Hz, S0 = 1.5 mm, and L1 = 2.5 cm). We see that for the BCLCE e3 ~ 30 nC/m is between the values for the pure BCN and the swollen elastomer, well within the giant flexoelectric regime. The temperature dependences of e3 for all three materials are similar as follows: an almost linear increase in cooling near the nematic-isotropic transition, almost constant through the middle of the nematic range, and a nearly linear decrease close to the glass transition in the elastomers or crystal phase in the bent-core LC. The range of large e3 approaches room temperature in the BCLCE and swollen elastomer films. Due to domain structure with varying transition temperatures, the nematic to isotropic transition is gradual in the elastomers—unlike the pure BCN which has weakly first order phase transition.19

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Figure 2 illustrates the electric current across the BCLCE sample induced by periodic flexing as a function of the flexing frequency. We find that there is a frequency threshold for the generation of flexoelectric current of approximately 0.35 Hz (0.2 Hz) while increasing (decreasing) the frequency during the measurement. This is due to ionic screening effects, which can be significant at low frequencies. With increasing frequency, the current increases roughly with the square root of frequency, while increasing frequency, the current decreases with the square root of frequency above 1 Hz. The sample was kept flexing for 10 min at 12 Hz before the current versus decreasing frequency measurements were started. During this procedure the flexoelectric current almost doubled, indicating that the flexing at high rates improves the alignment.

To confirm that the measured signal is not an artifact, we replaced our sample with pieces of the same dimensions as the BCLCE film of a conventional rubber band and a purely calamitic liquid crystal elastomer. We then repeated the temperature measurements illustrated in Fig. 1. For the calamitic elastomer the measured $\varepsilon_3$ was about 5 pC/m, typical of fluid calamitic nematics and over three orders of magnitude smaller than for the BCLCE (see Fig. S3 of the SI). The value of $\varepsilon_3$ of the simple rubber band was below our 1 pC/m sensitivity. To demonstrate the practical potential of our BCLCE we sandwiched a $4 \times 5$ mm$^2$ area sample (see picture in Fig. 3) between two brass electrodes covered on the outside with a flexible insulating layer. The electrodes of the sample were connected to an oscilloscope and the sandwich was repetitively flexed by hand. Figure 3 shows the time dependence of the electric current calculated from the voltage across the 1 M$\Omega$ oscilloscope input impedance. The period of the signal corresponds to the first harmonic of the flexure, indicating that it indeed has a flexoelectric origin, but the signal is also asymmetric since forward bending by hand was easier than backward bending (see Fig. S4 and the corresponding vide file in the SI). The sharp upward spikes recorded during forward bending are probably due to the electrodes touching at these large amplitude bends. The sinusoidal fit shown in Fig. 3 gives current amplitude of about 20 nA, and thus implies an upper limit of the current that can be achieved on cells of $\sim 20$ mm$^2$ areas at approximately 2 Hz. The video in the SI also shows that the control groups of a simple rubber and the pure calamitic nematic liquid crystal elastomer do not show any observable first harmonic response within the $\sim 1$ nA measurement noise.

In comparison with the giant flexoelectricity observed in ferroelectric ceramics, our results can be understood by assuming that the “giant flexoelectricity” ultimately has a piezoelectric origin due to constituent ferroelectric domains. In the solid ceramics, these domains build up within the entire material, whereas in bent-core nematic liquid crystals, recent experiments indicate their presence in the form of tilted smectic clusters, which occupy only a few percentages of the total sample volume.

Although the magnitude of the flexoelectric coefficient of our BCLCE material is much smaller than in the perovskite-type ferroelectric ceramics, we emphasize that the flexoelectric coefficient alone is not a sufficient indicator of possible applications when comparing solid and rigid inorganic ceramics with soft lightweight organic rubbers. Ferroelectric ceramics must be fabricated to a suitable shape in a costly and complex process, whereas BCLCEs are soft and easy to fabricate conformally. To compare the

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FIG. 1. The bend flexoelectric coefficient ($\varepsilon_3$) of the BCLCE (solid circles). For comparison, solid and open squares show, respectively, analogous results for the pure BCN monomer and calamitic liquid crystal elastomers swollen with the pure BCN (Ref. 12). The solid and dashed lines are guides to the eye. As the result of the preparation procedure (see SI) the liquid crystal elastomer film has a reasonably good planar alignment that was verified by polarizing microscope.

FIG. 2. Frequency response of the BCLCE sample studied in Fig. 1. Data points with squares (circles) were obtained for increasing (decreasing) frequency $f$. The fits (dotted lines) correspond to the equation $I=a+b-\sqrt{1+cf}$; the linear term in $f$ is much larger or the decreasing frequency curve. $S_y=1.5$ mm and $T=81$ °C (41 °C below the isotropic-nematic transition.

FIG. 3. The time dependence of the electric current induced by hand-flexing of the BCLCE sample at 1.7 Hz and approximately 35 °C. In the inset, the size of the BCLCE is illustrated next to a 18 mm U.S. coin.
potentials of these two different systems, we estimate the realistically achievable values of flexoelectric polarization. For example, in barium strontium titanate one can induce a polarization of about 1 μC/m² of a 1.8 mm thick slab with a strain gradient of 0.01 m⁻¹ (see Ref. 25), while with the 0.3 mm thick BCLCE we demonstrated a 100 nA/m² current density at 2 Hz with a 10 m⁻¹ strain gradient, which corresponds to a 100 μC/m² polarization. To increase the induced current per unit volume by another one to two orders of magnitude much thinner films are needed. This is possible in both areas, though thin flexoelectric ceramic composites are fragile and difficult to stress, whereas in liquid crystals production of several micron thick films, which could be readily stacked, is a routine process. These considerations, combined with the measurements presented in this work, suggest that BCLCEs have a realistic potential for inexpensive and highly processible electromechanical energy conversion devices.

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18See supplementary material at http://dx.doi.org/10.1063/1.3458391 for the synthesis of the bent-core liquid crystalline material used to create the side chains of the elastomer, and the preparation of the aligned side-chain bent-core liquid crystalline elastomer (BCLCE).