# Thermal Contraction and Ferroelectric Phase Transition in Vinylidene Fluoride–Trifluoroethylene Copolymers. 2. An Effect of Tensile Stress Applied in the Direction Perpendicular to the Chain Axis

**Kohji Tashiro,* Shin Nishimura, and Masamichi Kobayashi**

*Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan*

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ABSTRACT: Anisotropic thermal expansion under externally applied tensile stress has been measured for uniaxially oriented ferroelectric vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers with VDF 65% molar content. In the heating (cooling) process, the sample length along the drawing direction was found to contract (expand) largely in the vicinity of the structural phase transition temperature, while the dimension in the direction perpendicular to the draw axis has been found to expand (contract) in the same temperature region. The unoriented film exhibited a thermal expansion behavior intermediate between the dimensional changes in the parallel and perpendicular directions. A comparison of these thermomechanical curves with the data of X-ray, infrared and Raman, DSC, etc., revealed that the bulk dimensional changes of the sample reflect directly the structural phase transition occurring in the crystalline region in both directions. The transition temperature was found to shift to the lower side with an increasing applied stress: $\Delta T/\Delta\sigma = -1.0$ K/MPa (perpendicular) and $-4.6$ K/MPa (parallel). These results were interpreted reasonably based on a modified thermodynamical Clausius–Clapeyron equation.

## Introduction

Among many crystalline polymers, vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers may be unique in the point that the structural change occurring in the ferroelectric phase transition has been found to reflect directly on the change in the electrical and mechanical properties. This structural change is characterized by the large conformational change of the polymer chain between the trans and gauche forms.[1-4] Such a conformational change induces the large dimensional change along the chain axis. This phenomenon itself, i.e., the relation between the conformational change and the *c*-dimensional change, is general as often observed for the various crystalline polymers.[5] But there are few quantitative works that have revealed the intimate relationship between the microscopically occurring dimensional change in the crystalline region and the macroscopic dimensional change of the bulk sample. In the previous paper,[6] we have clarified that the macroscopic dimensional change along the draw direction of the uniaxially oriented bulk samples correlates intimately and quantitatively with the microscopic *c*-axis dimensional change induced by the trans–gauche conformational change; that is to say, the sample length along the draw axis contracts largely and reversibly in the temperature region corresponding to the structural transition point.

In the phase transition of the present fluorine copolymers, the intermolecular distances also change in the lateral direction.[1-4] Such a lateral dimensional change is expected to appear also as a large dimensional change in the direction perpendicular to the draw axis of the bulk sample. In this paper an intimate relationship of the dimensional change between the crystalline region and the bulk sample will be clarified in both the parallel and perpendicular directions to the draw axis. The transition temperature has been found to shift with a change in the applied tensile stress, which will be interpreted from the thermodynamic point of view.

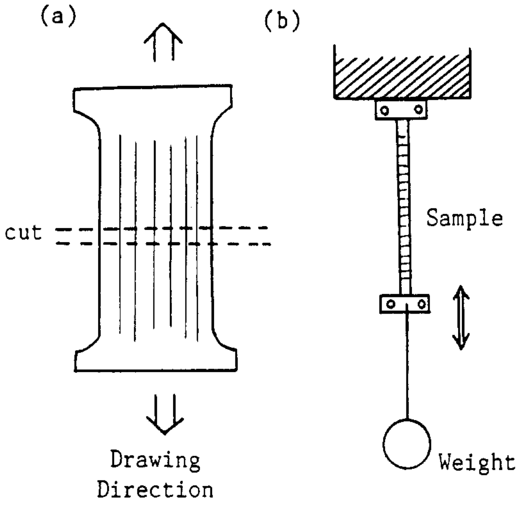

**Figure 1.** (a) Sectioning of the sample and (b) its setting in the thermomechanical cell for measurement of the thermal expansion along the lateral direction of the uniaxially oriented sample film.

## Experimental Section

The samples used were VDF–TrFE copolymers of 65 mol % VDF content supplied by Daikin Kogyo Co., Ltd., Osaka, Japan. Films cast from acetone solution were drawn at room temperature, and a rectangular strip was cut in the direction perpendicular to the draw axis (Figure 1a). This strip was hung vertically with a constant load applied and set into the thermomechanical measuring system made by us. The dimensional change of the sample was detected by a linear variable differential transformer (LVDT) and recorded by an X-Y recorder to obtain a curve of length vs temperature. The details of the apparatus were already described in the previous paper.[6] A strip of the as-cast unoriented film was also employed in the measurement.

