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## Measurement of the flexoelectric response in ferroelectric and relaxor polymer thin films

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We report measurements of the flexoelectric response (electric polarization induced by a strain gradient) in thin films of both ferroelectric and relaxor forms of vinylidene fluoride polymers. By using a simple cantilever measurement technique, while monitoring remanent polarization through the pyroelectric response, we are able to measure the flexoelectric response in thin films as well as isolate and correct for piezoelectric contributions, which would otherwise dominate the flexoelectric measurement. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4829622>]

The flexoelectric effect is a universal material response, whereby a strain gradient induces an electric polarization.<sup>1–3</sup> In most solids, however, the flexoelectric response is extremely small. For example, Tagantsev<sup>4</sup> estimated the flexoelectric coefficient  $\mu$ , the ratio of the induced polarization to the strain gradient in ionic crystals, to be of order  $ke/a$ , where  $k$  is the dielectric constant and  $e/a \approx 0.4$  nC/m, the ratio of the ionic charge to the lattice constant. This suggested that oxide ferroelectrics would be promising flexoelectric materials, because in the paraelectric phase just above the Curie temperature they can have very large dielectric constants, exceeding 10 000. Motivated by these considerations, Ma and Cross studied thin films of a variety of ferroelectric oxides, reporting flexoelectric coefficients ranging from  $2 \mu\text{C}/\text{m}$  to  $100 \mu\text{C}/\text{m}$ .<sup>5–9</sup> The higher values, which were obtained from strontium barium titanate, were significantly larger than the value of  $ke/a$  and also larger than the values calculated from first principles.<sup>10</sup> While the especially large values challenge the theoretical predictions, they also encourage work to exploit the effect in electromechanical devices that are freed of the constraint of noncentrosymmetry imposed on piezoelectric materials. Other opportunities for exploiting the flexoelectric effect at the nanoscale were well exemplified by the work of Lu *et al.*,<sup>11</sup> who used an AFM tip to produce large local strain gradients, and therefore large local electric fields, to mechanically produce polarization domain patterns in barium titanate thin films.

Unlike the oxide ferroelectrics, ferroelectric polymers based on polyvinylidene (PVDF) are dipolar order-disorder ferroelectrics, and therefore may not follow the ionic model. It is perhaps better to compare them to liquid crystals, where a simple mechanical model considers that wedge-shaped molecules with a dipole moment along the wedge axis exhibit a strong flexoelectric effect.<sup>12,13</sup> This may be the case with PVDF, where the net dipole moment points from the relatively bulky  $\text{CF}_2$  side to the  $\text{CH}_2$  side of the polymer chain. The dielectric constant of PVDF-based polymers, however, is relatively low, less than 100, even near the peak at the Curie

temperature.<sup>14</sup> Nevertheless, Baskaran *et al.* have reported high values for the flexoelectric coefficient  $\mu$  up to  $82 \mu\text{C}/\text{m}$  in nominally nonferroelectric PVDF samples.<sup>15–17</sup> It is difficult, however, to rule out piezoelectric contributions from residual ferroelectric beta and delta phases, because PVDF is, in general, a polymorphous material,<sup>14,18,19</sup> containing a substantial amorphous component<sup>20</sup> and various crystalline phases that depend strongly on synthesis and sample preparation procedures.<sup>21–23</sup> Therefore, we have made a study of thin films of VDF copolymer and a VDF terpolymer, which allow us to compare the flexoelectric response in three distinct states—ferroelectric, paraelectric, and relaxor.

