Polarization Inversion Current and Ferroelectric Phase Transition of Vinylidene Fluoride–Trifluoroethylene Copolymer

Kohji Tashiro,* Masanori Nakamura, Masamichi Kobayashi, Yozo Chatani, and Hiroyuki Tadokoro

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received September 16, 1983*

ABSTRACT: The temperature dependence of the polarization inversion current under a high electric field has been measured for a vinylidene fluoride–trifluoroethylene copolymer with 75 mol % vinylidene fluoride (VDF). The electric field E_{max} at the current peak decreases steeply in the vicinity of the ferroelectric phase transition temperature (ca. 125 °C). At the same time a new current peak begins to appear, shifts toward higher electric field, and disappears again in the paraelectric phase. This new peak might come from the forced phase transition from a paraelectric phase into the ferroelectric phase under high electric field. The observed temperature dependence of inversion current peaks has been interpreted by a phenomenological theory. An intimate relationship between the trans–gauche conformational change and the lowering of E_{max} has been discussed in connection with molecular motion.

In previous papers[1-3] we have investigated the structural changes occurring in the ferroelectric phase transition of vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers. The change in electric polarization observed in the ferroelectric transition is caused by a cooperative change in the arrangement of VDF (and TrFE) dipoles,[4-6] which originates from the large molecular conformational change between the trans-zigzag form and the gauche form with substantial molecular motion.[1-3,7,8] Such a structural change is characteristic of a polymeric material, where the dipoles are linked together by covalent bonding, and is observably different from the ferroelectric phase transition of low molecular weight ionic crystals, where the dipole changes are induced by small atomic displacements. From such a point of view it may be important to investigate the relationship between the dipole change and the structural transformation for this copolymer sample. We have measured the switching currents induced by the dipole inversion under high electric field at various temperatures successively, the result being related to the structural change revealed by X-ray diffraction and infrared spectroscopic measurements.

Experimental Section

The polarization inversion induced by the application of high electric fields to films is measured mainly by two kinds of methods.[9-13] One is the measurement of the so-called D–E hysteresis loop (D is an electric displacement and E is an electric field) and the other is the measurement of the inversion current as a function of E. These two methods are related as integral and differential, but the sensitivity for detecting the slight change in polarization seems higher for the inversion current measurement, as seen in Figure 1.

The method for the measurement of the inversion current is illustrated in the block diagram of Figure 2. A triangular wave with very low frequency, 0.3–0.0003 Hz, is amplified to a high voltage of 0–6 kV and applied to the sample. The relation between current I and applied voltage V is plotted by the X–Y recorder (I–V or I–E curve). As illustrated in Figure 2b, as the voltage of the triangular wave changes in the cycle 1–4, the inversion current I is observed in the same order of 1–4. In general, the dielectric material is considered to be equivalent to a parallel circuit of resistance R and dielectric capacity C_p. Then in Figure 2b, the I–E curve has a slope representing the contributions of the leak current due to Ohm's law ($I \propto E/R$) and also of the current due to the dielectric polarization ($I \propto \epsilon\, dE/dt$; ϵ is the dielectric constant and t is time). These contributions are estimated as being at most 10% in the temperature region under consideration (20–140 °C), even though the ϵ increases rapidly near the transition point ~125 °C.[14]

The sample used here was a VDF–TrFE copolymer containing 75 mol % VDF, which was supplied by Daikin Kogyo Co. Ltd. The unoriented films were prepared by pressing a molten film and cooling slowly to room temperature. The surfaces of the film were vacuum evaporated with gold or aluminum metal to prepare circular electrodes with a diameter of 1 cm. The samples were inserted into a high-temperature cell with a temperature controller.

