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Critical point in ferroelectric Langmuir-Blodgett polymer films

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The ferroelectric critical point has been found in a ferroelectric polymer by exploring the influence of the electric field on the paraelectric-ferroelectric phase transition. Dielectric and pyroelectric measurements on 30-monolayer-thick films of the crystalline copolymer poly(vinylidene fluoride-trifluoroethylene) grown by Langmuir-Blodgett deposition show a single hysteresis loop below the zero-field phase transition temperature $T_{c0} = 80 \pm 10$ °C, double hysteresis loops between T_{c0} , and the critical temperature $T_{cr} = 145 \pm 5$ °C, and no hysteresis above T_{cr} where the critical electric field is $E_{cr} = 0.93 \pm 0.1 \times 10^9$ V/m. [S0163-1829(98)08801-8]

Ferroelectricity has many features analogous to ferromagnetism including the appearance of spontaneous electric polarization in zero electric field at temperatures below zero-field Curie point T_{c0} , polarization hysteresis and reversal (switching), disappearance of the spontaneous polarization above the T_{c0} , and a shift of the phase transition temperature $T_c(E)$ with applied electric field.¹ Ferroelectricity was first established in crystalline polymers like poly-(vinylidene fluoride) (PVDF),² years after practical applications of piezoelectricity³ and pyroelectricity⁴ were recognized and realized commercially.⁵ These and other ferroelectric polymers were fabricated by casting or by solvent spin coating,⁵ methods that yield incompletely oriented polycrystalline polydomain films with a significant fraction of amorphous material.⁶ Ferroelectric polymers exhibit other properties characteristic of ferroelectric and noncentrosymmetric materials including bulk photovoltaic (photogalvanic) currents,⁷ electro-optic modulation,⁸ second harmonic generation,⁴ and possible photorefractive effects.⁹

A first-order ferroelectric phase transition has a critical point (E_{cr}, T_{cr}) in the electric-field-temperature (E - T) phase diagram as was shown by Devonshire¹⁰ using the Landau mean field theory of phase transitions and was observed by Merz in barium titanate.¹¹ The equilibrium ferroelectric-paraelectric phase transition temperature $T_c(E)$ is raised above the zero-field Curie temperature T_{c0} by application of an external electric field, but above the critical temperature T_{cr} the ferroelectric phase can no longer be sustained even at very high applied field. There are three important temperature ranges in the first-order ferroelectric phase transition. (1) Below the zero-field phase-transition temperature T_{c0} the ferroelectric polarization P exhibits a single ferroelectric hysteresis loop versus electric field E . (2) Between T_{c0} and T_{cr} the application of an electric field causes ferroelectricity to reappear along with double hysteresis. (3) Above T_{cr} hysteresis vanishes completely at all values of the electric field E ; the ferroelectric state is no longer stable. The shift of T_c with applied field, the observation of double hysteresis, and the existence of a critical point are perhaps the most striking

features of the first-order phase transition in ferroelectrics. We report here observations of these three features in a crystalline ferroelectric polymer, ultrathin films of P(VDF-TrFE 70:30), a copolymer of 70 mol. % vinylidene fluoride (VDF), and 30 mol. % trifluoroethylene (TrFE), grown by Langmuir-Blodgett (LB) deposition.¹²

The presence of a first-order ferroelectric phase transition in polymers was established by observation of thermal hysteresis of the dielectric constant¹³ and by the spontaneous polarization jump at T_{c0} .¹⁴ Ferroelectric polymers have also shown clear polarization reversal (switching) following application of a sufficiently large electric field opposite to the polarization direction.⁶ In addition, the shift of the Curie point with applied field was demonstrated along with indications of the onset of double hysteresis.¹⁵ The limited quality of the cast and spun films has been a major impediment to the precise measurement of ferroelectric properties. Ferroelectric P(VDF-TrFE) crystallizes in a orthorhombic $mm2$ structure with all-*trans*- $[(-\text{CH}_2\text{-CF}_2)_x(-\text{CH}_2\text{-CHF-})_{1-x}]_n$ -chains in parallel rows arranged in a quasihexagonal close packing.¹⁶ The net dipole moment, directed from the electronegative fluorine atoms to the electropositive hydrogen atoms, is perpendicular to the all-*trans* chains; ferroelectric switching coincides with rotation of the polar groups around the molecular chain axis. Both PVDF and P(VDF-TrFE) are proper ferroelectrics where the spontaneous polarization (about 0.1 C/m^2 at room temperature⁶) is the order parameter of the phase transition.