The samples consisted of thin film capacitors with structure Al/polymer/Al deposited on a glass cantilever, and were made as follows. The cantilever substrates were glass microscope cover slides measuring  $50 \text{ mm} \times 10 \text{ mm} \times 0.2 \text{ mm}$ . The top and bottom electrodes were aluminum stripes 2-mm wide and 25 nm thick deposited at right angles to each other using a thermal evaporator (BAL-TEC MCS 010) at vacuum base pressure of  $5 \times 10^{-5}$  mbar. The polymers for study were a ferroelectric random copolymer of vinylidene fluoride (70%) and trifluoroethylene (30%), P(VDF-TrFE), and a relaxor random terpolymer of vinylidene fluoride (55.8%), trifluoroethylene (35%), and chlorotrifluoroethylene (8.9%), both purchased in powder form from Kunshan Hisense Electronics (Shanghai) and used as received. The ferroelectric copolymer was dissolved in dimethylsulfoxide and the terpolymer in dimethylformamide, both to concentrations of 0.05% by weight. The thin films of 35 nominal monolayers were fabricated by the horizontal Langmuir-Blodgett (LB) method using a LB trough obtained from (NIMA-KSV). The copolymer samples were annealed for 90 min at  $135^\circ\text{C}$  and the terpolymer samples for 90 min at  $120^\circ\text{C}$ . The heating and cooling rate was  $0.5^\circ\text{C}/\text{min}$  for all samples. The method of sample preparation and the film properties thus produced are described in greater detail in the published reports.<sup>24–27</sup>

The flexoelectric measurements were made by flexing the cantilever back and forth along its long axis and measuring the current generated by the thin film capacitor, which was located approximately in the center of the cantilever. The cantilever geometry affords a simple means of producing a

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uniform strain and strain gradient in a thin film. Figure 1(a) shows the cantilever mounting and deflection method. The cantilever was held fixed at one end and deflected at the other end by knife edges driven by a cam and spring. Both the strain  $\varepsilon$  and strain gradient  $\varepsilon'$  of the film are approximately proportional to the displacement of the cantilever as follows:

$$\varepsilon = \frac{bY}{L^2}, \quad \varepsilon' = \frac{\partial \varepsilon}{\partial x} = \frac{Y}{L^2}, \quad (1)$$

where  $L = 30$  mm is the length of the cantilever from the fixed end to the knife edges,  $Y \ll L$  is the relative displacement of the cantilever at the contact point, and  $b = 0.2$  mm is the thickness of the cantilever. The cantilever oscillation was driven by an offset circular cam arrangement (Fig. 1(a)) mounted on the shaft of a dc motor. The center of rotation  $O'$  of the motor shaft was offset a distance  $c$  from the geometric center  $O$  of the circular cam of radius  $a$ . The off-center distance  $c$ , which ranged from 0.1 mm to 1.0 mm, defined the amplitude of oscillation. The net displacement undergoes sinusoidal motion according to  $Y = a + c \sin(2\pi ft)$ , where  $f$  is the frequency of rotation of the motor. This resulted in strains up to  $2 \times 10^{-4}$  and strain gradients up to  $1 \text{ m}^{-1}$ . The relative displacements were monitored by reflecting a He-Ne laser beam off the sample onto a quadrant photo detector. The cantilever signal from the sample was measured using a lock-in amplifier (Stanford Research Systems model SR 830) referenced to the cantilever oscillation frequency  $f$ , which was

