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Recent advances in ferroelectric polymer thin films for memory applications

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ABSTRACT

An overview of ferroelectric VDF/TrFE copolymer thin films is presented based on our recent work on their phase transition behavior and polarization switching dynamics. These properties originate in the hierarchical structures consisting of monomer dipoles, all-trans conformation, parallel chain packing and crystalline orientation in thin films. Successive loss of intermolecular and intramolecular orders yields multiple phase transitions from a ferroelectric phase to a molten phase via anti-ferroelectric and paraelectric phases. Polarization switching dynamics are shown to depend on a variety of factors not only applied field strength but also electrode, substrate, thickness and wave form of applied field. These results are discussed in relation to their hierarchical structures as well as nonvolatile memory applications.

1. Introduction

Copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) have attracted continuous attention last three decades because of their unique electrical properties comprising ferroelectricity and possible applications for actuators, sensors and nonvolatile memory elements. Their ferroelectricity originates from the molecular dipoles associated with positively charged hydrogen atoms and negatively charged fluorine atoms attached perpendicular to the chain axes. The all-trans conformation of chain molecules and their parallel packing induce an alignment of all molecular dipoles in one direction to produce a large spontaneous polarization [1]. Thin films prepared by spin-coating consist of relatively large crystalline grains in that molecular chain axes are aligned parallel to the film surface. Fig. 1 is a presentation of such hierarchical structures of VDF/TrFE copolymers which constitute the basis of their ferroelectric properties.

In this paper, we present an overview of ferroelectric VDF/TrFE copolymer thin films based on our recent studies with special interests on their phase transition behavior and polarization switching dynamics [2–7]. We first show that these properties markedly depend on the molar ratio of VDF and TrFE monomer units. We then summarize the entire features of multiple transitions among ferroelectric, anti-ferroelectric, paraelectric and molten phases. We finally describe in some details about the ferroelectric switching dynamics observed by using a variety of experimental techniques for well-defined VDF/TrFE copolymer thin films.

2. Experimental

The samples of polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (VDF/TrFE) used were kindly supplied by Koreha and Daikin, Japan. Most of them were dissolved into appropriate solvents and subjected to spin-coating to yield the film samples 20–1000 nm in thickness. Some of them were subjected to annealing to obtain highly crystalline films.

We conducted a variety of dielectric measurements in both linear and nonlinear regimes over a broad time and frequency ranges using the equipments developed in our laboratory. Most typically, they consist of an arbitrary wave generator, a power amplifier, a charge amplifier and data acquisition systems which are controlled by a computer system and yield linear and nonlinear dielectric spectra, D–E and ε–E hysteresis loops and switching transients.

3. Results and discussion

3.1. Composition dependence of ferroelectric characteristics of VDF/TrFE copolymers

Fig. 2 shows the D–E hysteresis loop and dielectric anomaly of the VDF/TrFE copolymers over the entire range of composition [2]. The 75/25 mol% copolymer exhibits a typical square hysteresis loop with a remanent polarization P_r of 100 mC/m^2 and a coercive field E_c of 50 MV/m. As the VDF content decreases, hysteresis tends to disappear after showing a propeller-type loop that is characteristic of anti-ferroelectrics. Dielectric anomaly at a Curie point moves towards the low temperature side with decreasing VDF content and then diminishes as the VDF content becomes smaller than

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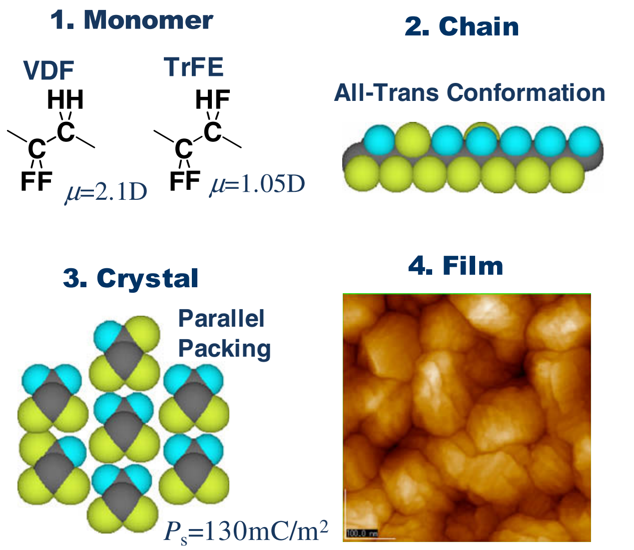

Fig. 1. Monomer, chain, crystal and film structures comprising the hierarchical structure of VDF/TrFE copolymer.