High-quality thin films of ferroelectric P(VDF-TrFE 70:30) have recently been fabricated by our group at the Institute of Crystallography using the Langmuir-Blodgett monolayer transfer technique, permitting precise control of the film nanostructure.¹² To date, these ferroelectric Langmuir-Blodgett polymer (FLP) films have shown strong thermal hysteresis of the dielectric constant,^{12,17} complete ferroelectric switching,¹⁷ and an increase of the coercive field with decreasing thickness.¹⁸ The FLP films exhibit a novel conductance switching controlled by the polarization direction, with potential application to nonvolatile computer memories.¹⁷ The structure and uniformity of the FLP films

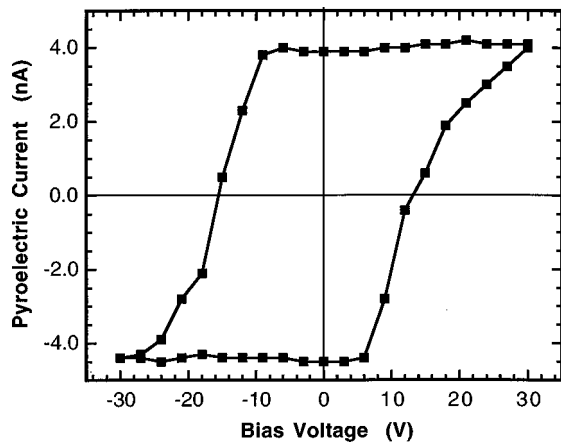


FIG. 1. Ferroelectric polarization reversal (switching) by an external electric field as probed by the pyroelectric response at $T=20^\circ\text{C}$ at zero bias after steady application of a constant bias voltage in a 30-monolayer FLP film of P(VDF-TrFE 70:30).

were checked by means of atomic-resolution tunneling microscopy, revealing high crystallinity and crystal orientation and close parallel packing of the all-*trans* polymer chains on the top layer of the films.¹⁹ The FLP films have an unmistakable first-order ferroelectric phase transition. This is demonstrated by thermal hysteresis of the dielectric constant,^{12,17} by polarization switching¹⁷ in films down to five monolayers in thickness,¹⁹ and by the observation of double hysteresis and the ferroelectric critical point to be described below. The LB technique has also been applied with success to prepare high-quality films²⁰ of polymer liquid crystals which show ferroelectric switching behavior in films as thin as six monolayers (ML).²¹

The 30-ML FLP films for the present study were prepared from a solution of the copolymer P(VDF-TrFE) (70:30) in dimethyl-sulfoxide at 0.01% weight concentration.¹² The copolymer was dispersed on a water subphase and the pressure-area isotherms measured to identify the conditions forming closest packing of a film of monolayer thickness. At room temperature, these conditions were satisfied at 5 mN/m surface pressure and 5.7 \AA^2 area per formula unit.¹² The films were transferred to aluminum-coated glass substrates one layer at a time by horizontal dipping in the LB trough, drying with warm nitrogen gas between layers. Aluminum electrodes were evaporated on the top of the films to form a sandwich structure ready for electrical measurements. Film preparation is described in greater detail elsewhere.^{12,22} The capacitance was measured by a Hewlett-Packard model 4192A impedance analyzer at 1 kHz frequency. The pyroelectric response was measured using the Chynoweth method²³ at zero-bias voltage, using a lock-in amplifier as the sample was periodically heated by an 80-mW laser beam (514.5 nm wavelength) chopped at 2 kHz.

The polarization hysteresis loop for a 30-ML film recorded is shown in Fig. 1. (The pyroelectric response is proportional to the net polarization.) The coercive field of $1.0 \pm 0.1 \times 10^9 \text{ V/m}$ is more than 20 times larger than the coercive field of much thicker films made by solvent spinning,⁶ confirming the general trend of increasing coercive field with decreasing film thickness.^{18,24}

Figure 2 shows the strong thermal hysteresis of the dielec-

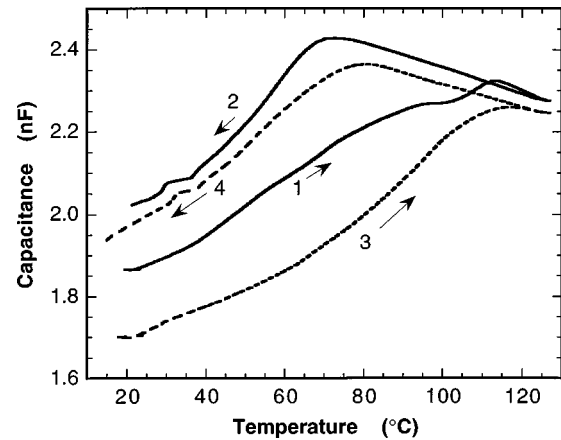


FIG. 2. Temperature dependence of the capacitance at zero-bias voltage (curves 1 and 2) and under bias voltage of 5 V (curves 3 and 4) in a 30-monolayer FLP film of P(VDF-TrFE 70:30).

