

Experimental Evidences for Field Induced Phase Transition of P(VDF/TrFE)(72/28)

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Abstract

P(VDF/TrFE) (VDF 50~80 mole %) has significant applications in the field of nonvolatile ferroelectric polymeric random access memory (FePoRAM) devices since they exhibit stable ferroelectric β -phase at room temperature with spontaneous polarization of the C-F dipoles below their Curie transition temperature (T_c). Many researchers have already reported the molecular structures and dynamics of the ferroelectric (F) crystalline phase and the unique change in chain conformation between polar F phase and non-polar paraelectric (P) phase near their T_c which is dependent on factors such as VDF content and annealing treatment conditions. In this paper, we have investigated the effect of external electric field strength on the $F \rightleftharpoons P$ crystalline phase transition in P(VDF/TrFE)(72/28) random copolymer samples of nanoscale thickness subjected to varying heat treatment conditions. Capacitance (C-T) of 250 nm thick sample measured as a function of heating-cooling under varying external electric field strength exhibited increasing T_c during heating (T_c^\uparrow) and cooling (T_c^\downarrow) under an applied electric field of more than 0.03MV/cm. Applying bias electric field (+1 to -1 MV/cm) for samples kept isothermally at just above their T_c during cooling, we were able to observe the field-induced $P \rightarrow F$ phase transition. With increasing cycles of the applied electric field for sample maintained just above T_c , the bistable C-E hysteresis was observed and the phase change from $P \rightarrow F$ is irreversible even after the electric field is removed. However, for samples kept well above T_c and near T_m (100°C and 120°C respectively) during cooling, the F -phase initially formed through the field-induced phase transition is reversibly transformed to the P -phase when the applied electric field is removed. Drastic changes were observed in both coercive field (E_c) and remnant polarization (P_r) values during heating and cooling near the T_c range due to the $F \rightleftharpoons P$ phase transition and the results are reported in detail here.

Keywords: P(VDF/TrFE); Nonvolatile memory, FePoRAM; Ferroelectric crystalline phase; Paraelectric crystalline phase; Field-induced phase transition.

1. Introduction

The copolymers of vinylidene fluoride-trifluoroethylene (P(VDF/TrFE)) with VDF content of 50~80 mol% are a special class of polymers exhibiting the so-called Curie transition temperature (T_c), where the electro-active ferroelectric (F) crystalline phase with all-*trans* chain conformation is transformed in the solid state to the electro-inactive paraelectric (P) crystalline phase consisting of molecules adopting irregular composition such as the statistical combination of *tg*, *tg'*, *tttg*, *tttg'*, etc [1-5]. Ferroelectric polymers also exhibit strong piezoelectricity and pyroelectricity, suitable for numerous electrical and electronic applications. For the F -phase, the material exhibits nonlinear electrical and mechanical behavior. The electric displacement (D) response to the electric field (E) forms a hysteresis loop and the mechanical strain (ϵ) response to the electric field forms a butterfly loop and strain response to the stress. However, in the P -phase, the material response to electrical and mechanical loads exhibits no hysteresis loops but exhibits a behavior similar to dielectric (non-polar) materials.

Among various ferroelectric polymers, the copolymers of VDF and TrFE have been widely reported for their possible applications to nonvolatile ferroelectric polymeric random access

memory (FePoRAM) devices [6,7]. Previous studies have used P(VDF/TrFE) films of several microns (~9 μ m or thicker) to study the ferroelectric characteristics [1,3] and the reduction of polymeric film thickness to nanoscale level is essential to fabricate FePoRAM devices which must be operated at below 5V to achieve less than 1 MV/cm for the switching of electrical dipoles. The $F \rightleftharpoons P$ phase transition in P(VDF/TrFE) depends on the VDF content, crystallization temperature, and annealing treatment conditions [8-10]. Unlike thick films, it is difficult to use calorimetric and x-ray diffraction studies to measure T_c and T_m in nano-scale films and hence other reliable, yet simple techniques have to be attempted. Affordable electrical techniques like capacitance and polarization measurements can be useful in evaluating the ferroelectric and dipole switching behavior quantitatively in even nanoscale thick films and have proved to be an effective tool for analyzing the FePoRAM devices [6,7].