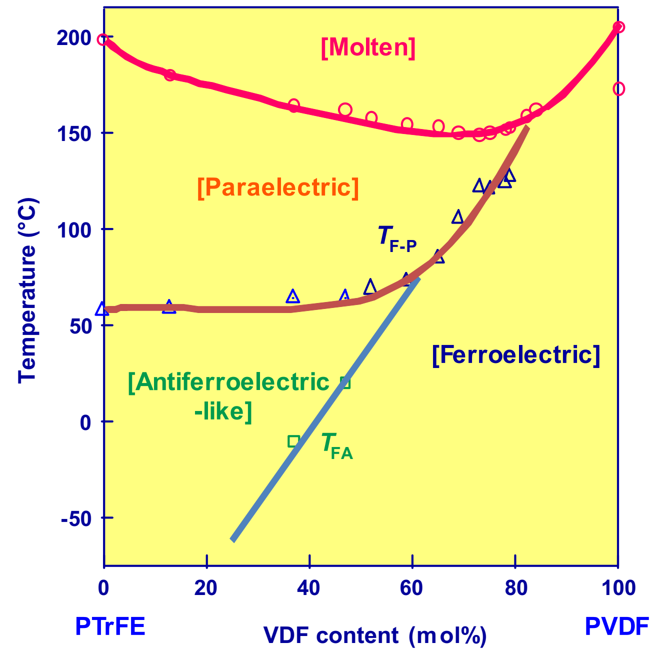

Fig. 3. Phase diagram of VDF/TrFE copolymers.

50%. The copolymers containing 60–80 mol% VDF are most commonly used for electro-mechanical and memory applications.

3.2. Successive phase transitions

PVDF is known to exhibit at least four crystalline polymorphs. Melt-crystallization yields nonpolar form II which is converted into ferroelectric form I by uniaxial drawing. On heating, form I PVDF undergoes a transition directly into molten phase and does not show a paraelectric phase at an atmospheric pressure. An introduction of TrFE into PVDF leads to a relative stabilization of all-trans conformation and induces direct crystallization into ferroelectric phase. However, the resulting all-trans phase is less stable compared to pure PVDF due to expansion of intermolecular distances. This instability causes a transition into an intramolecularly disordered paraelectric phase on heating. Further introduction of TrFE for more than 50 mol% causes an appearance of an anti-ferroelectric-like phase which consists of randomly packed all-trans molecules.

Fig. 3 shows the phase diagram of VDF/TrFE copolymers based on dielectric, thermal and X-ray data taken during heating [3]. The 50/50 copolymer undergoes a ferroelectric–paraelectric transition at a T_{F-P} of 65 °C. As the VDF content is increased to 80 mol%, T_{F-P} increases to reach 150 °C where it coincides with melting point T_M. As the VDF content becomes smaller than 50 mol%, T_{F-P} continues to decrease with decreasing VDF content and a new transition from a ferroelectric phase to an anti-ferroelectric phase appears. As a result, the VDF/TrFE copolymer exhibits four phases, i.e., ferroelectric, anti-ferroelectric, paraelectric and molted, whose structures are illustrated in Fig. 4. The transitions among these phases are strongly dependent on composition and occur as a result of partial loss of intermolecular and intramolecular orders.

3.3. Ferroelectric switching dynamics in MFM capacitor

The time domain measurements of polarization reversal induced by a stepwise electric field provide key information about switching dynamics. Fig. 5 shows the switching transients recently obtained for a 50-nm thick VDF(75)/TrFE(25) copolymer film with

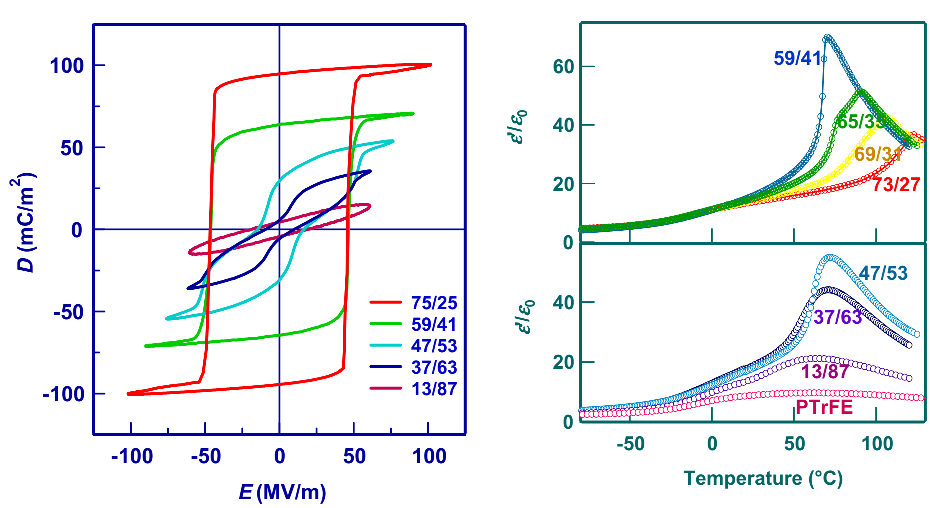

Fig. 2. D–E hysteresis loop and dielectric anomaly of VDF/TrFE copolymers with varying compositions.