

Correlation between Ferroelectric Phase Transition and Polarization Reversal Phenomena Observed through Nonlinear Dielectric Anomaly in Ferroelectric Fluorocopolymers

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ABSTRACT: Dielectric nonlinearities in a poled copolymer of vinylidene fluoride and trifluoroethylene (65/35 mol ratio) are discussed in terms of first and second order dielectric constants measured under bias electric fields E_b with an inverse direction to spontaneous polarization. Variation in phase transition temperature T_c obeys the Clausius–Clapeyron equation in a certain range of E_b . Under E_b beyond a certain range, however, T_c deviates from the linear T_c – E_b relation which is described by the Clausius–Clapeyron equation. It is concluded from the observation of the second order dielectric constant that the reason of the deviation is that the polarization reversal occurs before the phase transition.

KEY WORDS Ferroelectric Polymer / Ferroelectric Phase Transition / Polarization Reversal / Bias Electric Field / 2nd Order Dielectric Constant /

The ferroelectric–paraelectric phase transition of ferroelectric materials is affected by an external electric field. The effect of a positive external field, whose direction is the same as that of spontaneous polarization, on the phase transition of copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) has been reported in relation to the thermodynamical order of the phase transition.¹ Forced phase transition of a system whose transition is of the first order obeys the Clausius–Clapeyron equation.² When the external field is applied to samples opposite the direction of spontaneous polarization, the equation predicts a decrease in the phase transition temperature. Such a negative external field may induce two types of cooperative movement of molecules. Molecular motion preceding the ferroelectric phase transition occurs nonlocally and polarization reversal process occurs locally at boundaries between two domains with anti-parallel polarizations.

Date reported the effect of the external field

on the ferroelectric phase transition of VDF/TrFE (52/48) copolymer, observed by measurement of a pyroelectric coefficient.³ Two types of transitions he found are supposed to be related to the cooperative motion mentioned above.

In this paper, we describe temperature variation in first and second order dielectric constants of VDF/TrFE (65/35) copolymer under the external electric field. The 65/35 copolymer exhibits first order phase transition whose temperature hysteresis becomes about 30°C and polarization reversal phenomena, also, can be observed clearly.^{4,5} Since the second order dielectric constant is sensitive to the polarization state of the samples, it can be expected that correlation between phase transition and polarization reversal is observed in the experimental data.^{6,7}

EXPERIMENTAL

The copolymer of VDF and TrFE (65/35

mole ratio) was supplied by Daikin Kogyo Co. Films having about 20 μm in thickness was cast from DMA solution of the copolymer. After the film had been annealed at 140°C for 1 h, test sheets were cut out from the film. Gold was sputtered on both sides of the sheet as electrodes. Samples were poled after several times of polarization reversals by application of an alternating electric field with a frequency 0.05 Hz and an amplitude 100 MV m^{-1} at a room temperature. The system for measurement of dielectric constants was illustrated previously.⁶

PHENOMENOLOGICALLY DESCRIBED SECOND ORDER DIELECTRIC CONSTANT OF FERROELECTRIC MATERIALS

Phenomenological free energy of ferroelectric materials is expanded in power series of polarization P as:

$$G - G_0 = (1/2)\beta(T - T_0)P^2 + (1/4)\gamma P^4 + (1/6)\delta P^6 \quad (1)$$

where G_0 is a constant. β and δ are positive constants and γ is positive or negative constant according to whether the ferroelectric phase transition of the material is second or first order phase transition, respectively. An electric displacement including nonlinear responses is described in terms of power series of an electric field E :

$$D = \varepsilon_1 E + \varepsilon_2 E^2 + \varepsilon_3 E^3 + \dots \quad (2)$$

where ε_1 is a linear dielectric constant and ε_n is a n -th order nonlinear dielectric constant. From eq 1 and 2, we obtain the second order dielectric constant ε_2 .⁷

$$\varepsilon_2 = -(3\gamma + 10\delta P^2)P\chi^3 \quad (3)$$

where $\chi (= \varepsilon_1 - \varepsilon_0)$ is the electric susceptibility. The negative sign in this equation means that the polarization induced by this factor is oriented in the opposite direction to the

spontaneous polarization in a fully polarized ferroelectric state.

RESULTS AND DISCUSSION

First and second order dielectric constants for poled samples of VDF/TrFE (65/35) copolymer were measured under various bias electric fields. Results for the linear dielectric constant ε_1 are illustrated in Figure 1. Positive and negative signs of the bias field E_b in the figure stand for the directions of E_b parallel and anti-parallel to the spontaneous polarization P_s , respectively.