## Results and Discussion

**Relationship between Phase Transition and Dimensional Change.** Figure 2 shows the temperature depen-

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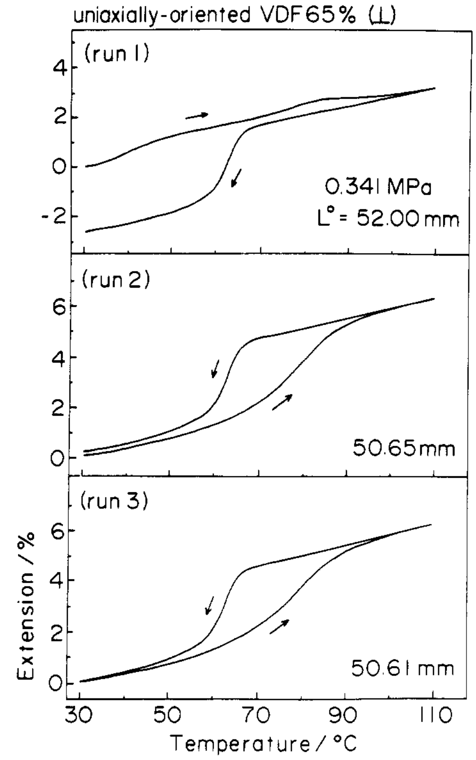

**Figure 2.** Thermal expansion curves measured along the lateral direction of the uniaxially oriented VDF 65% sample. The applied stress is 0.341 MPa.

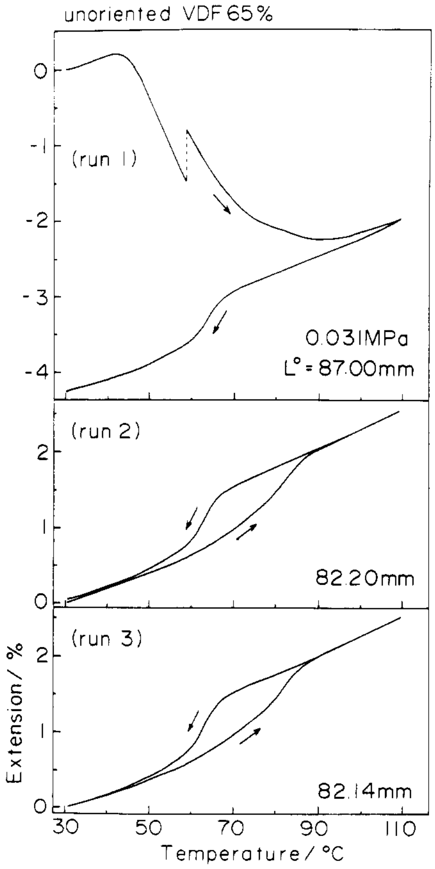

**Figure 3.** Thermal expansion curves measured for the as-cast unoriented VDF 65% sample. The applied stress is 0.031 MPa.

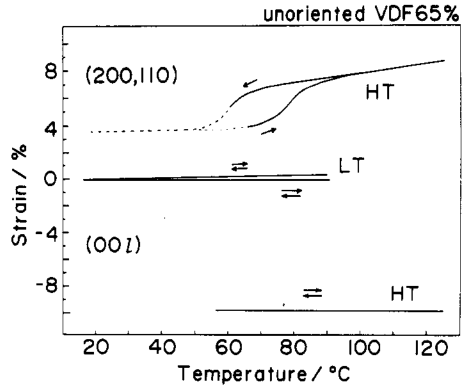

**Figure 4.** Temperature dependence of the lattice spacings along the *a* and *c* axes measured by the X-ray diffraction method for the VDF 65% copolymer.

dence of the dimensional change measured along the lateral direction of the oriented film. Except for the first run, the curve of which was deformed appreciably by an annealing effect in the heating process, reversible and closed curves are observed with a remarkable thermal hysteresis between the heating and cooling processes. The sample *expands* largely near 80 °C in the heating process and *contracts* steeply near 65 °C in the cooling process. In the case of the unoriented film, closed curves were also obtained after the first run (Figure 3), which are similar in shape to those of Figure 2 but the dimensional change is much smaller. In Figure 4 is shown the temperature dependence of the lattice spacings *d*(200, 110) and *d*(001) measured by the X-ray diffraction method for the VDF 65% oriented sample,[1] where the *c* axis is parallel to the chain axis. The macroscopically observed curves in Figures 2 and 3 change their slope steeply in the temperature region where the lattice spacing changes largely, indicating that the structural change occurring in the crystalline region reflects directly on the bulk dimensional change both in the directions parallel and perpendicular to the draw axis.