tric constant near the zero-field ferroelectric phase-transition temperature T_{c0} .^{12,17} The sample was heated and cooled with a constant rate of $2.8^\circ\text{C}/\text{min}$. The zero-field peaks in the capacitance are at 113 and 72°C on heating and cooling, respectively. The application of an electric field shifts the phase-transition temperature to higher temperature $T_c(E)$ as shown in Fig. 2, curves 3 and 4. The thermal hysteresis and the shift of T_c with electric field are clear indications of the first-order nature of the ferroelectric-paraelectric transition. Reports of a shift in T_c caused by applied electric field in any ferroelectric were first made by Merz in 1953,¹¹ and such an observation in a ferroelectric polymer was made independently by two groups in 1983.^{13,15}

The “butterfly” capacitance $C(E) \propto dD/dE$ curves recorded with a 2-mHz symmetric linear ramp shown in Fig. 3 demonstrate double hysteresis and identify the ferroelectric critical point in a ferroelectric polymer, conclusive evidence that this is a first-order ferroelectric phase transition. The peaks in capacitance occur at the switching transitions (the near-vertical sides of the hysteresis loop in Fig. 1) where the spontaneous polarization reverses direction, but at consistently smaller fields than the hysteresis loop transition because the dielectric response probes the fast dipolar response that is most evident at the beginning of switching, not at the point where the polarization crosses the horizontal axis. Below the zero-field ferroelectric phase-transition temperature of $T_{c0} = 80 \pm 10^\circ\text{C}$ [Figs. 3(a) and 3(b)], there is one hysteresis loop centered at zero field, giving two peaks in capacitance at the coercive field $E_c(T)$, one on each side of zero bias. Above the zero-field ferroelectric phase transition T_{c0} , but below the critical temperature T_{cr} [Figs. 3(c) and 3(d)] there are four peaks in the capacitance due to two hysteresis loops arranged antisymmetrically about zero bias.^{1,11} The dual hysteresis loops occur because the sample is not ferroelectric at zero field, but the ferroelectric state is induced at sufficiently high field. There is no hysteresis observed at 150°C [Fig. 3(e)] and therefore the sample is at or above the ferroelectric critical temperature T_{cr} . The sample showed no evidence of melting or degradation after repeat cycling to 155°C . Weak shoulders were observed in the capacitance versus field hysteresis of P(VDF-TrFE) spun films by Furukawa *et al.*,¹⁵ but the lack of four clear peaks like those in

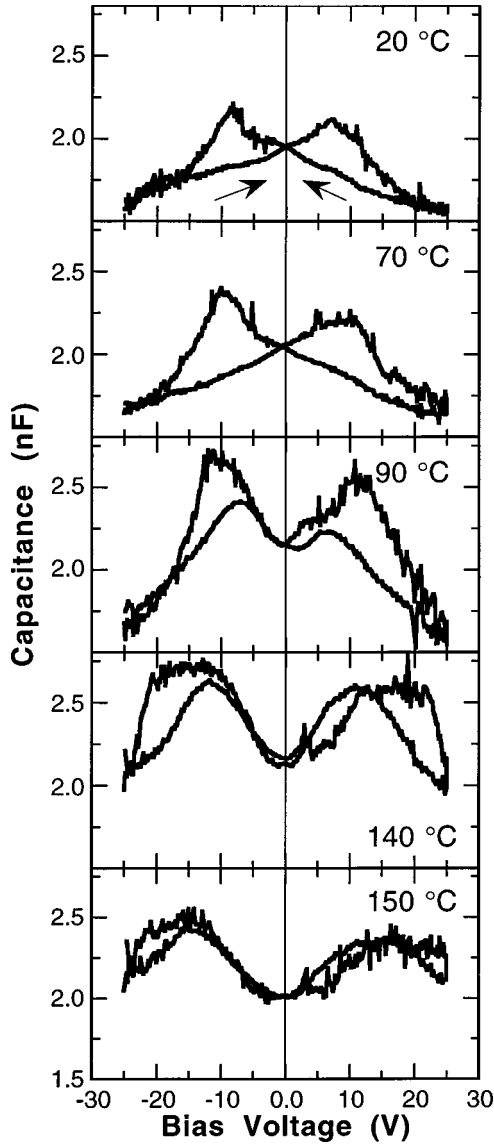


FIG. 3. “Butterfly” capacitance hysteresis curves at temperatures spanning both the Curie point $T_c=80\pm 10$ °C and the critical point $T_{cr}=145\pm 5$ °C. The field was ramped at 0.2 V/s during measurement.