Results and Discussion

In Figure 3 is shown the temperature dependence of the polarization inversion current observed for 75% VDF copolymer film. At room temperature a single peak with a small shoulder is observed. As the temperature rises, the peak becomes sharper and larger and the peak position shifts toward the lower electric field side. In the vicinity of the transition temperature, about 125 °C, the peak shift is particularly large. In the transition region this peak height becomes small and a new peak begins to appear, the position of which shifts to higher electric field side with increasing temperature. At higher temperatures this new peak disappears again and the I–E curve characteristic of the paraelectric phase is obtained. When the temperature is lowered, the curve of the original ferroelectric phase is obtained around 75 °C. In Figure 4 is plotted the electric field strength E_{max} at the current peak against temperature. E_{max} decreases markedly in the transition region and shows a large thermal hysteresis, corresponding closely to the hysteresis in structural changes observed by X-ray diffraction and infrared spectroscopic measurements (Figure 7).[1-3]

Phenomenological Interpretation of Temperature Dependence of Inversion Currents

In Figure 3 the rate of applying the electric field was very low and so the inversion is considered to be quasi-static. Therefore, an interpretation of Figure 4 will be attempted here based on static phenomenological theory.

As reported in the previous paper[3] the phase transition of the 75% VDF copolymer is typically first order between the low-temperature ferroelectric all-trans phase and the high-temperature paraelectric gauche phase. For the first-order ferroelectric phase transition, the phenomenological equation of polarization P is developed as follows. As is well-known, the free energy may be written as a function of P by

$$G = G_0 + (1/2)xP^2 + (1/4)yP^4 + (1/6)zP^6 \qquad (1)$$

Then the electric field E is expressed as

$$E = (\partial G/\partial P)_T = xP + yP^3 + zP^5 \qquad (2)$$

where

$$x = (T - T_0)/C \qquad (3)$$

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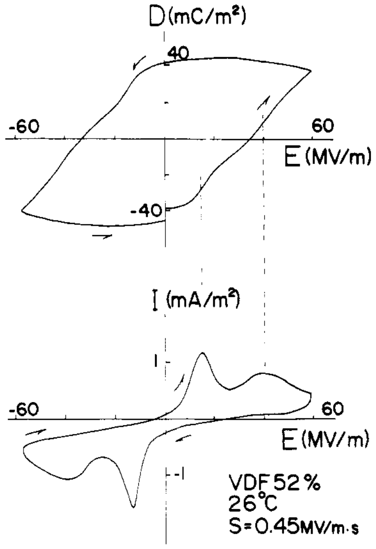

Figure 1. Comparison of *D–E* hysteresis loop and *I–E* curve for 52 mol % VDF copolymer (room temperature). *S* is an impressing rate of voltage.

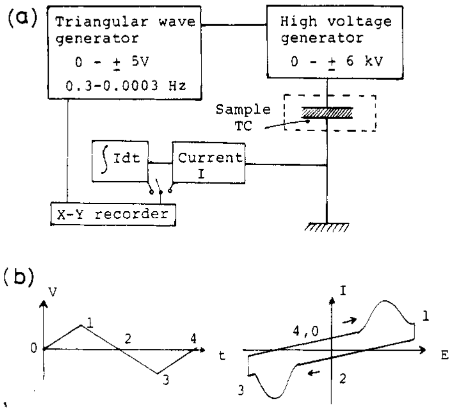

Figure 2. (a) Block diagram for measurement of the polarization inversion current. (b) Correspondence of the applied triangular electric field and the resultant inversion current.

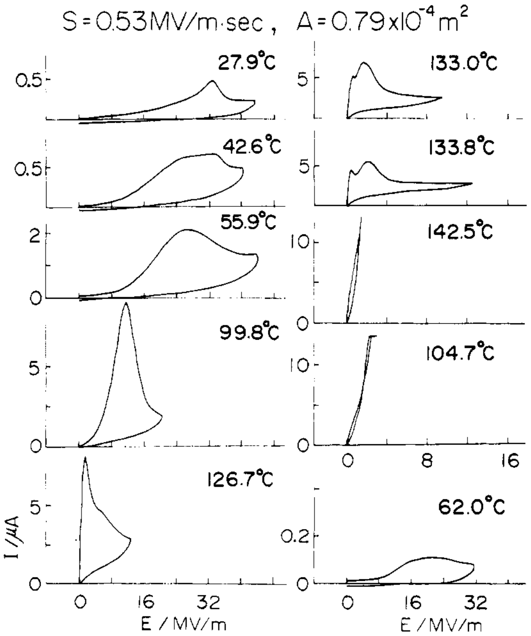

Figure 3. Temperature dependence of the polarization inversion current for 75% VDF copolymer. *A* is the area of the electrode.