In real ferroelectric materials, ε_1 exhibits a sharp peak at the phase transition temperature T_c in many cases. In the case of the VDF/TrFE (65/35) copolymer, we can also see peaks specified in Figure 1, although the peak lost sharpness because of the successive phase transition which is usually observed in 65/35 copolymer.^{8,9} The figure shows that the transition temperature under the condition $E_b = -5 \text{ MV m}^{-1}$, $T_{c(-5)}$, is lowered from T_c due to the bias field, as is expected in the scope of the Clausius-Clapeyron equation. The

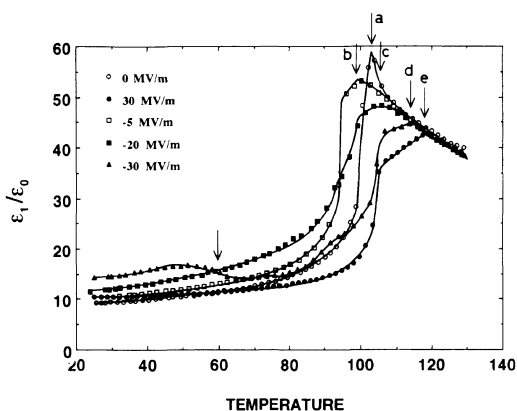


Figure 1. Dielectric constants of poled 65/35 VDF/TrFE copolymer measured under various bias electric fields. Arrows indicate the ferroelectric phase transition temperatures determined at the peak point: a, no bias; b, -5 MV m^{-2} ; c, -20 MV m^{-1} ; d, -30 MV m^{-1} ; e, 30 MV m^{-1} . The arrow at 60°C under -30 MV m^{-1} indicates the temperature at which the polarization reversal occurs.

curves under the conditions $E_b = -20$ and -30 MV m^{-1} , however, exhibit the phase transition at temperatures higher than T_c . Furthermore, the ϵ_1-T relation under $E_b = -30 \text{ MV m}^{-1}$ exhibits a relatively sharp decrease at about 60°C . Except for the decrease, the shape of the curve is similar to the curve for $E_b = 30 \text{ MV m}^{-1}$, where $T_{c(30)}$ shifts to a higher temperature the Clausius–Clapeyron equation predicts. $T_{c(30)}$ nearly equals $T_{c(-30)}$.

Figure 2 illustrates the temperature dependence of the second order dielectric constant ϵ_2 . ϵ_2 shows a negative value in the low temperature region and a positive peak at T_c indicated in the ϵ_1-T curve in Figure 1. The negative value of ϵ_2 at room temperatures agrees well with the negative sign in eq 3. If the spontaneous polarization vanishes perfectly at T_c , ϵ_2 should become zero because ϵ_2 is a third rank tensor and eq 3 becomes zero when $P_s = 0$. ϵ_2 in this case, however, overshoots the value $\epsilon_2 = 0$ and reveals the sharp positive peak. If the reversed polarization remains at T_c , ϵ_2 might have a large positive value because of the contribution of χ^3 . Heterogeneous space charge distribution which cancels partly the depolarization field below T_c seems to remain even after the dipole orientation vanishes and makes ϵ_2 positive for a while because of its relaxation time longer than the polarization reversal switching time. In such a case, ϵ_2 reaches the positive maximum value at T_c . We conclude that the positive maximum of ϵ_2 comes from the peak of the factor χ^3 and an existence of the polarization opposite the initial poling direction.

ϵ_2 measured under $E_b = -5 \text{ MV m}^{-1}$ has the peak at $T_{c(-5)}$ which was determined at the peak of ϵ_1 . The ϵ_2-T relation under $E_b = -20 \text{ MV m}^{-1}$ exhibits a change in the sign fairly below $T_{c(-20)}$ which is specified by the arrow in the figure. The ϵ_2-T curve under -30 MV m^{-1} also has a change in sign at about 60°C which is much lower than $T_{c(-30)}$. In this case, after the change in the sign, the ϵ_2-T

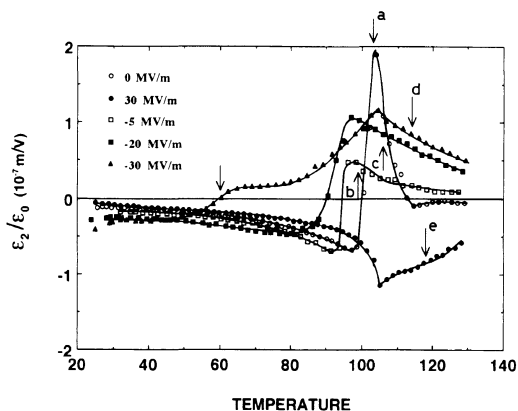


Figure 2. Second order dielectric constants of the same samples and under the same conditions as those in Figure 1. Arrows in the figure appear at the same temperatures as those in Figure 1.

relation has a similar shape and opposite sign to those of the system under $E_b = 30 \text{ MV m}^{-1}$ existing in the ferroelectric state below $T_{c(30)}$. Therefore, the sample is in the ferroelectric state even after the change in the sign of ϵ_2 . What happened at about 60°C is merely polarization reversal without phase transition.