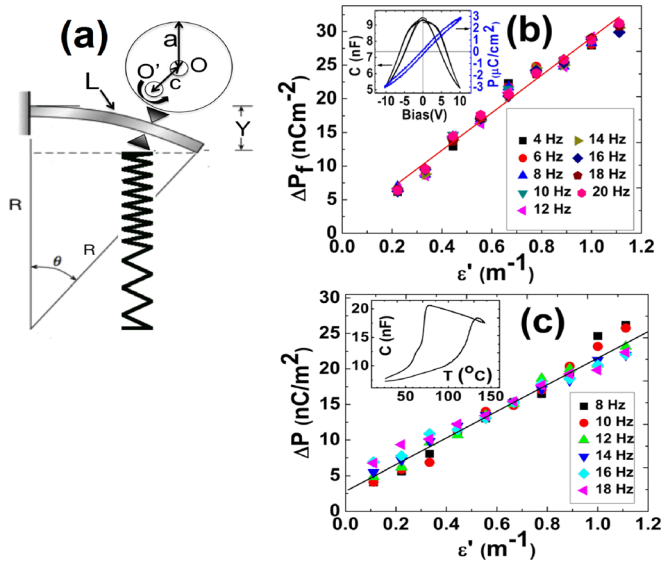


FIG. 1. (a) Schematic diagram of the experimental apparatus showing the beam geometry and the cam arrangement. The cantilever is attached to a rigid mount at left and moved by an eccentric cam of radius  $a$  and offset  $c$ , such that the cam center  $O$  rotates at constant angular velocity about the cam shaft  $O'$ . The cantilever is displaced by distance  $Y$ , resulting in a radius of curvature  $R$ . A spring keeps the cantilever in contact with the cam for both positive and negative displacements. (b) The net change in surface polarization is plotted as a function of the strain gradient for the relaxor ferroelectric. The slope of the linear fit gives a value of the flexoelectric coefficient  $\mu$ . The inset shows the sample capacitance and the polarization as a function of the external bias for the terpolymer sample. (c) The net change in surface polarization  $\Delta P$  as a function of the strain gradient measured at several oscillation frequencies in the paraelectric phase of the ferroelectric copolymer sample. The inset shows the variation of the sample capacitance as a function of temperature.

varied between 4 Hz and 20 Hz, well below the approximately 194 Hz fundamental resonance frequency of the cantilever. The pyroelectric response was measured by the modulation method, where a He-Ne laser–chopper arrangement modulated the sample temperature at 1 kHz and the current was measured by a second SR 830 lock-in amplifier.<sup>28</sup> The sample temperature was controlled by enclosing the cantilever apparatus in a homemade Teflon™ oven and controlled to within  $\pm 1^\circ\text{C}$  by a proportional feedback temperature controller (Brand-Gaus model 611). The cams were machined from solid Ultem™ blocks.

The change in electric polarization  $\Delta P_i$  in a material due to a combination of strain and strain gradient is

$$\Delta P_i = e_{ijk}\varepsilon_{jk} + \mu_{ijkl} \frac{\partial \varepsilon_{jk}}{\partial x_l}, \quad (2)$$

where  $e_{ijk}$  is the piezoelectric tensor,  $\varepsilon_{jk}$  is the strain tensor,  $x_l$  is the position vector, and  $\mu_{ijkl}$  is the flexoelectric tensor.<sup>4</sup> The first term in Eq. (2) is the piezoelectric contribution, which is present in a material that lacks inversion symmetry, and the second term is the flexoelectric contribution, which is present in all materials. The thin film capacitor deposited on one side of the cantilever will undergo a strain along the cantilever length and a strain gradient normal to the film. We omit the detailed tensor notation for the remainder of the analysis and work with effective scalar values appropriate to the simple planer geometry of the thin film capacitor, where only the polarization component normal to the film surface is detectable as charge on the electrodes. The change in surface polarization  $\Delta P$  is given by the sum of the two contributions, piezoelectric and flexoelectric, according to the expression

$$\Delta P = \Delta P_p + \Delta P_f = d\lambda\varepsilon + \mu\varepsilon' = (d\lambda b + \mu) \frac{c}{L^2}, \quad (3)$$

where the subscripts  $p$  and  $f$  denote the piezoelectric and flexoelectric contributions, respectively, and  $\lambda$  is the Young's modulus of the polymer. For the cantilever geometry (Fig. 1(a)), the strain  $\varepsilon$  is along the cantilever axis and the strain gradient  $\varepsilon'$  is the strain gradient perpendicular to the film, and  $\mu$  and  $d$ , without subscripts, are the effective values of the flexoelectric and piezoelectric coefficients for this geometry. With the deflection  $Y$ , and therefore the strain  $\varepsilon$  and strain gradient  $\varepsilon'$ , modulated sinusoidally at frequency  $f$ , the amplitude of the polarization modulation is proportional to the current  $J$  measured, as by the lock-in amplifier, according to  $\Delta P = J/(2\pi fA)$ , where the capacitor area  $A = 4 \text{ mm}^2$  for all samples.