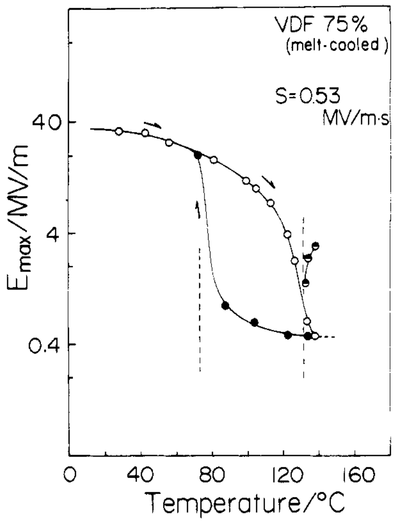

Figure 4. Temperature dependence of electric field $E_{\max}$ at the current maximum.

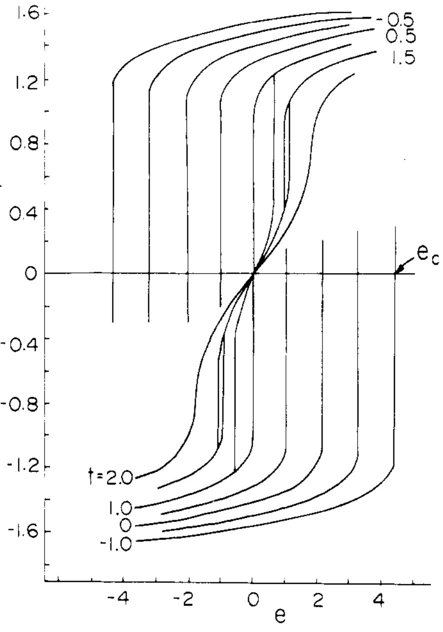

Figure 5. Plot of the reduced polarization *p* against the reduced electric field *e* for the various values of *t*.

is the linear electric susceptibility, T_0 and C are constants, y and z are nonlinear electric susceptibilities, independent of temperature, and $y < 0$ and $z > 0$ for the first-order transition. By utilizing the new variables p and e defined in eq 4 and 5 instead of P and E, one can reduce eq 2 to eq 6.

$$p = (-2z/y)^{1/2}P \tag{4}$$

$$e = -(4/y)(-2z/y)^{3/2}E \tag{5}$$

$$e = 2tp - 4p^3 + 2p^5 \tag{6}$$

where

$$t = (4z/Cy^2)(T - T_0) \tag{7}$$

and the Curie temperature T_c is given by

$$T_c = T_0 + (3Cy^2/16z) \tag{8}$$

In eq 6 the parameter t corresponds to the temperature. Figure 5 shows the plot of p vs. e for the various t. For the negative value of t, i.e., for the temperature range of ferroelectric phase ($T < T_0$), a large p–e hysteresis loop is seen and the coercive electric field e_c is given at the point where the curve crosses the $p = 0$ line. For positive but

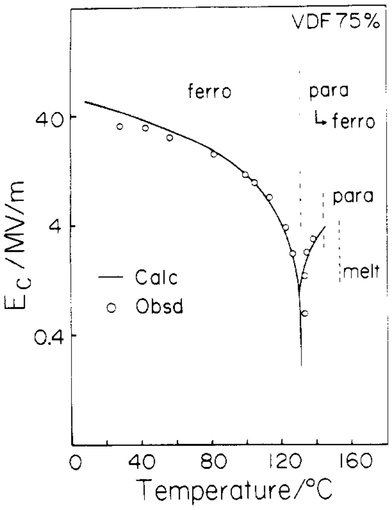

Figure 6. Comparison of the calculated E_{max} values with the observed ones as a function of temperature. Only the heating process is shown.

small values of t, corresponding to the temperature immediately above the transition point T_c, the so-called double hysteresis loop is formed; the e_c value becomes higher with a rise of temperature, contrary to the case in the ferroelectric phase. Such a double hysteresis loop is said to originate from the transition of the paraelectric phase to the ferroelectric phase induced by the external electric field. As the temperature rises further, i.e., for larger positive values of t, the linear curve characteristic of the paraelectric phase is manifested. The inversion current corresponds to the differentiation of Figure 5 with respect to e. The current peak of the ferroelectric phase may shift toward lower electric field with increase of temperature, but in the vicinity of the transition point the peak position shifts instead to higher electric field, and finally the paraelectric curve is obtained. This theoretically predicted behavior of the current peak corresponds well to the present experimental result for the 75% VDF copolymer.

