

**Ducharme and Fridkin Reply:** We have reviewed carefully the Comment [1] by Bratkovsky and Levanyuk (BL) concerning our recent Letter [2] reporting measurements of the intrinsic coercive field in ferroelectric Langmuier-Blodgett films of vinylidene fluoride-trifluoroethylene copolymers. Their thesis is that the paraelectric-ferroelectric phase transition in PVDF and its copolymers is of the strong first-order type, and therefore cannot be modeled with the Landau-Ginzburg-Devonshire (LGD) formalism [3], but the results of many detailed studies over the past 30 years confirm the LGD predictions in exquisite detail. There is insufficient space here to review this evidence, but the interested reader can begin with recent reviews [4]. BL cite several apparent incongruities in the data, but each fails their thesis on close scrutiny. The orthorhombic  $mm2$  ferroelectric phase is indeed a subgroup of the symmetries favored in the literature for the paraelectric phase, orthorhombic  $mmm$  or hexagonal  $6/mmm$ , though other structures have been proposed. Further study is necessary before the correct structure of the paraelectric phase can be confidently assigned. BL misapply the observed doubling of the 2D electronic Brillouin zone across a distinct *surface* phase transition [5] to their arguments concerning the structure change across the *bulk* ferroelectric-paraelectric transition. The ferroelectric phase already has a two monomer in-chain period due to the well-known  $7^\circ$  dihedral tilt instability [4]. BL also misinterpret the significance of the disorder evident in one STM image (Fig. 1 of Ref. [5]) of a bilayer that was not annealed. Proper annealing is critical for obtaining good crystallinity and stable ferroelectric properties. Well-annealed LB films are too dense for this amount of disorder and are fully crystalline [6], not a “mixture of amorphous and crystalline phases.” The presence of amorphous material in thick solvent-cast films certainly makes some measurements difficult, but as sample crystallinity has improved over the years, so has the quantitative agreement between the data and the predictions of LGD. BL assert that the observed strain at the phase transition is unreasonably large compared to other ferroelectrics, but precise measurements of the electrostriction in the paraelectric phase and piezoelectricity in the ferroelectric phase accurately account for the spontaneous strain [4,7]. Quantitative comparison of the ferroelectric properties of polymers with “usual ferroelectrics” such as the perovskites is clearly inadequate because the atomic interactions are fundamentally different. This is not to say that the LGD nature of ferroelectricity in the copolymers is absolutely proven, only that the preponderance of the evidence is strongly in favor of this hypothesis.

The existence of the intrinsic coercive field does not depend on the nature or even the existence of the phase transition because the defining characteristic of a ferroelectric

is the existence of a spontaneous polarization that can be reversed by an external electric field. The maximum value of the intrinsic coercive field can be estimated directly from electrostatic energy considerations and is about  $1/2$  the depolarization field [3,8], in agreement with the data reported in [2]. The microscopic mechanism underlying the LGD phenomenology can be obtained from a two-dimensional Ising approach [3,9], and is not restricted to three dimensions. Intrinsic switching in the films is very slow, 10 sec or more, which is indeed puzzling, but hardly “astronomical.” The polarization relaxation time is relevant only for small perturbations, not for switching. The films can also be made to switch in about  $1 \mu\text{s}$ , but only at much lower extrinsic coercive fields [6]. We did not claim that the films have neither domains nor nucleation sites, only that nucleation and domain dynamics are not limiting the coercive field in the films of 15 nm or thinner. The intrinsic and extrinsic switching processes are controlled by fundamentally different interactions, and therefore cannot be compared.

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