Fig. 3 and the possibility of contributions from dielectric loss shed doubt on the suggestion that those data were evidence of ferroelectric double hysteresis. The shift of T_c with electric field and the presence of a critical point have been clearly demonstrated in BaTiO_3 (Ref. 11) and KDP (KH_2PO_4),^{25,26} both proper ferroelectrics with first-order phase transitions, and also in a ferroelectric liquid crystal,²⁷ a first-order improper ferroelectric in which the order parameter is molecular tilt, not electric polarization.

The “butterfly” curves in Fig. 3 permit us to construct the E - T phase diagram at atmospheric pressure for the 30-monolayer FLP film (Fig. 4). The electric field at the boundary between the ferroelectric and paraelectric phases is the center of the hysteresis loop, or the midpoint between the pairs of peaks at both positive and negative bias, and is plotted against temperature in Fig. 4. Since we observed double

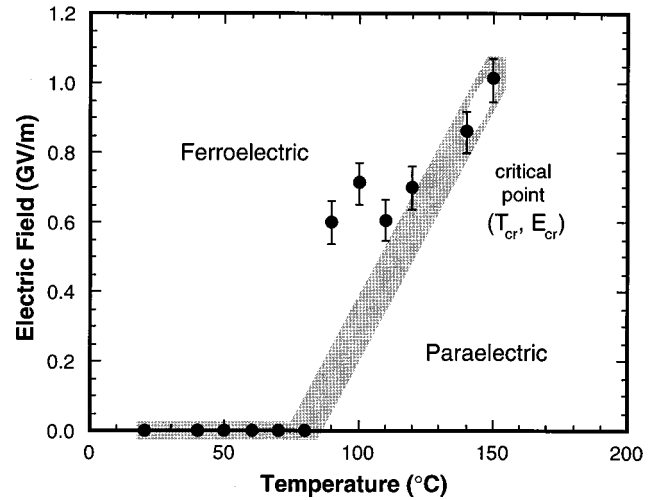


FIG. 4. Ferroelectric E - T phase diagram of a 30-monolayer FLP film of P(VDF-TrFE 70:30) at atmospheric pressure showing the zero-field phase transition temperature $T_c=80\pm 10$ °C and the ferroelectric critical point $T_{cr}=145\pm 5$ °C. The data points were derived from hysteresis curves like those in Fig. 3.

hysteresis at 140 °C and not at 150 °C, the critical point is contained within the ellipse centered at $T_{cr}\approx 145\pm 5$ °C and $E_{cr}=0.93\pm 0.1\times 10^9$ in Fig. 4. Table I gives values of dT_c/dE , E_{cr} , and T_{cr} , for ultrathin FLP and thick spun films of copolymer P(VDF-TrFE) (70:30 mol. %) as well as BaTiO_3 , KDP, and a ferroelectric liquid crystal. As Table I shows, ferroelectric polymers have a relatively large span of the field-induced phase transition temperatures $T_{cr}-T_{c0}=65\pm 11$ °C as compared to other ferroelectric materials like BaTiO_3 ,^{1,11} KDP,^{25,26} and ferroelectric liquid crystals,²⁷ because of the relatively weak van der Waals interaction in the polymers.⁶

In conclusion, we have demonstrated three important features of the first-order phase transition in a ferroelectric polymer: the shift of the Curie point with applied electric field, double hysteresis above the Curie point, and the existence of the critical point (T_{cr}, E_{cr}) in the E - T phase diagram. These observations were made possible by the high quality and

TABLE I. Ferroelectric phase transition parameters for P(VDF-TrFE 70:30) films made by Langmuir-Blodgett deposition and solvent spinning, potassium dihydrogen phosphate (KDP), barium titanate (BaTiO_3), and a ferroelectric liquid crystal (FLC).

	T_{c0} (°C)	T_{cr} (°C)	E_{cr} (V/m)	dT_c/dE (m °C/V)
LB polymer	80 ± 10	145 ± 5	$0.93\pm 0.1\times 10^9$	$7.0\pm 2\times 10^{-8}$
Spun polymer ^a	102	no data	no data	12×10^{-8}
BaTiO_3 ^b	108	116	0.6×10^6	6.5×10^{-4}
DKDP ^c	-61	-60	0.83×10^6	1.25×10^{-6}
FLC ^d	55.0	55.8	5.0×10^6	1.6×10^{-7}

^aReference 6.

^bReference 11.

^cReferences 25 and 26.

^dReference 27.

uniformity of the films of P(VDF-TrFE 70:30) made by Langmuir-Blodgett deposition. The FLP films offer an exciting new medium in which to study the ferroelectric phase transition in great detail and, in particular, the ferroelectric state in a reduced-dimension system.

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