For the ferroelectric copolymer, both the piezoelectric and flexoelectric terms of Eq. (3) contribute to the polarization change. In this case, the piezoelectric response is directly proportional to  $P_r$ , the remanent sample polarization. Since the pyroelectric response is also proportional to the remanent polarization  $P_r$ ,<sup>28,29</sup> the pyroelectric current at each poling voltage is therefore a measure of the relative piezoelectric contribution. Taking these facts into consideration, we can reframe Eq. (3) to read

$$\Delta P = (\kappa P_r + \mu)\varepsilon', \quad (4)$$

where  $\kappa$  is a constant that is independent of the polarization state, but is proportional to the product of the electrostriction coefficient and the dielectric constant.<sup>28</sup>

The terpolymer P(VDF-TrFE-CTFE) exhibits primarily relaxor behavior, so there should be little to no remanent polarization or piezoelectric response,<sup>30</sup> and therefore the induced polarization change in the cantilever measurement should be dominated by the flexoelectric response, as shown by Eq. (4) when  $P_r$  is zero. The cantilever signal was measured as a function of frequency and amplitude, and then plotted as function of the amplitude of the strain gradient  $\epsilon'$  (see Eq. (4)), as summarized in Fig. 1(b). The data agreed well with linear dependence on amplitude expected from Eq. (4), with an effective flexoelectric coefficient  $\mu = 30 \pm 1.5$  nC/m that was determined from a least-squares linear fit to the data. To probe for ferroelectric polarization in the relaxor polymer capacitor, we made both polarization and dielectric hysteresis measurements, as shown in the inset in Fig. 1(b). We found a small amount of hysteresis in the dielectric constant by measuring the capacitance at 1 kHz using an impedance analyzer (Hewlett Packard 4192 LF) while cycling the voltage between  $\pm 10$  V at a rate of 0.5 V/s. The polarization hysteresis was measured by recording the polarization switching charge with a Sawyer-Tower<sup>31</sup> circuit with a reference capacitor of 118 nF and a sinusoidal test signal of 10 V peak at a frequency of 10 Hz. The inset in Fig. 1(b) shows the dependence of the capacitance of the thin film terpolymer as a function of the applied field superposed with the P-E loop. The results show little hysteresis with a remanent polarization of  $0.18 \pm 0.01$   $\mu\text{C}/\text{cm}^2$ , about 2% of the spontaneous polarization of the copolymer, and are consistent with measurements done elsewhere on the same composition terpolymer,<sup>30</sup> showing that it has negligible ferroelectric hysteresis. We also tested the assumption that there was negligible piezoelectric contribution to the cantilever signal by confirming that the terpolymer capacitor had negligible pyroelectric response, even after poling at  $\pm 10$  V for 15 min.<sup>28</sup>

The copolymer P(VDF-TrFE), on the other hand, is ferroelectric at room temperature, and therefore we must account for the piezoelectric contribution represented by the first term in Eq. (4). We first measured the induced cantilever signal from the sample in the as-grown state, before a dc bias had been applied to the capacitor. The dependence of the induced polarization on strain gradient was linear, as shown in Fig. 2(a), but with a much larger slope of 248 nC/m. But, this result was likely dominated by the unavoidable remanent polarization found in nominally unpoled ferroelectric polymer films,<sup>32</sup> so we proceeded to investigate this point further, sampling the full range of remanent polarization states by cycling the applied voltage between  $\pm 12$  V in steps, each applied for 10 min. After removing the DC bias at each step, the induced polarization change obtained from the cantilever signal was measured as a function of amplitude  $Y$  (see Fig. 2(b)) and the slope  $\Delta P/\epsilon'$  determined for each remanent polarization state. Figure 2(c) shows the resultant hysteresis loop formed by the slope  $\Delta P/\epsilon'$  along with corresponding pyroelectric response for each remanent polarization state. These data exhibit hysteresis because both the piezoelectric and pyroelectric coefficients are proportional to the remanent polarization.<sup>28</sup> The flexoelectric contribution to the cantilever signal should, however, be independent of the remanent polarization state and show up as an offset in the  $\Delta P/\epsilon'$  hysteresis loop. This offset is evident in the dependence of the slope  $\Delta P/\epsilon'$  on the remanent polarization state represented by the pyroelectric signal  $\Delta P_{pyro}$ , as shown in Fig. 2(d). The flexoelectric coefficient was extracted by applying a least-squares linear fit to the unsaturated data in Fig. 2(d). (For this determination, we excluded the values corresponding to saturated polarization states at the top and bottom of the hysteresis loops, because they are far from the nominally unpoled state.) The intercept of this fit is an upper limit on the value of the flexoelectric coefficient  $\mu \leq 191 \pm 17$  nC/m for the 70/30 ferroelectric copolymer P(VDF-TrFE) film at room temperature. We have therefore found that in the ferroelectric