Referring to the theoretically predicted relationship between the coercive electric field e_c and temperature t, obtained from eq 6, and using the observed value of remanent polarization $P_r \approx 80$ mC/m^2 at room temperature,[16] we can reproduce the observed curve of E_{max} vs. T as shown in Figure 6. The numerical values of the parameters thus obtained are as follows. For the units of E (V/m) and P (C/m^2), $y = -1.457 \times 10^{12}$ (V m^5)/C^3, $z = 4.256 \times 10^{14}$ (V m^9)/C^5, $C = 1.20 \times 10^{-8}$ (C K)/(V m), $T_0 = 390.3$ K = 117.2 °C, and $T_c = 401.5$ K = 128.3 °C. The order and sign of y and z seem reasonable but much larger than the values for ionic crystals; e.g., $y = -2.3 \times 10^9$, $z = 3.9 \times 10^{10}$, and $C = 1.5 \times 10^{-6}$ for BaTiO$_3$.[17] The high values of y and z for the 75% VDF copolymer correspond to a high electric field for the dipole reorientation, reflecting a characteristic feature of polymers, where the dipoles are covalently linked.[18,19]

Structural Change and Inversion Currents

Although the above phenomenological theory has apparently been able to interpret the observed temperature dependence of E_{max} with good success, we must take into account some additional significant factors. One is the existence of a domain structure lowering the total free energy of the ferroelectric material. Furukawa et al.[9,10] and Odajima et al.[12] have discussed the polarization inversion of copolymer samples measured at room temperature in terms of the motion of domain walls. Increasing the temperature may accerelate the motion of the wall greatly, and the coercive electric field may thus be much decreased.

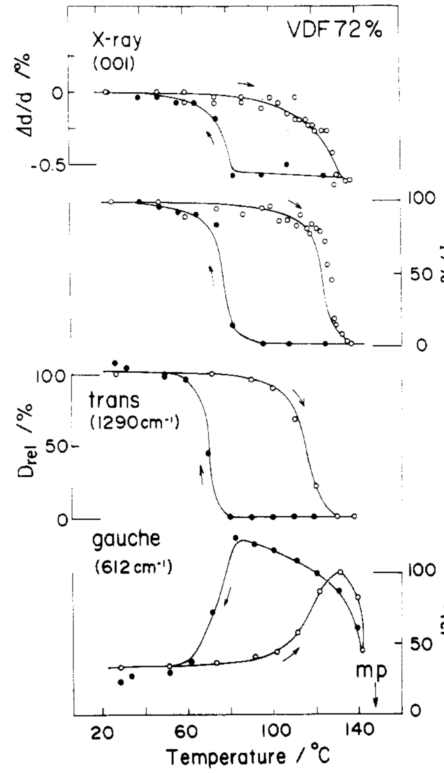

Figure 7. Temperature dependence of the fiber period and X-ray (001) reflection intensity for the low-temperature trans phase and of the relative absorbances of infrared trans and gauche bands for the 72% VDF copolymer.

