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**Novel Polymer Ferroelectric Behavior via Crystal Isomorphism and Nanoconfinement Effect<sup>1</sup>**

LEI ZHU, Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH 44106-7202

Despite comprehensive understanding of novel ferroelectric [i.e., relaxor ferroelectric (RFE) and antiferroelectric (AFE)] behaviors for ceramics, RFE and double hysteresis loop (DHL) behaviors have just emerged for ferroelectric crystalline polymers since the past 15 years. A number of applications such as electrostriction, electric energy storage, and electrocaloric cooling have been realized by utilizing these novel ferroelectric properties. However, the fundamental understanding is still lacking. In this invited talk, we intend to unravel the basic physics behind these novel ferroelectric behaviors via systematic studies of poly(vinylidene fluoride-co-trifluoroethylene) [P(VDF-TrFE)]-based terpolymers and e-beam irradiated copolymers. It is found that both crystal internal structure and crystal-amorphous interaction are important for achieving the RFE and DHL behaviors. For the crystal internal structure effect, friction-free dipole switching and nanodomain formation by pinning the polymer chains are essential, and they can be achieved via the mechanism of crystal repeating unit isomorphism. Physical pinning [e.g., in P(VDF-TrFE)-based terpolymers] induces a reversible RFE $\leftrightarrow$ FE phase transition and thus the DHL behavior, whereas chemical pinning [e.g., in e-beam irradiated P(VDF-TrFE)] results in the RFE behavior. Finally, the crystal-amorphous interaction (or the nanoconfinement effect) results in a competition between the polarization and depolarization local fields. When the depolarization field becomes stronger than the polarization field, a DHL behavior can also be observed. Obviously, the physics is different from ceramics and can be largely attributed to the long chain nature of semicrystalline ferroelectric polymers. This understanding will help us design new ferroelectric polymers with improved electroactive properties and/or better applications.

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