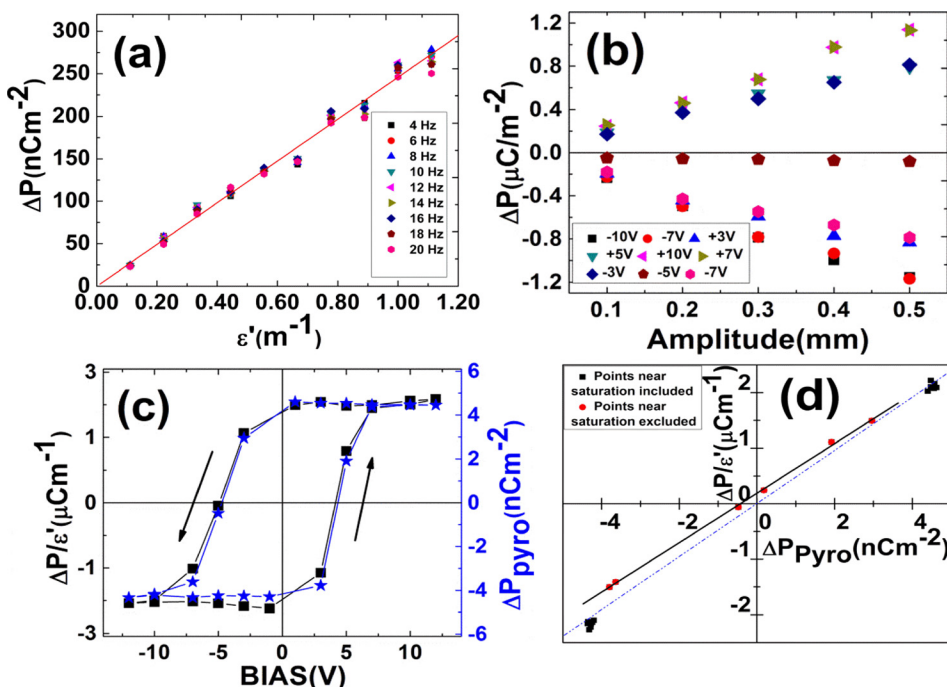


FIG. 2. The experimental results for the ferroelectric copolymer. (a) The net change in surface polarization  $\Delta P$  as a function of the amplitude of deflection of the cantilever. (b) The net change in surface polarization  $\Delta P$  as a function of amplitude for different poling voltages. (c) Hysteresis loops showing the ratio of the induced surface polarization  $\Delta P$  to strain gradient  $\epsilon'$  (squares) and the pyroelectric current  $\Delta P_{pyro}$  (stars) as a function of the different poling voltages. (d) The ratio of the induced surface polarization  $\Delta P$  to strain gradient  $\epsilon'$  plotted against the pyroelectric current  $\Delta P_{pyro}$  from the data in (c). The intercept of the linear fit gives an upper limit of  $\mu$ . The solid line is the linear fit including the data point near saturation (see plot, Fig. 2(c)), while the dotted line is the linear fit excluding those data points.



TABLE I. Flexoelectric coupling coefficients for ferroelectric and relaxor polymers.

