Ferroelectric behavior in the high temperature paraelectric phase in a poly(vinylidene fluoride-*co*-trifluoroethylene) random copolymer

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ABSTRACT

In this report, ferroelectric behaviors were investigated as a function of temperature and poling frequency for a uniaxially stretched poly(vinylidene fluoride-*co*-trifluoroethylene) 50/50 (mol./mol.) film. A variety of ferroelectric behaviors, including normal ferroelectric, antiferroelectric-like, and paraelectric behaviors, were observed by varying temperature, poling frequency, and poling electric field. Especially, the ferroelectric (FE) to paraelectric (PE) transition and ferroelectric behaviors of the high temperature PE phase were studied in detail by electric displacement-electric field loop measurements. At a high poling frequency (e.g., 1000 Hz) and 100 °C (above the Curie temperature at 64 °C), a paraelectric behavior was obtained due to the nucleation of electric field-induced FE nanodomains inside the PE phase matrix. These FE nanodomains were highly reversible and they quickly depolarized upon removal of the poling field. At an intermediate poling frequency (e.g., 10 Hz) and 100 °C, an antiferroelectric-like behavior was observed, which could be attributed to the competition between depolarization and polarization fields upon reverse poling. Finally, at a low poling frequency (e.g., 1 Hz) and 100 °C, a normal ferroelectric behavior with rectangular hysteresis loops was seen because the small, reversible FE domains had enough time to grow into large irreversible ones. The presence of electric field-induced FE domains in the PE matrix was proved by field dependent Fourier transform infrared study. On the basis of this study, understanding of the paraelectric behavior in polar crystalline polymers will help us design new materials to meet the requirements for high energy density and low loss dielectric applications.

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1. Introduction

Ferroelectric polymers, such as poly(vinylidene fluoride) (PVDF) and its random copolymers, have received significant research interest in the past several decades because of their ferroelectric, piezoelectric, and pyroelectric properties, which are useful for numerous practical applications [1,2]. Similar to ferromagnetic materials, ferroelectric polymers exhibit spontaneous polarization, i.e., a net electric dipole moment in the absence of an external electric field. This spontaneous polarization can be reversibly switched by an external field, resulting in a normal electric displacement-electric field (D–E) hysteresis loop (see Scheme 1A). This rectangular-shaped D–E loop enables applications such as non-volatile capacitor- and transistor-type ferroelectric memories

(FeRAMs) [3–7]. The advantages of these non-volatile FeRAMs include fast read/write speed, minimum energy consumption, and long cycle life. P(VDF-*co*-trifluoroethylene) [P(VDF-TrFE)], with a VDF content of 70–75 mol.%, is usually chosen for polymer FeRAMs because of its large polarization ($\sim$0.1 C/m^2), excellent polarization stability, fast switching time (e.g., 20 ns at 840 MV/m for 20 nm thin film [8]), and easy processing [3,7]. In addition, all ferroelectric polymers also possess piezoelectric properties, which have been used for transducers [2,9], piezo-actuators [2,10,11] and mechanical energy harvesting devices [12–14]. For these applications, high piezoelectric responses benefit from a large remanent polarization (P_r), and thus a normal ferroelectric behavior is required.

Not all applications, however, require normal ferroelectricity. There are quite a few applications requiring not rectangular-shaped but slim hysteresis loops with a minimum P_r. In our recent report [15], it is indicated that both relaxor ferroelectric and antiferroelectric-like behaviors show narrow hysteresis loops with a minimum P_r (see Scheme 1B and C). First, for electrostriction application, a large deformation at high fields but a minimum

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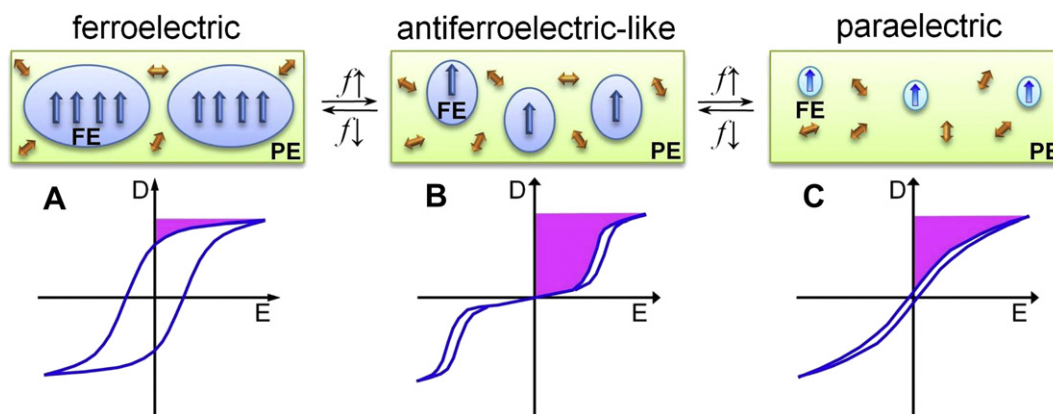
Scheme 1. Schematic illustration of (A) normal ferroelectric, (B) antiferroelectric-like, and (C) paraelectric behaviors of the high temperature PE phase in P(VDF-TrFE) under different poling frequencies (*f*).

deformation at a zero field is required. Therefore, relaxor ferroelectric rather than normal ferroelectric polymers exhibit extraordinarily high electrostrictive constants [16–20]. Second, all ferroelectric polymers are also pyroelectric. Direct applications include electricity generation from heat [2,21–23] and solid-state refrigeration (or the electrocaloric effect) [24–26]. These applications require slim hysteresis loops and large difference in the D/E slope at different temperatures. Around the ferroelectric-to-paraelectric (i.e., the Curie) transition, the hysteresis loop changes its shape dramatically. Therefore, at the Curie temperature (T_C), high energy conversion and electrocaloric coefficients can be obtained. Third, for electric energy storage applications such as dielectric film capacitors, a high spontaneous polarization and a minimum P_r are also required [27,28]. Obviously, relaxor ferroelectric and antiferroelectric-like loops release more stored energy densities than the normal ferroelectric behavior and thus have high discharge efficiencies and a minimum energy loss [15,27,29].

