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Finite-size scaling of flexoelectricity in Langmuir-Blodgett polymer thin films

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The flexoelectric effect, which is a linear coupling between a strain *gradient* and electrical polarization, is a fundamental electromechanical property of all materials with potential for use in nanoscale devices, where strain gradients can be quite large. We report a study of the dependence of the flexoelectric response on thickness in ultrathin films of polar and non-polar polymers. The measurements of the flexoelectric response in non-polar polyethylene and the polar relaxor polymer polyvinylidene-*co*-trifluoroethylene-*co*-chlorofluoroethylene were made using a bent cantilever method and corrected for the contribution from the electrode oxide. The results show that the value of the flexoelectric coefficient increases with decreasing thickness, by up to a factor of 70 compared to the bulk value, reaching such enhanced values in films of only 10 nm thickness. These results are consistent with a model accounting for interfacial contributions, and underline how large electro-mechanical coupling can be produced at the nanoscale. The results also distinguish the surface flexoelectric response from that coming from the volume. © 2016 AIP Publishing LLC.

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A common method of electromechanical coupling in materials is through piezoelectric response, the linear coupling of strain and electric field, which requires a material that lacks inversion symmetry.^{1,2} It is not always practical, however, to use piezoelectric materials, especially at the nanoscale, where device design can compromise material response. An alternative approach to nanoscale electromechanical coupling is to exploit the flexoelectric effect, which is a linear coupling of strain gradient and electric field.^{3–5} The dependence on the strain gradient makes flexoelectricity functionally different from piezoelectricity in two key ways. First, the flexoelectric response is present in *all* materials, not just in materials that lack inversion symmetry. In the case of flexoelectricity, the inversion symmetry is broken by the applied strain gradient, and hence, the limitation of the crystal being non-centrosymmetric is lifted.^{4–6} In liquid crystals,⁷ upon application of a strain gradient, the ordering of the large bulky molecules is strongly dependent on the shape anisotropy of the molecular species. In the case of polymers,^{8–11} and elastomers,¹² the ordering of the polymer chains depends on the size and rigidity of the side groups and cross-linked functional groups. While in inorganic amorphous materials,¹³ a distortion in the random network of local bonding units renders the system polar. In these materials the inversion symmetry breaking is strictly not crystalline but more geometrical in nature. This geometrical symmetry breaking leads to the creation of bound charges on the surface and hence induces a net change in surface polarization. Formally, the polarization P_i induced by a strain gradient is expressed in tensor notation as: $P_i = \mu_{ijkl} \frac{\partial \varepsilon_{jk}}{\partial x_l}$, where μ_{ijkl} is the flexoelectric coefficient tensor, ε_{jk} is the strain tensor, and the x_l is the coordinate along the l th direction. Second, the dependence of the induced polarization on the strain

gradient makes flexoelectricity a promising approach in designing new devices to exploit nanoscale functionality. For example, a large strain gradient achieved by pressing a scanning probe tip onto the surface of barium titanate (BT) thin film has been shown to induce ferroelectric polarization reversal.¹⁴ Polarization rotation has also been reported to result from large strain gradients engineered into epitaxial films of lead zirconium titanate (PZT).¹⁵

The earliest works by Kogan for crystalline dielectrics¹⁶ aimed at explaining the role of electrostatic fields arising from inhomogeneous defects in the crystal lattice. He showed that such inhomogeneous deformation potentials would polarize the medium even for centrosymmetric crystals and estimated the flexoelectric coefficient to be of the order of 0.1 nC/m. Marvan's work with the elastomers¹² considered a model of dipolar reorientation in anisotropic free volume to give an order of magnitude estimate of the flexoelectric coefficient between 0.1 nC/m and 1 nC/m. In a later theoretical work based on a rigid ion model, Tagantsev showed that the flexoelectric coefficient should also be proportional to the dielectric constant of the material since a high dielectric constant leads to larger ionic polarizability.^{3,17,18} In a series of experiments, Ma and Cross showed that for high dielectric constant ceramic perovskites like barium strontium titanate (BST),¹⁹ barium titanate,²⁰ lead magnesium niobate (PMN),²¹ and lead zirconium titanate,^{22,23} the flexoelectric coefficients are 2–4 orders of magnitude greater than the phenomenological estimates and may be related to the scaling of the effect with the material dielectric constant. We recently reported experimental results that showed that in vinylidene-fluoride based polymer films with both ferroelectric and relaxor character, the flexoelectric effect did scale with the dielectric constant of the material in a narrow temperature range near the phase transition temperatures.²⁴ In static bending experiments on strontium titanate