The bias field -30 MV m^{-1} thus caused the polarization reversal at temperatures far from the phase transition. On the other hand, the bias field -5 MV m^{-1} is presumed to induce the phase transition because the positive peak of ϵ_2 under $E_b = -5 \text{ MV m}^{-1}$ is located at the temperature predicted by the Clausius–Clapeyron equation. The polarization reversal under -20 MV m^{-1} begins at a temperature slightly below 90°C . The polarization reversal is supposed to be accompanied by transition, because the Clausius–Clapeyron equation predicts that phase transition will occur near 90°C as is shown in Figure 5. This case seems to be between the two cases $E_b = -30 \text{ MV m}^{-1}$ and -5 MV m^{-1} . Polarization reversal may occur by way of the paraelectric phase, as Date suggested.³

ϵ_2 measured under 30 MV m^{-1} (-30 MV m^{-1}) shows a negative (positive) peak at a temperature lower than $T_{c(30)}$, where ϵ_2 decreases (increases) up to the peak tempera-

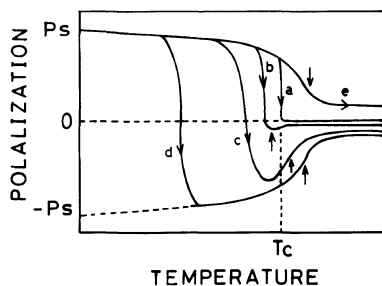


Figure 3. Temperature dependence of the spontaneous polarization for the VDF/TrFE copolymer under various bias fields. Characters in the figure have the same meaning as in Figure 1.

ture and then increases (decreases) slowly. The first relatively sharp decrease (increase) stems from the positive (negative) polarization and steep increase in ϵ_1 . The following slow increase (decrease) until $T_{c(30)}$ means the slow increase in ϵ_1 and steep decrease in the remanent polarization before $T_{c(30)}$.

Figure 3 illustrates temperature variation in spontaneous polarization of the system. The polarization reversal process under -30 MV m^{-1} occurs at about 60°C , where the system is in the ferroelectric state. In this case, the reversal process is localized on the domain boundary. In the case of the bias field of -5 MV m^{-1} , the reversal of dipoles occurs nonlocally as the process preceding the ferroelectric phase transition resulting in lowering of the transition temperature predicted by the Clausius–Clapeyron equation. The bias field -20 MV m^{-1} has effect between these two bias fields. In this case, polarization reversal occurs by way of the paraelectric state. In Figure 4, free energy diagrams representing such situations are schematically depicted. Diagrams (a), (b), and (c) correspond to the cases of the bias fields -30 , -20 , and -5 MV m^{-1} , respectively. The diagram (a) illustrates the polarization reversal process coming from the growth of the domain with the polarization ($-P_s$) parallel to the applied electric field. In this case, the paraelectric state is bypassed due to concentration of the strain

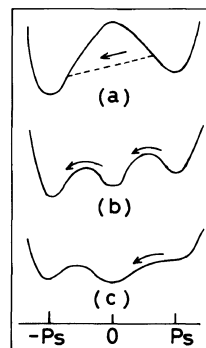


Figure 4. Free energy diagram at the instant when polarization reversal occurs. (a), (b), and (c) correspond to processes occurring at -30 MV m^{-1} , -20 MV m^{-1} , and -5 MV m^{-1} , respectively.

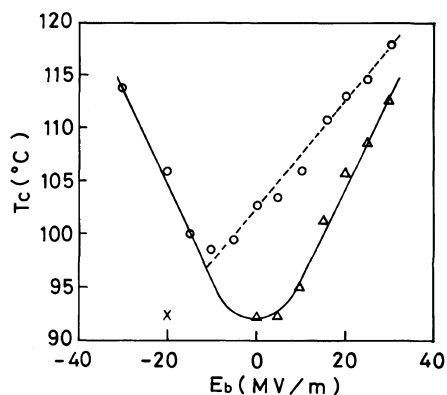


Figure 5. Bias electric field dependence of the phase transition temperature. \circ , poled samples; \triangle , unpoled samples. The solid line representing a trace of unpoled samples in the negative bias field was pictured by reversing that in the positive bias field symmetrically about the longitudinal axis passing through $E_b = 0$. The broken line represents the Clausius–Clapeyron relation for the poled sample. If the spontaneous polarization is not reversed previously, under -20 MV m^{-1} , the phase transition would occur near a temperature marked with a cross.

energy into the boundary between the two domains with P_s and $-P_s$. The diagram (b) shows the polarization reversal process occurring by way of the paraelectric state, which Date proposed.³ In the diagram (c), polarization reversal does not occur but the phase transition occurs with the aid of the bias field.

Figure 5 illustrates the external field dependence of the phase transition temperature

determined as the peak temperature of the linear dielectric constant. In this figure, two sorts of samples are illustrated: circles correspond to the poled samples and triangles stand for T_c of the unpoled samples. A trace of T_c 's of the poled samples has a linear relation to the external field as the Clausius–Clapeyron relation predicts. But below -15 MV m^{-1} the trace deviates from the straight line and shifts to higher temperatures. The trace which deviated from the straight line agrees with the trace of the unpoled samples. It is presumed that the state which was transformed by the polarization reversal is similar to the state of the unpoled samples, because the bias field used here is fairly low and, therefore, reversed polarization and the crystal state are not so perfectly ordered.

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