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The Landau-Ginzburg theory of ferroelectricity predicts the intrinsic coercive field for polarization reversal, but the observed extrinsic coercive field is always much smaller as a result of nucleation, dynamic processes not covered by the static theory. We have realized the intrinsic coercive field for the first time, in two-dimensional Langmuir-Blodgett polymer films as thin as 1 nm. The measured coercive field is in good agreement with the theoretical intrinsic value, exhibits the expected dependence on temperature, and does not depend on thickness below 15 nm.

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The experimentally measured value of the ferroelectric coercive field, the magnitude of an external electric field required to reverse the macroscopic polarization, is invariably much smaller than the *intrinsic* value predicted by the Landau-Ginzburg (LG) mean-field theory [1]. The low *extrinsic* coercive field observed in real ferroelectrics is caused by localized nucleation of domains with reversed polarization, which then grow and coalesce by domain wall motion [2,3]. Relatively little energy is required to reverse (switch) polarization in a small nucleation volume around a defect compared to the energy needed for collective polarization reversal of an entire crystal. Reducing the number of nucleation defects does not necessarily increase the coercive field, but generally slows switching [3]. A more effective way to increase the coercive field is to make a particle small enough or a film thin enough to inhibit nucleation [3–6]. Several mechanisms for this finite-size effect have been proposed, including reduction of nucleation volume, space charge near the electrodes, and surface pinning [2,6,7]. Even in the thinnest ferroelectric films obtained previously, the measured extrinsic coercive field is much smaller than the intrinsic value calculated from the LG theory [1], and consequently there has been relatively little published discussion of the intrinsic coercive field. Here we report the first measurements of the intrinsic ferroelectric coercive field, achieved in ultrathin films of a vinylidene fluoride copolymer fabricated by the Langmuir-Blodgett (LB) deposition, films in which nucleation is inhibited by finite-size effects.

The ferroelectric equation of state can be derived from the Gibbs free energy density G, which is appropriate when the independent thermodynamic variables are stress, electric field, and temperature. The free energy density may be described by the LG expansion in the electrical polarization P [1,8]:

$$G = F_0 + \frac{\alpha}{2}P^2 + \frac{\beta}{4}P^4 + \frac{\gamma}{6}P^6 - PE, \qquad (1)$$

where $\alpha = \alpha_0(T - T_0)$, T is the temperature, E is the electric field, and F_0 is the free energy density of the paraelectric phase at zero electric field. The LG free energy coefficients α_0, T_0, β, and γ are assumed independent of temperature. We consider here the first-order ferroelectric where α_0, T_0, and γ are all positive, β is negative. The stable polar state exists at temperatures below the phase transition temperature $T_C = T_0 + \frac{3}{16}\beta^2/\alpha_0\gamma$. The equilibrium polarization in zero field, the spontaneous polarization $P_S = P(E = 0) = \pm\sqrt{-\beta(1 + \sqrt{1 - t})/2\gamma}$, is found at the minimum of the free energy density G and can have two values with opposite directions. Here, $t = 4\alpha\gamma/\beta^2$ is the reduced temperature.

The electric field E is calculated from the minimum in the free energy density G,

$$E = \alpha P + \beta P^3 + \gamma P^5, \qquad (2)$$

and inversion of this relation gives the intrinsic polarization hysteresis function $P(E)$ for the ferroelectric state, at temperatures below T_C, as shown in Fig. 1. The $P(E)$ curve illustrates the bistable nature of the polarization; intrinsic polarization reversal occurs only when the magnitude of the electric field exceeds the intrinsic coercive field E_C (dashed lines) at the turning points in the function $P(E)$. The magnitude of the intrinsic coercive field E_C is readily calculated from the extrema of Eq. (2):

$$E_C = E_{C0} f(t), \qquad (3a)$$

$$E_{C0} = \frac{6}{25}\sqrt{\frac{3}{5}}\,\frac{|\beta|^{5/2}}{\gamma^{3/2}}, \qquad (3b)$$

$$f(t) = \left[\frac{1}{\sqrt{2}}\sqrt{1 + \sqrt{1 - \frac{5}{9}t}}\right]\left[\frac{1}{2}\left(1 + \sqrt{1 - \frac{5}{9}t} - \frac{5}{3}t\right)\right]. \qquad (3c)$$

The magnitude of the intrinsic coercive field at temperature T_0 is E_{C0}, about 1/10th of the depolarization field, P_S/(dielectric permittivity), the electric field in the absence of free charge.