On the basis of this idea, i.e., an intimate relationship between the bulk dimensional change and the lattice spacing change, we can simulate the observed curves of Figures 2 and 3. In the calculation a series arrangement of the crystalline and amorphous regions was assumed along the direction of the applied force, and the thermal expansions of these two phases and the large dimensional change at the transition point within the crystalline region (Figure 4) were taken into account. As discussed in the previous paper,[6] a bulk strain, $\epsilon$, is expressed by

$$\epsilon = x\epsilon_c + (1-x)\epsilon_a \tag{1}$$

where $\epsilon_c$ and $\epsilon_a$ are the strains in the crystalline and amorphous phases, respectively, in the direction just in question. $x$ is a degree of crystallinity. $\epsilon_a$ is assumed to be expressed as

$$\epsilon_a = \alpha_a(T - T_0) \tag{2}$$

Here $\alpha_a$ is a thermal expansivity and $T_0$ is a reference temperature (starting temperature, for example). In such a thermodynamically first-order phase transition as the present case, the low-temperature (LT) and high-temperature (HT) phases are coexistent in the transition temperature region. Thus $\epsilon_c$ is assumed to be written as

$$\epsilon_c = f\epsilon_{LT} + (1-f)\epsilon_{HT} \tag{3}$$

where $f$ is a fraction of the LT phase. The strains of the LT and HT phases, $\epsilon_{LT}$ and $\epsilon_{HT}$, respectively, are given as

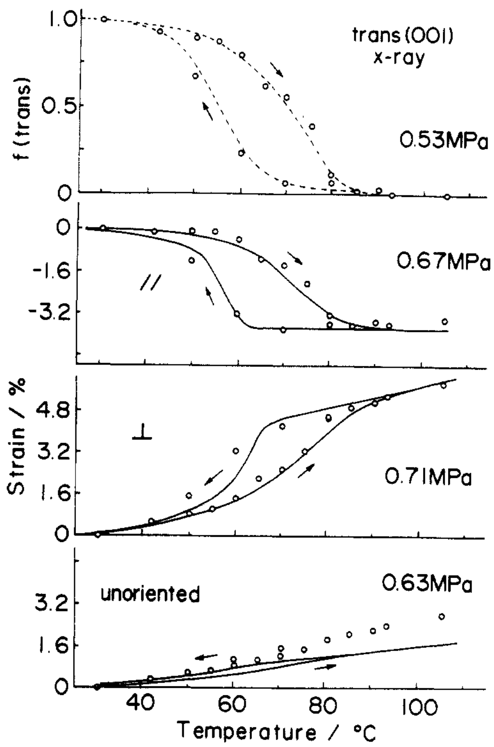

**Figure 5.** Comparison of the observed results (—) and the calculated points (O) for the thermal expansion curves in the parallel, perpendicular, and unoriented samples of the VDF 65% copolymer. The calculations were based on the experimental data of the temperature dependence of the relative trans content in the crystalline region,[6] which were measured by the X-ray diffraction method under the tensile stress similar to those in the thermomechanical experiments (top figure).