Kimura's group [11,12] studied the ferroelectric, piezoelectric, and pyroelectric characteristics in thin films of P(VDF/TrFE)(74/26) and were found to exhibit remarkable ferroelectricity similar to that found in much thicker films of this copolymer. In our previous report [3], we have studied the effect of external field strength upon the $F \rightleftharpoons P$ phase transition behavior

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with heating and cooling, respectively. During heating (Fig. 4(a)), with increasing the temperature just above T_c and maintaining at 100 and at 120°C (well above T_c), the ferroelectric response was diminished showing no hysteresis with simultaneous reduction in both P_r and E_c compared to the P-E hysteresis measured for sample kept at temperature lower than its T_c . At temperatures higher than T_c , the P-E curve is similar to that exhibited by a dielectric material. The P_r value was also very low because of the formation of the P -phase via the $F \rightarrow P$ crystalline phase transition. However, the ferroelectric response was observed to increase with decreasing temperature during cooling down to R.T. due to the formation of F -phase via $P \rightarrow F$ crystalline phase transition as shown in Fig. 4(b). These results indicate that the clear P-E hysteresis loop appears only in the ferroelectric phase of P(VDF/TrFE) and can be used for non-volatile FePoRAM applications only in the temperature range below its T_c .

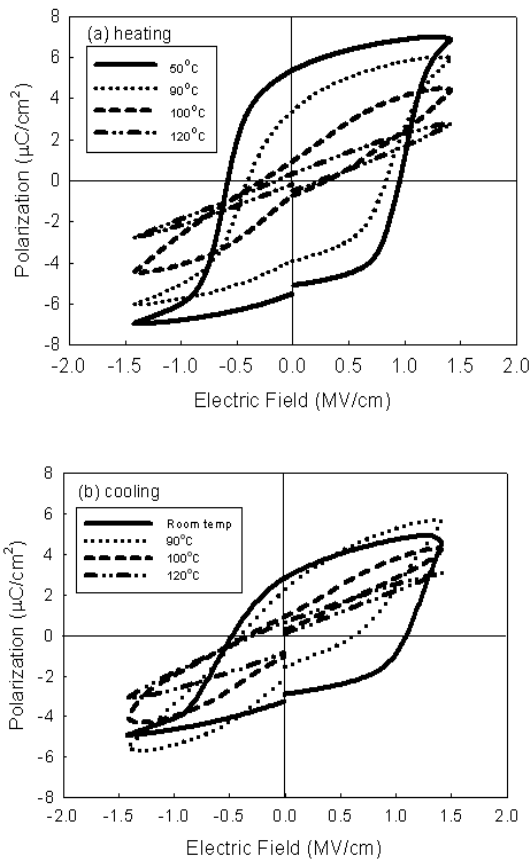


Fig. 4. P-E hysteresis loops of P(VDF/TrFE)(72/28) 245 nm thick film during (a) heating and (b) cooling respectively.

3.3 Inter and intra-molecular conformational changes with T_c

The origin of the Curie transition of P(VDF/TrFE) is entirely associated with intra-molecular conformational change from *trans* and *gauche* [3]. Thus, the T_c is highly dependent on the relative value of the energy difference between the *trans* and *gauche* rotational isomers ($J = U_{ig} - U_{it}$). When an electric field is applied on heating and cooling through the Curie transition, the electric field increases the total polarization in the crystalline lattice and thus inter-molecular interaction plays an important role in the F -phase transition as well as in the intra-molecular conformational change. Since an electric field interrupts the intra-molecular chain rotation about bonds from *trans* to *gauche*

conformation due to an increase in inter-molecular interaction of the F -crystal phase with all *trans* conformation under the field, an increase in the T_c is predicted; but the intra-molecular chain rotation from *gauche* to *trans* is expected to be much easier upon subsequent cooling under the electric field. In other words, an electric field, on heating through the Curie transition, increases the energy barrier for the transformation from *trans* to *gauche* but reduces the energy barrier for the transformation from *gauche* to *trans* upon cooling. Consequently, an electric field will increase both the two Curie transition temperatures, T_c^\uparrow for heating and T_c^\downarrow for cooling.

3.4 Effect of electric field on T_c behavior using C-E studies

To study the effect of external electric field upon heating-cooling on the T_c behavior, the capacitance was measured as a function of temperature with different external electric fields. Fig. 5 shows T_c behavior at varying external electric field (0, 0.3, 0.5 and 0.8 MV/cm) during heating-cooling cycle. T_c^\uparrow and T_c^\downarrow upon heating and cooling were increased significantly under the field of more than 0.3 MV/cm. These results are the same as in infrared spectroscopic results obtained by our previous report [3] to observe the effect of electric field on the Curie transition of P(VDF/TrFE) thicker films. The phase-transition behavior in the present study also shows a first-order-like transition irrespective of the applied electric field.