Ferroelectric polymers based on vinylidene fluoride (PVDF) and its copolymers with trifluoroethylene and tetrafluoroethylene, P(VDF-TrFE) and

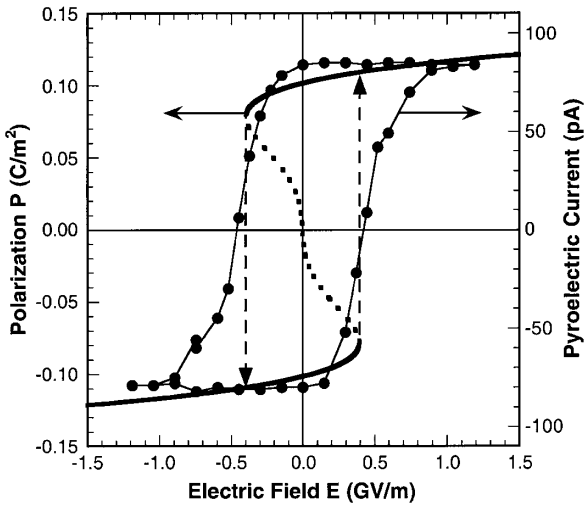

FIG. 1. The theoretical polarization $P(E)$ at 25 °C (thick-solid line) of P(VDF-TrFE 70:30) calculated from the LG expression [Eq. (3)] and the hysteresis in the pyroelectric response at 25 °C (circles) in a 30-ML LB film of P(VDF-TrFE 70:30). The solid lines in the $P(E)$ response represent stable or metastable minima in the free energy density [Eq. (1)], but the dotted line joining them represents an unstable maximum.

P(VDF-TeFE), have been a fertile field for the study of ferroelectricity for over twenty years [9,10]. The ferroelectric phase of P(VDF-TrFE) consists of all-trans—$(CH_2 - CF_2)_x - (CH_2 - CHF)_{1-x}$—chains arranged in parallel rows in a quasihexagonal crystalline packing. Studies of ferroelectricity in polymers have previously been made on polymorphous films formed by solvent spinning or casting, films which contain incompletely oriented microcrystals embedded in an amorphous phase [10]. The polymorphous films have shown strong finite-size effects with the highest coercive fields of any ferroelectric, up to 100 MV/m [11], about $\frac{1}{5}$ of the expected intrinsic coercive field, showing that it might be possible to reach the intrinsic coercive field in a suitably thin sample. The polymorphous films, like all other ferroelectric materials studied to date, did not exhibit a coercive field as large as the intrinsic coercive field, because nucleation could not be completely inhibited.

In 1995 we succeeded in making highly crystalline ferroelectric copolymer films of P(VDF-TrFE) as thin as 0.5 nm (one monolayer) by LB deposition [12,13]. These films are highly crystalline and oriented with the polarization axis perpendicular to the film as confirmed by scanning tunneling microscopy [13,14], x-ray diffraction [15], and neutron diffraction [16]. Dielectric measurements confirm polarization reversal [13], and a first-order paraelectric-ferroelectric phase transition at $T_C = 80$ °C [12,14]. They also exhibit a double hysteresis above T_C, field-induced increase in the transition temperature and a critical point [17], encouraging confirmation of the universal applicability of the theory of first-order phase transitions represented by Eq. (1). These films permitted us to demonstrate for the first time that bulk ferroelectricity can persist in two dimensions [14], and to discover a distinct surface phase transition [14]. Here we report the first study of the intrinsic ferroelectric coercive field made possible by the outstanding crystallinity and nanometer thickness of the LB films of P(VDF-TrFE).

The films for the present study consisted of 2 to 30 monolayers (ML) of the 70% vinylidene fluoride copolymer, P(VDF-TrFE 70:30), deposited by horizontal LB deposition on aluminum-coated glass substrates with evaporated aluminum top electrodes, as detailed elsewhere [12,18]. Potentials were applied across the film thickness. All films showed the first-order phase transition near 80 °C and repeatable polarization hysteresis loops similar to the example in Fig. 1. The time of switching varied from 1 to 10 s, so hysteresis loops were recorded by quasistatic pyroelectric [19,20] and capacitance [17] methods. The remanent polarization hysteresis loop measured by the Chynoweth pyroelectric method [19] at 25 °C on a 30-ML is shown in Fig. 1, along with the theoretical curve for $P(E)$ calculated from Eq. (2) [21]. The agreement between the theoretical and experimental hysteresis loops, though very good, is insufficient evidence that the intrinsic coercive field has indeed been measured, because there is some uncertainty in the precise value of the measured coercive field and because of uncertainties in the values of the LG coefficients used to calculate the theoretical value [21].