$$\epsilon_{\mathrm{LT}} = (l_{\mathrm{LT}} - l^{\circ}_{\mathrm{LT}})/l^{\circ}_{\mathrm{LT}} = \alpha_{\mathrm{LT}}(T - T_0) \qquad (4\text{-}1)$$

$$\epsilon_{\mathrm{HT}} = (l_{\mathrm{HT}} - l^{\circ}_{\mathrm{LT}})/l^{\circ}_{\mathrm{LT}} = \Delta\epsilon + (1 + \Delta\epsilon)\alpha_{\mathrm{HT}}(T - T_0) \qquad (4\text{-}2)$$

where $l_i$ is the length of the $i$th phase ($i$ = LT and HT) and $\Delta\epsilon$ is the dimensional change occurring at the transition temperature, $T_c$, between the LT and HT phases (refer to Figure 4). $\alpha_i$ is the thermal expansion coefficient of the $i$th phase. When reasonable experimental values for the parameters,[6] i.e., $x = 0.5$, $T_0 = 30$ °C, $\alpha_a = 4 \times 10^{-4}$ K$^{-1}$, $\alpha_{\mathrm{LT}}(\|) = \alpha_{\mathrm{HT}}(\|) = -1 \times 10^{-5}$ K$^{-1}$, $\alpha_{\mathrm{LT}}(\perp) = 1.3 \times 10^{-4}$ K$^{-1}$, $\alpha_{\mathrm{HT}}(\perp) = 4 \times 10^{-4}$ K$^{-1}$, $\Delta\epsilon(\|) = -9.8\%$, and $\Delta\epsilon(\perp) = +5.5\%$, are used and when the $f$ value from the observed temperature dependence of the X-ray (001) reflectional intensity of the trans phase (Figure 5), which was measured under the similar tensile stress (0.53 MPa) with that used in the present thermomechanical measurements,[6] is evaluated, the observed curves (solid lines in Figure 5) and the calculated results (open circles) are found to be in relatively good agreement with each other. In this figure the result for the unoriented sample is also plotted, where the strain is averaged as $\epsilon = (2\epsilon_{\perp} + \epsilon_{\|})/3$. In this case, the calculated points deviate somewhat from the observed curve, possibly because the utilized film specimen might be not so perfectly unoriented but oriented to some extent: in other words, the above-mentioned averaging process between $\epsilon_{\perp}$ and $\epsilon_{\|}$ may not be so suitable. [Such an effect of orientation must be also taken into account in the calculation of $\epsilon_{\perp}$ and $\epsilon_{\|}$. In the above discussion of $\epsilon_{\perp}$ and $\epsilon_{\|}$, we have assumed the films are perfectly uniaxially oriented. Strictly speaking, such an assumption may not be applicable in the actual sample, but some contribution from the other directions ($\epsilon_{\|}$ in the $\epsilon_{\perp}$ case, for example) should be taken into consideration.]

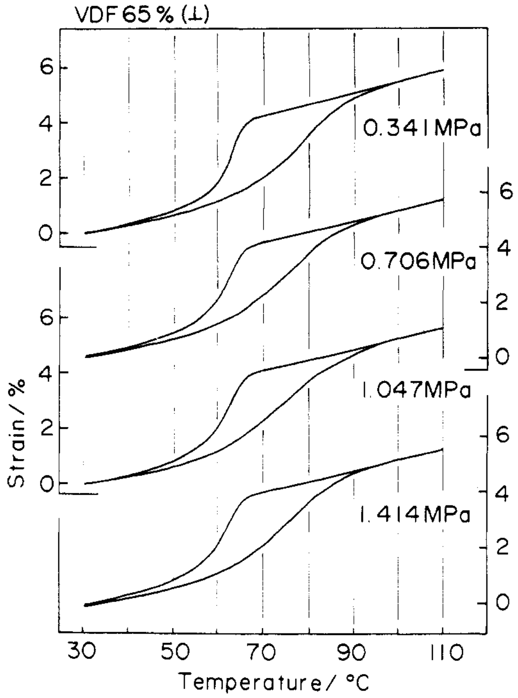

**Figure 6.** Stress dependence of the thermal expansion curve in ther lateral direction of the uniaxially oriented VDF 65% copolymer.