Materials	Coefficient $\mu$ (nC/m)	Dielectric constant $k$	Coefficient $F$ (V)
Ferroelectric copolymer	$\leq 191 \pm 17$	10 (Ref. 21)	$\leq 2146 \pm 192$
Paraelectric copolymer	$18 \pm 1$	13	$159 \pm 6$
Relaxor terpolymer	$30 \pm 1.5$	50 (Ref. 26)	$67 \pm 3$

phase, the piezoelectric is by far the dominant contribution to the cantilever measurement response, even when great care is taken to minimize the remanent polarization.

In order to determine the value for the flexoelectric coefficient for the ferroelectric copolymer, we heated the ferroelectric film to 135 °C, well into the paraelectric phase above the Curie temperature of approximately 100 °C.<sup>14,24</sup> From the slope of a least-squares fit of the plot of the polarization change vs. the strain gradient (Fig. 1(c)), we determined flexoelectric coefficient  $\mu = 18 \pm 1$  nC/m in the paraelectric phase, less than one tenth than the value obtained in the ferroelectric phase, and slightly smaller than the value  $30 \pm 1.5$  nC/m obtained for the terpolymer. The figure in the inset shows the variation of sample capacitance with temperature indicating that the sample works consistently even at such high temperature. These results are comparable to values measured by Chu *et al.*<sup>33</sup> with PVDF (13 nC/m) and several thermosetting polymers (2 nC/m to 10 nC/m). We did not find evidence for giant flexoelectric coefficients of up to 82  $\mu$ C/m as reported by Baskaran *et al.* with nominally unpoled samples of PVDF.<sup>15–17</sup> Although they corrected their data for piezoelectric contributions, a small error in the correction may have had a large effect on the extracted value of the flexoelectric coefficient, as we found in our studies.

To compare the measurements from three distinct states—relaxor, ferroelectric, and paraelectric—we consider the more general principle that the flexoelectric coefficient should be proportional to the relative dielectric constant of the material,<sup>4</sup> and so it is useful to compare values of the flexoelectric coupling coefficient

$$F = \frac{\mu}{k\epsilon_0}, \quad (5)$$

which should be nearly independent of the dielectric constant. At room temperature, the dielectric constant is approximately 10 for the ferroelectric copolymer<sup>28</sup> and 50 for the terpolymer.<sup>30</sup> Table I compares the results of the flexoelectric measurements for the three cases. The value of the flexoelectric coupling coefficient  $F$  is 67 V for the relaxor terpolymer at room temperature and 159 V for the paraelectric phase of the copolymer at 135 °C. For the ferroelectric phase of the copolymer, the value of  $F$  is much larger, 2146 V at room temperature. The  $F$  values are, therefore quite different, probably because they represent three distinct states, ferroelectric, paraelectric, and relaxor, and therefore there are differences that go beyond the dielectric response. The values of  $F$  are also in reasonable agreement with those of Chu *et al.*,<sup>33</sup> which were obtained from PVDF at room

temperature (158 V) and several thermosetting polymers (89 V to 287 V). In particular, we note that the measured flexoelectric coupling  $F$  ranges from approximately 60 to 160 V in the nonferroelectric phases of VDF-based polymers, while it is somewhat larger, approximately 272 V, in polyethylene,<sup>33</sup> whereas the mechanical wedge model used for liquid crystals<sup>12</sup> would predict that the dipolar VDF materials should have much larger flexoelectric response than non-polar polyethylene. The fact that this expectation is not met is likely due to that fact that liquid crystals are nearly always operating in a plastic regime, where molecular displacements are relatively large, whereas the measurements reported here are well in the elastic range, where the wedge shape would be less important.

In summary, we investigated the flexoelectric effect in thin film capacitors of VDF-based polymer. We used mechanical bending methods to measure the value of the flexoelectric coefficient  $\mu$ , which we found to be approximately two to three orders of magnitude larger than the Tagantsev estimate of approximately 0.1 nC/m. Although the values of the flexoelectric coefficient  $\mu$  vary considerably among the different polymer states, the ratio  $F$  covers a somewhat narrower range (Table I) and are comparable to values obtained for PVDF and several other thermosetting polymers,<sup>33</sup> demonstrating that the dielectric constant is an important parameter distinguishing flexoelectric response among similar materials.

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