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single crystals, Zubko *et al.* also showed definitive scaling of the effect with the device capacitance at finite temperatures.²⁵ At the nanoscale, strain gradients can be relatively large, and therefore flexoelectricity can have dramatic effects on the properties of ultra thin films and nano-structured devices. There has, however, been limited experimental work reported on the thickness dependence of the flexoelectric effect. Sharma *et al.* have also simulated the thickness dependence of the flexoelectric effect for ferroelectric and paraelectric barium titanate nanobeams and given expressions for the effective size-dependent piezoelectric coefficient, which is quite high even in the paraelectric phase.^{26–29}

Here, we report the results of an experimental investigation into the dependence of the flexoelectric response on thickness for thin films of relaxor poly(vinylidene-trifluoroethylene-chlorofluoroethylene), P(VDF:TrFE:CTFE). The relaxor terpolymer films contain nanopolar regions that lack long-range ordering and as such will have negligible piezoelectric response.^{30,31} A non-polar polymer system of polyethylene (PET) was also studied for comparison since the basic structure is very similar to the ferroelectric and relaxor polymers of the vinylidene fluoride family.^{32,33} In order to compare the scaling behavior with a reference inorganic material, we have used thin films of silicon dioxide in the same thickness range as the polymer films.

The samples used in the reported measurements were in the form of thin film capacitors consisting of one or more dielectric layers between aluminum electrodes as shown in Fig. 1(a). The cantilever device was made on a glass microscope cover slide measuring 50 mm × 10 mm × 0.2 mm. The bottom aluminum electrode was 2 mm wide, 30 mm long, and 20 nm thick, deposited using a thermal evaporator (BAL–TEC MCS 010) at a vacuum base pressure of 5×10^{-5} mbar. The polymers that were used to make thin films consisted of medium density polyethylene (0.94 g/cm³) purchased from Sigma Aldrich and terpolymer poly(vinylidene fluoride (56%):trifluoroethylene (36.5%):chlorofluoroethylene (7.5%)), or P(VDF:TrFE:CFE) purchased from Kunshan Hisense Electronics, Shanghai. The medium-density

polyethylene was dissolved in benzene while the terpolymer powder was dissolved in dimethylformamide ($\geq 99\%$, reagent grade) purchased from Sigma Aldrich. The details of solution preparation method are discussed in greater detail in previous reports.^{11,34} The thin films of terpolymer were fabricated using a Langmuir-Blodgett (LB) deposition trough (NIMA 622) at a target pressure of 10 mN/m. The films of the polyethylene were also fabricated by LB method at a target pressure of 15 mN/m.¹¹ The films were transferred onto the substrate by the horizontal Schaefer's method.³⁵ Silicon dioxide thin films were made using an rf magnetron sputtering system at 2×10^{-3} Torr argon pressure. A top aluminum electrode 20 nm thick and 2 mm wide deposited by thermal evaporation, orthogonally crossed to the bottom electrode, capped all the thin film cantilever devices providing an effective electrode area of $A = 4 \text{ mm}^2$.

The cantilever sample was oscillated periodically by an off-center cam arrangement, as shown in Fig. 1(b). The detailed experimental set up is discussed in prior report.¹¹ The cantilever capacitors were oscillated with amplitudes ranging from 0.6 mm to 1.0 mm and at frequencies ranging from 2 Hz to 12 Hz. The flexoelectric current I was measured using the lock-in amplifier at the oscillation frequency f and the flexoelectric coefficient was extracted from the slope of polarization $P = I/(2\pi fA)$ and the strain gradient ($\epsilon' = Y/L^2$),¹¹ where $L = 30 \text{ mm}$ is the length of the bottom electrode.

The polymer films fabricated by Langmuir-Blodgett deposition had thicknesses ranging from 3 to 35 nominal monolayers. The thickness calibration used for polyethylene LB films was approximately 4 nm per nominal monolayer³⁴ and for the terpolymer it was 4.4 nm per nominal monolayer.³⁶ The silicon dioxide films fabricated by sputtering had thicknesses ranging from 5 nm to 100 nm. The dielectric measurements, device capacitance and loss tangent, were measured using a HP impedance analyzer LF 4192A.