To enable the above applications, numerous experimental and theoretical efforts have been dedicated to achieve relaxor ferroelectric and antiferroelectric-like behaviors in ferroelectric polymers. The antiferroelectric-like (or strictly speaking, it should be ferrielectric [30,31]) behavior with double hysteresis loops (DHLs) was first reported for β-PVDF at temperatures below −60 °C [32] and P(VDF-TrFE) with the TrFE content more than 50 mol.% [33–35]. The DHL consisted of a dipole depolarization step at low fields and a polarization reversal step at high fields, and it only appeared in the first several cycles and eventually transformed into a single hysteresis loop upon repeated cycling. Therefore, this behavior was attributed to imperfect P(VDF-TrFE) crystals cooled from the melt with coexistence of both FE and PE phases [35]. Later, it was attributed to the nonpolar "antiferroelectric-like phase" in P(VDF-TrFE) [7,36–38]. Recently, we explained the antiferroelectric-like behavior as a more or less universal phenomenon for semicrystalline ferroelectric polymers, rather than for specific samples and/or specific phases [15,29]. According to this explanation, DHL would take place as long as $D = (Q + P_{comp}) < P_{in}$, where Q is the polarization in vacuum ($Q = \varepsilon_0 E$ with ε_0 being the vacuum permittivity), P_{comp} the compensation polarization in the amorphous phase at the amorphous/crystal interface, and P_{in} the induced polarization inside the ferroelectric crystal at the crystal/amorphous interface. In other words, when the local depolarization field ($E_{depol} = P_{in}/\varepsilon_0$) became higher than the local polarization field ($E_{pol} = D/\varepsilon_0$) during discharging, part of the aligned dipoles or domains in the poled ferroelectric crystal would depolarize and revert back to their original direction, resulting in a minimum P_r at zero electric field.

This explanation was further tested in a P(VDF-TrFE-CTFE)-*g*-PS (CTFE stands for chlorotrifluoroethylene) graft copolymer, where the ferroelectric PVDF crystal was confined by a thin layer of low polarizability PS to reduce the P_{comp} at the amorphous/crystal interface [15]. Consequently, a nearly perfect antiferroelectric-like behavior with a nearly zero remanent polarization at $E = 0$ was achieved at a poling field of 150 MV/m.

Relaxor ferroelectric behavior in polymers was first reported in electron beam (e-beam) irradiated P(VDF-TrFE) with a broad Curie relaxation and a substantially decreased T_C [16–18]. With gradually increasing the e-beam dose, structural changes happened in both amorphous and crystalline phases. In the amorphous phase, primarily crosslinking took place with the formation of a certain amount (2 mol.%) of short side groups such as >CH-CF$_3$ in the main chain [39,40]. From an electron diffraction study on P(VDF-TrFE) single crystals, the low temperature ferroelectric (FE) phase gradually transformed into the paraelectric (PE) phase upon irradiation, and eventually crystallinity was lost at high doses [41,42]. However, no irradiation-induced phase transformation could be seen for neat PVDF. It was proposed that the enlarged lateral unit cell dimensions of P(VDF-TrFE), as compared to those of PVDF, was responsible for the introduction of structural defects in the crystalline phase upon irradiation [41,42]. These structural defects decreased the size of the ferroelectric or crystalline domains, and thus relaxor ferroelectric behavior was obtained [16–18]. However, questions are still remaining: What are the structural defects in P(VDF-TrFE) crystals and how do they effectively decrease the ferroelectric or crystalline domains? Later, structural defects were purposely introduced into P(VDF-TrFE) by copolymerization with a third bulky comonomer such as chlorofluoroethylene (CFE), chlorodifluoroethylene (CDFE), CTFE, and hexafluoropropylene (HFP) [43–45]. Relaxor ferroelectric behavior was reported in P(VDF-TrFE-CTFE) terpolymers with specific compositions, and high dielectric constants at room temperature were observed [46–48]. Again, questions are remaining for these relaxor ferroelectric terpolymers: How are the bulky comonomers incorporated in P(VDF-TrFE) crystals and how do they decrease the size of ferroelectric or crystalline domains and then induce the relaxor ferroelectric behavior?

To the best of our knowledge, there are few reports on the ferroelectric properties of the PE phase in P(VDF-TrFE) [2]. In this work, we systematically studied the ferroelectric behavior of a P(VDF-TrFE) random copolymer with 50 mol.% VDF as a function of temperature and poling frequency. By increasing the poling frequency from 1 Hz to 1000 Hz in the pure PE phase, normal ferroelectric, antiferroelectric-like, and paraelectric behaviors were observed. On the basis of an electric field dependent Fourier