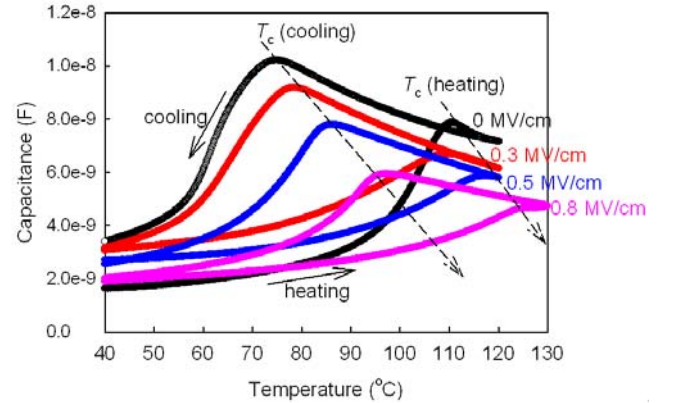


Fig. 5. Curie transition (T_c) behavior at varying external electric fields (0, 0.3, 0.5 and 0.8 MV/cm) during heating-cooling cycle.

3.5 Electric field-induced phase transition during heating and cooling

To study the effect of varying temperatures (below T_c , at T_c and above T_c) on the ferroelectric dipole switching behavior upon applying bias electric field (+1 to -1 MV/cm), the capacitance was measured as a function of electric field with heating-cooling cycle. Fig. 6 shows C - E curve observed upon applying bias electric field to P(VDF/TrFE)(72/28) 250 nm thick film with heating (Fig. 6(a)) and cooling (Fig. 6(b)) cycle. Though a bistable C - E hysteresis was observed clearly much below its T_c^\uparrow , the bistability was gradually reduced and coercive field (E_c) also decreased with increasing temperature up to T_c^\uparrow . At 120°C (well above T_c^\uparrow), bistable ferroelectric dipole switching behavior completely vanished, showing a behavior similar to that exhibited by dielectric materials. However, for the same sample when cooled to 100°C, which is still even 25°C higher than the T_c^\downarrow in the absence of an electric field, a bistable C - E hysteresis was again observed due to the formation of the F -phase via a field-induced phase transition. At the cooling temperature of 90°C,

the bistable C - E hysteresis was well observed and the F -crystalline phase once transformed from the P -crystalline phase through the field-induced phase transition, is not re-transformed back to the P -crystalline phase even after the electric field is removed, i.e., the field-induced $P \rightarrow F$ phase transition is an irreversible process in this case.

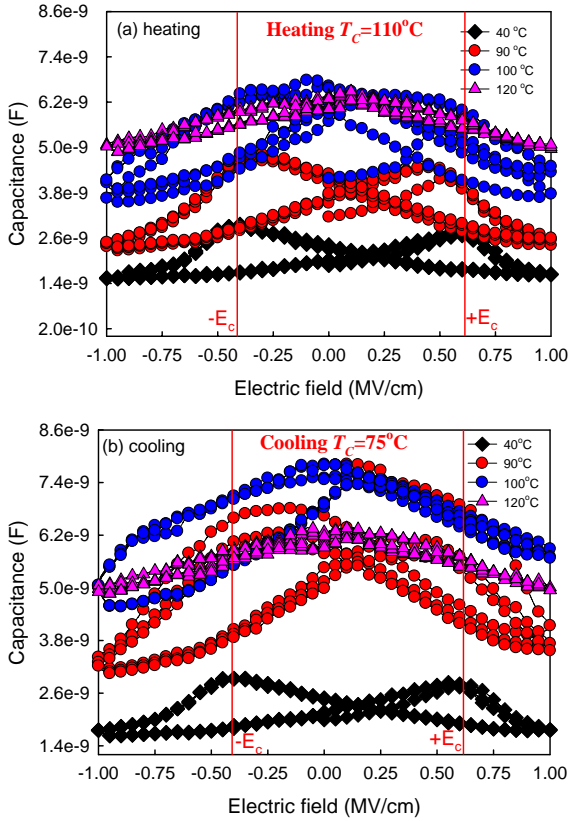


Fig. 6. Field-induced phase transition observed upon bias electric field for 250 nm thick P(VDF/TrFE)(72/28) film with heating and cooling cycle

4. Conclusion

In this work, we have used affordable electrical techniques like capacitance and polarization measurements for evaluating the $F \rightleftharpoons P$ phase transition in P(VDF/TrFE)(72/28) 250 nm thick films. Polarization (P - E) measurements were used to study the effect of varying frequencies under applied bias voltage on remnant polarization (P_r) and coercive field strength (E_c). With increasing frequency, P_r was increased whereas E_c decreased. The hysteresis and bistability of P - E curve diminished as a function of increasing temperature.

C - E measurement was used to study the effect of varying heating-cooling temperatures (below T_c , at T_c and above T_c) on the ferroelectric dipole switching behavior upon applying bias electric field (+1 to -1 MV/cm) as a function of electric field. Though a bistable C - E hysteresis was observed clearly much below the Curie transition, the bistability was lost gradually and E_c was decreased with increasing temperature. When the sample in the paraelectric state is cooled to 100°C, which is still even 25°C higher than the T_c in the absence of an electric field, the application of an external electric field showed a bistable C - E hysteresis again due to the formation of the F -phase via a field-induced phase transition.

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