The bottom electrode of aluminum always develops an unavoidable layer of aluminum oxide (Al_2O_3) on air exposure,

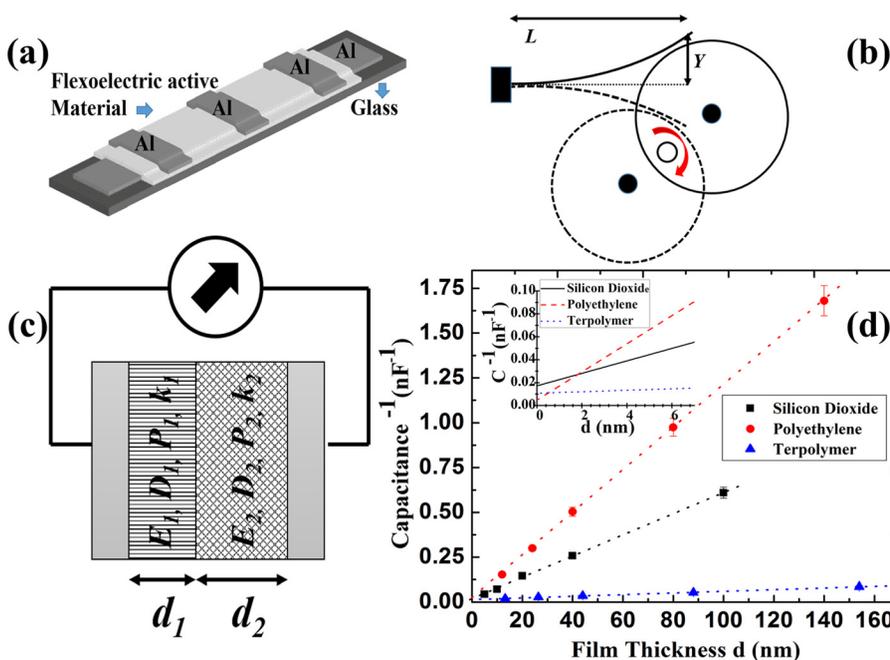


FIG. 1. (a) Sample geometry of the cantilever capacitor. (b) Schematic diagram of the cantilever oscillation with off-center cam. (c) The schematic view of the sample showing the aluminum oxide layer and the flexoelectric active layer (subscript 1 denotes the aluminum oxide layer while subscript 2 denotes the active layer). (d) Linear fitting of the reciprocal capacitance value with the device thickness for silicon dioxide, polyethylene, and terpolymer thin films. The inset is a zoomed-in area near the intercept.

TABLE I. Native aluminum oxide layer thicknesses in different material devices.

Material	Silicon dioxide	Polyethylene	Terpolymer
Al ₂ O ₃ thickness (nm)	5.7 ± 1.3	5.3 ± 1.2	4.6 ± 0.6

which could affect the net flexoelectric current. The schematic diagram of a sample device with the oxide layer is shown in Fig. 1(c). The capacitances of the films were measured with an HP 4192A impedance analyzer at a test ac voltage of 0.1 V at 10 kHz. The sample capacitance C measured is the capacitance of the oxide layer and the active layer capacitance in series as follows:³⁷

$$C^{-1} = \frac{d_1}{k_1 \epsilon_0 A} + \frac{d_2}{k_2 \epsilon_0 A}, \quad (1)$$

where subscripts 1 and 2 refer to the aluminum oxide and the active polymer layer, respectively, d is the thickness, and k is the dielectric constant. The intercept of a linear fit using Equation (1) gives the value of the native aluminum oxide layer thickness as is shown in Fig. 1(d) and listed in Table I. The inset shows a zoomed in area near the intercept. The bulk value of the dielectric constant, $k_1 = 9$, was used for the aluminum oxide layer.³⁸

Electrostatic boundary condition across the interface between aluminum oxide layer and the active material of the device was used to model the system. The normal component of the electric displacement D must be continuous across this interface in the absence of free charge

$$D_1 = D_2 \rightarrow \epsilon_0 k_1 E_1 + P_1 = \epsilon_0 k_2 E_2 + P_2. \quad (2a)$$