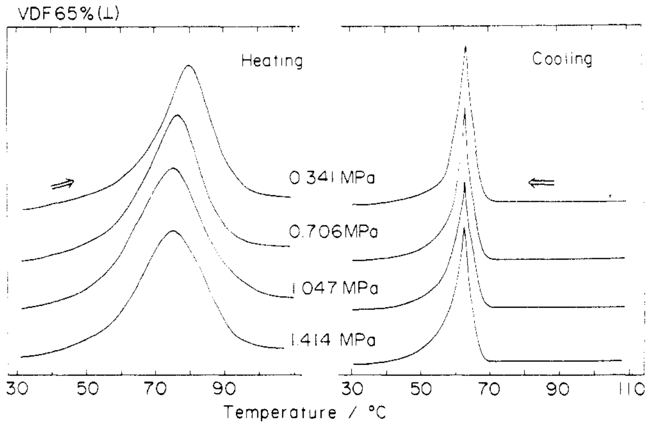

**Figure 7.** Differentiated curves of Figure 6 with respect to temperature.

**Stress Dependence of the Transition Point $T_c$.** Figure 6 shows the thermal expansion curves measured under the various tensile stresses applied in the direction perpendicular to the draw direction. By differentiating these curves with respect to temperature, as shown in Figure 7, a transition point was estimated from the peak position of the resultant curves.[6] Figure 8 shows the case of the unoriented sample. Thus revealed peak temperatures are plotted against the stress as shown in Figure 9, where the three cases of the parallel, perpendicular, and unoriented samples are compared with each other. As the stress is increased, the transition point is found to shift toward the lower temperature side for all the three cases, although the magnitudes of the temperature shift are different from each other.

As likely as in the previous paper,[6] the thermodynamically derived Clausius–Clapeyron equation may be useful for the interpretation of this stress-induced transition temperature shift in the crystalline phase. Under the application of the external force field, the free energy of the system is changed: the free energy change per unit volume of crystal $d\bar{G}$ is given as follows under constant

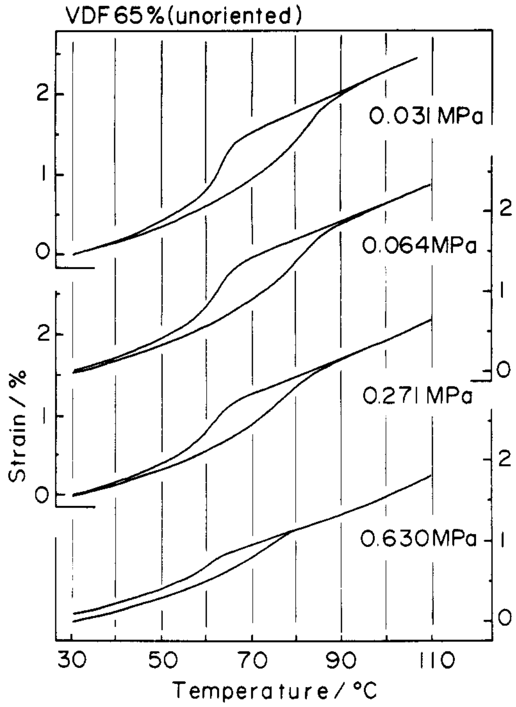

**Figure 8.** Stress dependence of the thermal expansion curve for the unoriented VDF 65% copolymer.

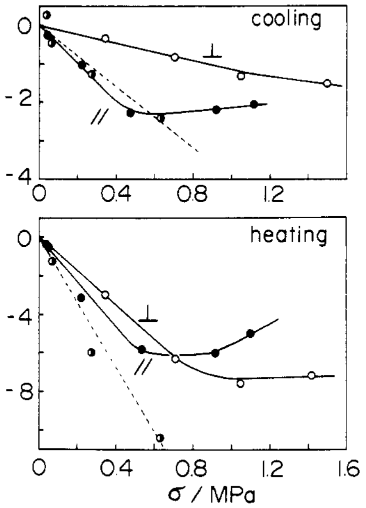

**Figure 9.** Stress dependence of the transition point observed for the oriented (‖ and ⊥) and unoriented (- - -) VDF 65% samples.