Another factor concerns molecular motion of polymer chains accompanying the trans–gauche conformational change. In Figure 7 are shown the fiber period and X-ray (001) reflection intensity for the low-temperature trans-zigzag phase and the relative intensities of the infrared trans and gauche bands as a function of temperature.[3] As the temperature approaches the transition point, a decrease of trans band intensity and an increase of gauche band intensity are observed, and at the same time the X-ray intensity of the (001) reflection for the low-temperature phase is also decreased. On cooling, the transformation from the gauche to the trans form occurs at about 80 °C, showing a large thermal hysteresis. The remarkable temperature dependence of E_{max} in Figure 6 is parallel to these structural changes, indicating an intimate relation between the trans–gauche conformational change and the ease of dipole inversion. It should be noted here that in the vicinity of the transition point the fiber period of the trans-zigzag form contracts slightly from the value at room temperature but more than the amount predicted for a simple negative thermal expansion of the chain. This may originate from the circumstance that the gauche bonds generated near the transition point not only assemble together to form the high-temperature crystal phase but also appear within the trans-zigzag chain as a kind of defect. Analyzing the temperature dependence of broad-line NMR spectra of 72% VDF copolymer, Ishii et al.[20] proposed a diffusional motion of gauche bonds along the chain axis, which is associated with the rotation of VDF segments near the transition temperature. The contraction of the zigzag chain shown in Figure 7 may be consistent with their proposition. The great lowering of E_{max} may be caused by such a thermal motion of gauche bonds within the trans-zigzag chains. Hopfinger et al.[21,22] analyzed the polarization inversion mechanism of PVDF form I under high electric field based on a soliton model, i.e., the motion of a defect composed of a complicated sequence of trans and gauche bonds. Intercorrelation of Figures 6 and 7 suggests the possibility of the application of such a hypothesis to the analysis of the polarization inversion mechanism and its temperature dependence for the copolymer samples.

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Solid-State ^{19}F NMR Investigations of Annealed Poly(tetrafluoroethylene)

Anita J. Brandolini,[†] **Karen J. Rocco, and Cecil R. Dybowski***

Department of Chemistry, University of Delaware, Newark, Delaware 19716.

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ABSTRACT: Solid-state ^{19}F NMR spectroscopy is used to follow the disorientation of crystallites in poly(tetrafluoroethylene) during annealing at 300 °C. The rapid shrinkage is accompanied by disorientation of crystallites. Over prolonged periods, NMR indicates that a totally random orientation is not achieved. The NMR technique is exceptionally sensitive to the nonrandom orientational distribution.

Introduction

During the processing of polymeric materials, annealing at temperatures near the melting point is often performed in order to relieve internal stresses induced during fabrication. Such processing results in a material whose properties, such as impact strength, dimensional stability, and heat resistance, are frequently superior to those of the unannealed material.[1] When a drawn semicrystalline polymer is annealed, shrinkage of the sample is accompanied by a rapid relaxation of strained tie molecules that connect crystalline lamellae.[1] This relaxation process causes rapid disorientation of the crystallites.[1] The nature of the changes that occur during annealing of semicrystalline polymers is, therefore, complex and requires analytical techniques sensitive to subtle structural and motional changes. Techniques such as mechanical testing, electron microscopy, and X-ray diffraction have been used to monitor structural changes accompanying annealing, and these applications have been reviewed elsewhere.[1-3] Each technique suffers from certain limitations. Some methods yield only limited orientation information; others are sensitive to ordering in only the crystalline or amorphous fraction of the material. Solid-state nuclear magnetic resonance (NMR) spectroscopy is sensitive to molecular motion (through the study of relaxation times) and structure (through the analysis of orientation-dependent interactions).[4,5] The chemical-shift interaction has been shown to be valuable for studying orientation in drawn[6-13] and annealed[14] semicrystalline polymers. This approach can be used to derive a complete orientation distribution function, and the NMR spectrum does contain information about both phases. The analysis is limited, however, to spectra in which unobscured resonances may be observed. We report here a quantitative NMR spectroscopic study of the annealing of poly(tetrafluoroethylene) (PTFE) at 300 °C. Our results confirm that the observed sudden shrinkage of the polymer that occurs during annealing is accompanied by rapid disorientation of the crystallites. Even after extended periods of time at this temperature, the NMR analysis reveals that the crystallites do not relax back to the totally random distribution that the material had before drawing.

Theory

A static anisotropic distribution of crystallite orientations in a sample of a drawn polymer produces an NMR spectrum characteristic of the distribution of crystallite axes relative to the magnetic-field direction, $\vec{B}_0$. Analysis of the changes in the spectral line shape produced by varying the angular position of the draw axis relative to

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[†] Current address: Mobil Chemical Co., Research and Development, Edison, NJ 08818.

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