In the short circuit condition, the voltage across the device must vanish³⁹

$$E_1 d_1 + E_2 d_2 = 0. \quad (2b)$$

Here, E represents the electric field, P the flexoelectric contribution to polarization; k_1 and k_2 are the dielectric constant of the Al₂O₃ and the polymer, respectively. The polarization in the polymer layer mainly originates from the applied strain gradient ϵ' , i.e., $P_{1,2} = \mu_{1,2} \epsilon'$, where μ_1 and μ_2 are the flexoelectric coefficients of interfacial oxide layer and the polymer layer, respectively. The electric fields in the two layers can now be evaluated as

$$E_1 = (\mu_2 - \mu_1) \frac{d_2}{\epsilon_0 k_2 d_1 + \epsilon_0 k_1 d_2} \epsilon', \quad (3a)$$

$$E_2 = -(\mu_2 - \mu_1) \frac{d_1}{\epsilon_0 k_2 d_1 + \epsilon_0 k_1 d_2} \epsilon'. \quad (3b)$$

Since there is no electrical field outside the device, and under short circuit condition we measure the charge (or the current), the electric displacement also satisfies: $D_1 = D_2 = \mu_{\text{eff}} \epsilon'$ where μ_{eff} is the effective value of the flexoelectric coefficient for bilayer. μ_{eff} of the active polymer layer/Al₂O₃ bilayer is given by: $\mu_{\text{eff}} = (\frac{\mu_1 d_1}{k_1} + \frac{\mu_2 d_2}{k_2}) / (\frac{d_1}{k_1} + \frac{d_2}{k_2})$. The expression for the flexoelectric effect of only the active material is as follows:

$$\mu_2 = \mu_{\text{eff}} + (\mu_{\text{eff}} - \mu_1) \frac{k_2 \cdot d_1}{k_1 \cdot d_2}. \quad (4)$$

A control cantilever sample of Al/Al₂O₃/Al was fabricated by natural oxidation of bottom aluminum electrode.^{40,41} The dc resistance for the reference capacitor was approximately 300 Ω . The capacitance and the tangent loss of the control aluminum oxide device were measured as function of frequency, as shown in Fig. 2(a). The flexoelectric current was recorded for the control sample under same experimental conditions. The flexoelectric coefficient μ for the aluminum oxide sample with an average thickness of approximately 5 nm was 45 nC/m ± 0.97 nC/m at 27 °C, as shown in Fig. 2(b).

The effective flexoelectric response was measured as a function of the film thickness for all three materials, namely, the relaxor terpolymer, the polyethylene film, and the silicon dioxide layer, using the dynamic beam bending method.¹¹ The flexoelectric coefficient μ_2 was calculated using Equation (4) for each thickness since the native oxide thickness of aluminum d_1 and the flexoelectric coefficient μ_1 are now known. The value of the dielectric constant used for aluminum oxide,³⁸ polyethylene,³⁴ terpolymer,²⁴ and silicon dioxide⁴² were 9, 2.3, 40, and 3.9, respectively. The effective flexoelectric coefficient μ_{eff} (solid black squares) and the material flexoelectric coefficient μ_2 (solid red dots) are plotted as a function of the film thickness, as shown in Figs. 3(a)–3(c).

The data indicate that the effective flexoelectric coefficient increases with the decreasing thickness. The increase in the effective flexoelectric coefficient is highest for the terpolymer/native oxide films. The flexoelectric coefficient (μ_2) for the materials alone after correcting for the native oxide layer (viz., Equation (4)) showed enhancements too, and these values are even greater than the effective values for the two layers taken together. The phase information from the

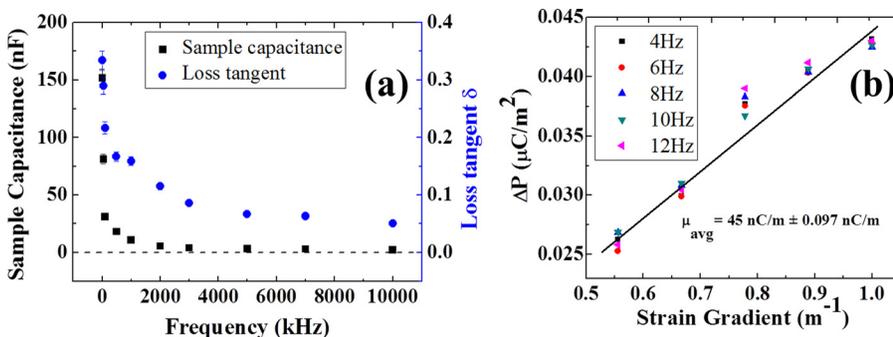


FIG. 2. (a) The capacitance values and the loss tangent for the control aluminum oxide device. (b) The strain gradient induced change in polarization for the control sample of aluminum oxide.