electric field strength

$$d\bar{G} = -\bar{S}\,dT - \sum_{i=1-3} \epsilon_{ci}\,d\sigma_{ci} \tag{5}$$

where $\bar{S}$ is an entropy, $T$ is a temperature, and $\epsilon_{ci}$ and $\sigma_{ci}$ are the strain and stress components of the crystal, respectively. In order to develop this equation, we need to obtain a relation among the $\epsilon_{ci}$ and $\sigma_{ci}$. The process is just the same as in the previous paper.[6] In the present paper, therefore, the details on such a derivation of equations will not be mentioned but only some comments are described below. First of all, it is assumed that the mechanical series model is applicable also to the direction perpendicular to the draw axis; i.e., $\sigma_{c1} = \sigma_{a1}$, where $\sigma_{c1}$ and $\sigma_{a1}$ are the stresses of the crystalline and amorphous phases in the 1 direction or the lateral direction. Since the crystallite is connected to the amorphous phase, the sides of the crystallite are not necessarily free of stress, but the stress tensor components $\sigma_{c2}$ and $\sigma_{c3}$ also work on the crystallite as inner stress, where the 3 axis is parallel to the draw axis. These assumptions and the other necessary conditions will be summarized as follows: (i) concerning the strains at the boundary, $\epsilon_{c3} = \epsilon_{a3}$ and $\epsilon_{c2} = \epsilon_{a2}$; (ii) concerning the stresses at the boundary, $\sigma_{c3} + \sigma_{a3} = 0$, $\sigma_{c2} + \sigma_{a2} = 0$ (stress-free sides) where the degree of crystallinity is assumed as 0.5, and $\sigma_{c1} = \sigma_{a1}$ (series model); (iii) concerning the Poisson's ratios, $\nu_{13} = \nu_{23} = \nu$, $\nu_{21} = 0.5$, and $\nu_a = 0.5$; and (iv) concerning the Young's modulus, $E_3 = 1/s_{33}$, $s_{11} = s_{22} = s_{a11}$, and $E_a = 1/s_{a11} = 1/s_{a22} = 1/s_{a33}$. Under these conditions, the relations among the stress, $\sigma_{ci}$, and strain components, $\epsilon_{ci}$, of the crystallite and the stress of the bulk sample, $\sigma_1$, are obtained. When these relations are substituted into eq 5, $d\bar{G}$ is expressed finally as follows:

$$d\bar{G} = -\bar{S}\,dT - k\epsilon_{c1}\,d\sigma_1 \tag{6}$$

Here $\epsilon_{c1}$ is the thermal strain in the direction 1 perpendicular to the $c$ axis of the crystallite and

$$k = 1 + q_1/q_2 \tag{7}$$

Here

$$q_1 = [E_3 - 2\nu E_a][9E_3^{\,3} + 8\nu^3E_a^{\,3} + (54\nu + 40)E_aE_3^{\,2} - (52\nu^2 - 16\nu)E_3E_a^{\,2}]$$

and

$$q_2 = [15E_3^{\,2} - 28\nu^2E_a^{\,2} + 16E_3E_a][7E_3^{\,2} - 4\nu^2E_a^{\,2} + 4(2 - \nu)E_3E_a]$$

In these equations $\nu$ is the Poisson's ratio ($=\nu_{23}$) of the crystalline region, and $E_3$ and $E_a$ ($=E_1 = E_2$) are the Young's moduli of the crystalline and amorphous regions, respectively, as described above. At the transition temperature, the free energies of the LT and HT phases are equilibrated to each other, i.e.

$$d\bar{G}_{LT} = d\bar{G}_{HT} \tag{8}$$

and then, when eq 6 is used, the following equation is finally obtained:

$$dT_c/d\sigma_1 = -k_{HT}\Delta\epsilon_{c1}/\Delta\bar{S} \tag{9}$$

Here $\Delta\epsilon_{c1}$ is the dimensional change in the lateral direction of the crystallite at the transition point and $\Delta\bar{S}$ is an entropy change between the LT and HT phases ($=\bar{S}_{HT} - \bar{S}_{LT}$). For the parameters in these equations, the following numerical values are used as explained in the previous paper:[6] $E_a = 2$ GPa, $E_3 = 15$ GPa, $\nu = 4.5$, $\Delta\bar{S} = -12.4 \times 10^4$ J/K m$^3$, and $\Delta\epsilon_{c1} = -0.075$ (see Figure 4) in the cooling process. (The value of $\Delta\bar{S}$ employed here is the one obtained for the unoriented sample[7] with a correction for the degree of crystallinity. Although the $\Delta\bar{S}$ in the oriented sample might be, strictly speaking, different from it, we use this value also in the calculation here as the first approximation.) As a result we obtain

$$dT_c/d\sigma_1 = -0.48 \text{ K/MPa} \tag{10}$$

For the stress applied along the draw direction, we already have the calculated result of

$$dT_c/d\sigma_3 = -5.7 \text{ K/MPa} \tag{11}$$

If an apparently averaged shift between $dT_c/d\sigma_1$ and $dT_c/d\sigma_3$ is assumed to appear for the unoriented sample, then we have

$$dT_c/d\sigma = -2.2 \text{ K/MPa} \tag{12}$$

These calculated values are in good agreement with the actually observed values of ca. −1.0 K/MPa (⊥), −4.6

K/MPa (‖), and −3.9 K/MPa (unoriented), respectively.