A more stringent test of the intrinsic nature of switching is the dependence of the measured coercive field on temperature, according to the definite theoretical prediction of Eq. (3). The temperature dependence of the coercive field in a 20-ML LB film of P(VDF-TrFE 70:30) was determined using the "butterfly" technique, where the coercive field is assigned at the capacitance peaks that appear during a slow sweep of the hysteresis loop [17]. The results shown in Fig. 2 demonstrate excellent agreement with the prediction of Eq. (3). The solid line is a fit to

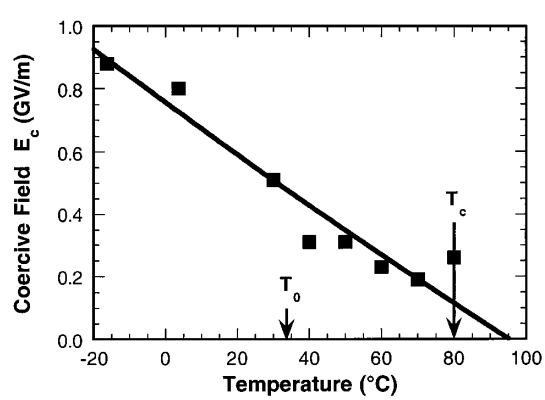

FIG. 2. The intrinsic coercive field of a 20-ML LB film of P(VDF-TrFE 70:30). The solid line is the LG expression [Eq. (3)] calculated with only one adjustable parameter, the value of the coercive field E_{C0} at the temperature $T_0 = 33.7$ °C.

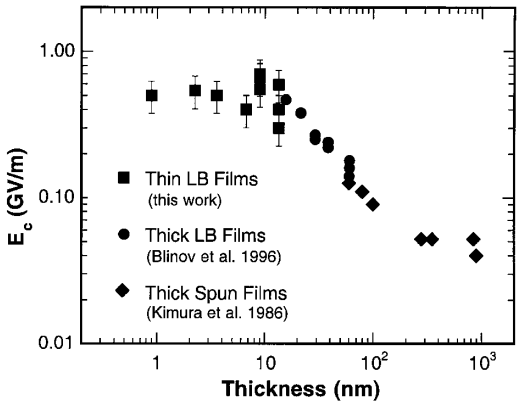

FIG. 3. The finite-size effect for the coercive field E_C in P(VDF-TrFE) over three decades in thickness, from 1 nm to 1 μm. The diamonds are data from P(VDF-TrFE 65:35) films made by solvent spinning [11]. The circles and squares are data from P(VDF-TrFE 70:30) films made by LB deposition reported previously [23] (circles) and for the first time in this study (squares).

Eq. (3) with only one fitting parameter, the coercive field at T_0, $E_{C0} = 0.48 \pm 0.1$ GV/m. This is in good agreement with the value $E_{C0} = 0.35 \pm 0.1$ GV/m calculated from the LG coefficients obtained from measurements of the P(VDF-TrFE 70:30) LB films [21] and with the value $E_{C0} = 0.55$ GV/m calculated from the LG coefficients of P(VDF-TrFE 65:35) reported by Furukawa [22].

The final question concerns the transition from the nucleation-limited extrinsic coercive field to the nucleation-independent intrinsic coercive field. A finite-size effect was already apparent in the thinnest ferroelectric copolymer films made by solvent spinning, as reported by Kimura and Ohigashi in 1986 [11]. The data in Fig. 3 taken from that work show a maximum coercive field $E_C \approx 0.1$ GV/m was achieved in a thin (60 nm) spun film, still well below the LG intrinsic coercive field of approximately 0.5 GV/m [22]. More recent studies of the finite-size effect reported by Blinov *et al.* in 1996 extended the thickness range down to 18 nm and determined that the coercive field scaled at the -0.7 power of the thickness [23]. This behavior is consistent with the nucleation mechanism and finite-size scaling; as the films are made thinner, nucleation volume is reduced and becomes energetically less favorable [7,24].

The finite-size scaling ceases for films 30 ML (15 nm) and thinner, as shown in Fig. 3, reaching the intrinsic coercive field of approximately 0.5 GV/m (at 25 °C). This indicates that polarization reversal is no longer initiated by nucleation, but depends only on the intrinsic properties of the ferroelectric state represented by Eq. (1). It also shows that the critical size for nucleation is approximately 15 nm. The absence of the finite-size effect on the bulk ferroelectric state in copolymer films 30 ML (15 nm) and thinner was previously shown in the constancy of the values of the dielectric constant, polarization, and the phase transition temperature [14].

In summary, we have for the first time measured the intrinsic ferroelectric coercive field, found in ultrathin LB films of the copolymer P(VDF-TrFE 70:30). The intrinsic nature of the coercive field is demonstrated by three key tests: (i) The magnitude of the coercive field is in good quantitative agreement with the theoretical prediction based on independent measurements of the LG coefficients; (ii) the temperature dependence is in excellent agreement with the theoretical prediction; (iii) the coercive field is independent of sample thickness in the range 1–15 nm. The results further promote the utility of the Landau theory of phase transitions as applied to ferroelectricity, where the basic free energy expansion [Eq. (1)] unifies the dielectric properties, the nature of the phase transition, and the polarization bistability (switching). The Landau theory is an equilibrium framework and does not address dynamics; the detailed mechanism of switching at the intrinsic coercive field in ferroelectric polymers remains unknown.

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