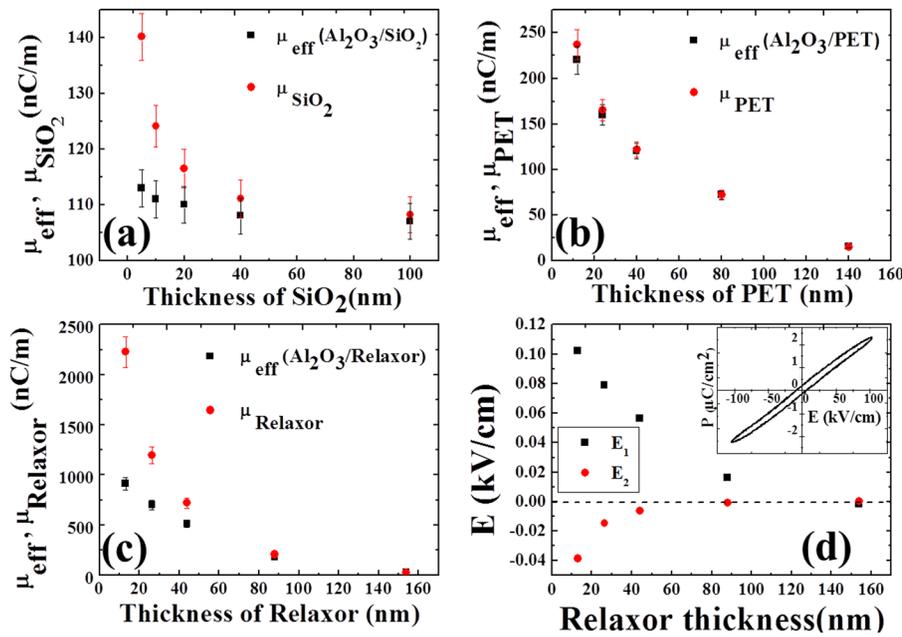


FIG. 3. The effective flexoelectric coefficient and the flexoelectric coefficient of the active material plotted as a function of film thickness: (a) silicon dioxide, (b) polyethylene, (c) terpolymer, and (d) the e-field induced by the maximum strain gradient of 1.0 m^{-1} for different film thickness of relaxor terpolymer in both the aluminum oxide and the relaxor terpolymer. The inset shows the P-E loop for a 20 ML relaxor film.

lock-in amplifier used to measure the flexoelectric current indicates a positive sign for the value of μ_{eff} , indicating that the material by itself ought to have higher coefficients for thinner films than a bilayer film. The data also indicate that for thicker films ($d_2 \geq 100 \text{ nm}$), the effective flexoelectric coefficient and the polymer flexoelectric coefficient converge. The flexoelectric coefficient values for the minimum thickness (d_{min}) for the active polymer layer to the effective flexoelectric coefficient for the maximum thickness (d_{max}) are compared in Table II. It is customary to define a flexoelectric coupling constant as: $f = \mu/(k\epsilon_0)$. The values of f for ceramic ferroic materials is estimated to be between 1 and 10 V.⁴³ The values of flexoelectric coupling coefficient f for the materials used in this manuscript range from 14 V for thick films to 10 kV for thinner films. The high flexocoupling constant for the polymer materials reported in the manuscript have been quantified empirically based on experimental observation due to lack of sufficient theory of flexoelectricity on molecular systems at such small length scales. It is clear that there are enhancements based on the model proposed but the difference from one material to the other is unclear. In ceramic ferroic thin films, the dielectric constant

decreases in comparison to the bulk values, and hence, the flexoelectric coupling constant values are preserved as shown by Ocenasek *et al.*,⁴⁴ but in the polymer films under investigation in the current work, there is no change in dielectric constant from the bulk for films down to 2 monolayers.^{34,45}