At this stage we will consider the physical reason for the negative values of the $\mathrm{d}T_c/\mathrm{d}\sigma_i$ ($i$ = 1, 3, and unoriented). The polymer substance is often treated as one-dimensional linear chain system. But the actual polymer crystal is a three-dimensional system with mechanically anisotropic properties. As stated in the previous paper,[6] the tensile stress may deform not only the crystallites but also the surrounding amorphous matrix, which affects in the feedback way the mechanical deformation of the crystalline region. In other words, the boundary condition at the crystal–amorphous interface must be necessarily taken into account in the discussion of the mechanical behavior of the three-dimensionally anisotropic system. Such an interface effect is included finally in a form of the parameter $k$ in eq 9 (and in eq 17 in the previous paper), which is a function of the Young's moduli of the crystalline and amorphous phases and the Poisson's ratio $\nu$ of the crystalline region. The sign of the $\mathrm{d}T_c/\mathrm{d}\sigma_i$ is determined by the sign of the $k$, in particular by the value of $\nu$: The large value 4.5 of $\nu$ results in the negative shift of both the parallel and perpendicular directions. Such a large value of $\nu$ is characteristic of the polymer chain system, the reason for which has been already discussed in the previous paper.[6]

In this way we can interpret the stress-induced shift of the transition point based on the modified Clausius–Clapeyron equation both in the parallel and pependicular directions. But we still have an unresolved problem at this stage; why is the temperature shift different between the heating and cooling processes? This might be only apparent and due to the broadness of the transition behavior in the heating process, as seen in Figure 2, where the dimensional change in the cooling process is very sharp compared with that in the heating process. The reason why we compared the observed and calculated values of the temperature shift *in the cooling process* stands on this situation. Such a difference in the thermomechanical behavior between the heating and cooling processes becomes smaller for the copolymer samples of the higher VDF content as seen in the case of VDF 73% copolymer.[6] Therefore we may consider that the difference may be originated from the characteristics of the crystalline phase transition itself. In fact, the X-ray diffraction and the infrared and Raman spectral data indicate that the intensity change also differs between the heating and cooling processes.[1] The sharpness of the transition behavior is dependent on various factors including the VDF content of the copolymers, the heat-treatment conditions, the casting conditions, etc.[1,8] In the present case, where the copolymer sample with a specific VDF content is treated under fixed annealing conditions, however, these factors are not applicable. One of the possible factors might be a difference in the initial state of the transition. In the above calculation, the transition has been assumed, as a rough approximation, to occur between the LT and HT phases. Strictly speaking, however, the trans phase of the VDF 65% sample at room temperature consists of the mixture of the regular LT phase and the irregular cooled (CL) phase.[1,2] (Some authors assign this cooled phase as the mixture of the regular trans phase and the irregular gauche phase[3,4,9]). Therefore, we may think that in the cooling process the transition occurs from a unique gauche phase to the trans phase, but in the heating process the transition to the high-temperature gauche phase occurs from the mixture of the LT and CL phases. Such a difference in the transition behavior between the heating and cooling processes is considered to result in the large difference in sharpness of the thermal expansion curves. The external tension induces the forced transition from the CL to the LT phases. Therefore, the relative content of the CL and LT phases is dependent on the applied stress. That is to say, the broadness of the transition in the heating process might be changed depending on the applied external force, influencing the apparent transition–temperature shift under the external tensile stress.

## Conclusions

In the present paper we have confirmed that the structural phase transition occurring in the crystalline region of the ferroelectric VDF–TrFE copolymers is reflected directly on a bulk property such as thermal expansion of the bulk sample in both parallel and perpendicular directions to the draw axis, as well as in the unoriented samples. This intimate relation may be detected also for the properties such as elasticity, piezoelectricity, dielectricity, and so on, although the direct measurements of these properties in the crystalline region have not yet been carried out as successfully as the measurement of the dimensional change discussed in the present paper.

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