The electric fields induced for the maximum strain gradient of 1.0 m^{-1} (Equation (3)) as a function of film thickness for the relaxor terpolymer film are shown in Fig. 3(d). The inset shows a representative P-E loop for a 20-monolayer relaxor terpolymer sample having negligible remnant polarization at zero field. The E-fields induced by the strain gradient are 3 orders of magnitude smaller than the external E-fields needed to cycle between the saturated polarization states. This shows that the charge generation in the relaxor is primarily due to the low field induced by the mechanical strain gradient. It is also worth mentioning that recently it was shown by Lee *et al.*⁴⁶ that a fixed unidirectional strain gradient produced a flexoelectric diode rectification effect in epitaxially grown films. However, our samples are not grown epitaxially, and hence, the strain gradient is homogeneously distributed throughout the thickness. The asymmetric structure of our device might lead to a built in voltage via the Schottky barrier effect but its effect is mitigated by periodic oscillation of the cantilever as such at any point of time the average built in voltage attenuates to zero.

In previous theoretical treatments by Shen and Hu⁴⁷ and Dai *et al.*,⁴⁸ the contribution of surface piezoelectricity to the effective flexoelectric response was shown to scale as the reciprocal of the material thickness. In the present work, we have measured a dependence of the flexoelectric response on thickness that could be attributed to pronounced surface effects, such that the effective coefficient rises. However, the increase in the flexoelectric response for diminishing film thickness cannot be solely attributed to surface layer effects as suggested by Stengel.⁴⁹ The substrates used in all these experiments were cover slip glass of thickness $200 \mu\text{m}$. For substrates thicker than that the substrates would crack for the same strain gradient; whereas thinner substrates tend to be too

TABLE II. Enhancement factors for the material alone after correcting for the native aluminum oxide layer.

Material	SiO ₂	Polyethylene	Relaxor
d_{min} (nm)	10	12	13.2
d_{max} (nm)	105	140	154
Permittivity (k)	3.9	2.3	40
$\mu_2(d_{\text{min}})$ (nC/m)	140	238	2222
$f_2(d_{\text{min}})$ (V)	4000	11692	6270
$\mu_{\text{eff}}(d_{\text{min}})$ (nC/m)	113	220	912
$f_{\text{eff}}(d_{\text{min}})$ (V)	3273	10808	2576
$\mu_{\text{eff}}(d_{\text{max}})$ (nC/m)	107	14	29
$f_{\text{eff}}(d_{\text{max}})$ (V)	3100	687	82
$\frac{\mu_2(d_{\text{min}})}{\mu_{\text{eff}}(d_{\text{min}})}$	1.2	1.1	2.4
$\frac{\mu_2(d_{\text{min}})}{\mu_{\text{eff}}(d_{\text{max}})}$	1.3	17	76

floppy for the dimensions of the cantilever. It is for this reason that different materials were used as the flexoelectric active material in this work for a fixed substrate thickness. It is possible that the high f values for decreasing film thickness could be coming from contributions beyond intrinsic flexoelectricity mainly from polar inclusions in the bulk for the relaxor polymer case and/or the surfaces for the non-polar polymer case. But even if the extrinsic factors were accounted for, the absence of any scaling effect in the dielectric permittivity as a function of film thickness in these materials would lead to a flexoelectric enhancement for thinner films. Furthermore, we tried measuring pyroelectric current by the chopper-laser modulation method but could not get a stable pyroelectric current.

To summarize, we have studied the thickness dependence of the flexoelectric response in two non-piezoelectric polymers and in silicon dioxide. A two-layer model was employed to explain the results based on electrostatic boundary conditions, where one layer is the material under investigation and the other layer is the native oxide layer, which was separately characterized. We found that the flexoelectric response increased as the film thicknesses decreased, either with or without accounting for the surface layer. There was a significant enhancement in the value of the flexoelectric coefficient with decreasing film thickness for all three materials, with enhancement factors of 76, 17, and 1.3 in terpolymer, polyethylene, and silicon dioxide films, respectively. This fundamental result is important for understanding the role of multilayer devices exhibiting enhanced flexoelectric response in the absence of purely piezoelectric materials.

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