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Notes

Detection of Sharp DSC Peak during the Phase Transition from the Low-Temperature Phase to the Cooled Phase of Vinylidene Fluoride−Trifluoroethylene Copolymers

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Introduction

The structural changes occurring in the ferroelectric phase transition of vinylidene fluoride−trifluoroethylene (VDF−TrFE) copolymers have been investigated widely with an aim to clarify the essential features of the transitional mechanism.[1−12] The transition is associated with the three types of crystalline phases: the low-temperature (LT) phase, the high-temperature (HT) phase, and the cooled (CL) phase. The transitional behavior depends largely on the type of samples used in the experiments. The copolymer sample with VDF content 70−80 mol % shows a clear and discontinuous first-order transition between the LT and HT phases at relatively high temperature close to the melting point. For the sample of VDF content less than 50%, on the other hand, the transition occurs apparently continuously between the CL and HT phases in a second-order manner. The VDF 50−60% samples show more complicated transitional behavior.[1−8] For the unoriented sample, the reversible transition is observed between the CL and HT phases. But, in the oriented sample, the LT phase transforms at first to the CL phase and then to the HT phase. This HT phase is cooled to the CL phase, not to the LT phase. Once the CL phase is obtained, the reversible transformation is seen between the CL and HT phases. The LT phase can be obtained again by applying the tension to the CL phase at room temperature.

The LT phase takes the structure of all-trans-zigzag chains packed in a regular way just like in PVDF form I.[1] The CL phase is characterized by an observation of the tilting phenomenon in the X-ray fiber pattern. The CL phase was proposed to take a kind of superstructure of the LT phase, in which the trans-zigzag chains are packed together to form a domain, and these domains are gathered to form a whole crystallite through the linkage of trans−gauche defects between the neighboring domains along the chain direction.[1,7,8] This phase was also proposed to take a molecular structure containing both the regular trans-zigzag sequence and the disordered helical sequence.[3−6]

The difference in the phase transitional behavior between the LT and CL phases may be considered to come from such a difference in the orderliness of the structure. The gauche defect contained in the CL phase may work as a trigger for the trans-to-gauche conformational change, making the phase transition easier and continuous. On the other hand, the regular trans-zigzag chains require a high barrier to jump from the trans to gauche forms, leading to the transition at higher temperature. In the copolymer samples of VDF 50−60%, the trans-zigzag chains transfer once to the irregular trans form of the CL phase, which changes relatively easily to the HT phase of the random gauche conformation. This large structural change between the regular trans conformation of the LT phase and the irregular trans conformation in the CL phase is expected to require a large thermal energy. But no thermal data have been reported so far about the transition between the LT and CL phases. This type of thermal data is also important to reconfirm the existence of the disordered CL phase itself from the thermodynamic point of view. Recently, we have found a quite sharp thermal energy change in the LT-to-CL phase transition, as reported in this paper. Besides, the relation between these thermal behaviors and the trans-to-gauche conformational change during the phase transition between the LT and CL phases is confirmed by measuring the temperature dependence of the X-ray diffraction and Fourier transform Raman spectra.

Experimental Section

Samples. The sample used in the experiments was the copolymer with VDF 55 mol % content. The unoriented samples were prepared by cooling the melt slowly to room temperature. The uniaxially oriented samples were prepared by stretching the films cast from the acetone solution by 4−5 times the original length at room temperature. The samples were annealed above T_c and cooled to room temperature, giving the samples of the CL phase. The pure LT phase was prepared by applying the tension to the CL-phase sample at room temperature.

Measurements. The differential scanning calorimetry (DSC) measurements were performed at the heating rate 2 °C/min by using a Seiko DSC 120 controlled by a SSC200H disk station. The X-ray fiber diagrams were taken by using an imaging plate system with a Mo−Kα radiation at $\lambda = 0.710\ 73$ Å (DIP1000 of Mac Science Co. Ltd., Japan). The temperature dependence of the fiber diagrams was measured by setting the sample into the homemade heater. The temperature of the sample was monitored by contacting a thermocouple directly with the sample. The Fourier transform Raman spectral measurements were carried out with the 180° scattering geometry. The spectra were taken by using a BIO RAD FTS-60A/896 FT-Raman system, where the 1064 nm line from a Nd:YAG laser was used as an excitation source. The data were taken at a resolution of 2 cm^{-1}.

Results and Discussion

The oriented VDF 55% samples annealed above the ferroelectric transition point T^o_c show a tilting phenom-

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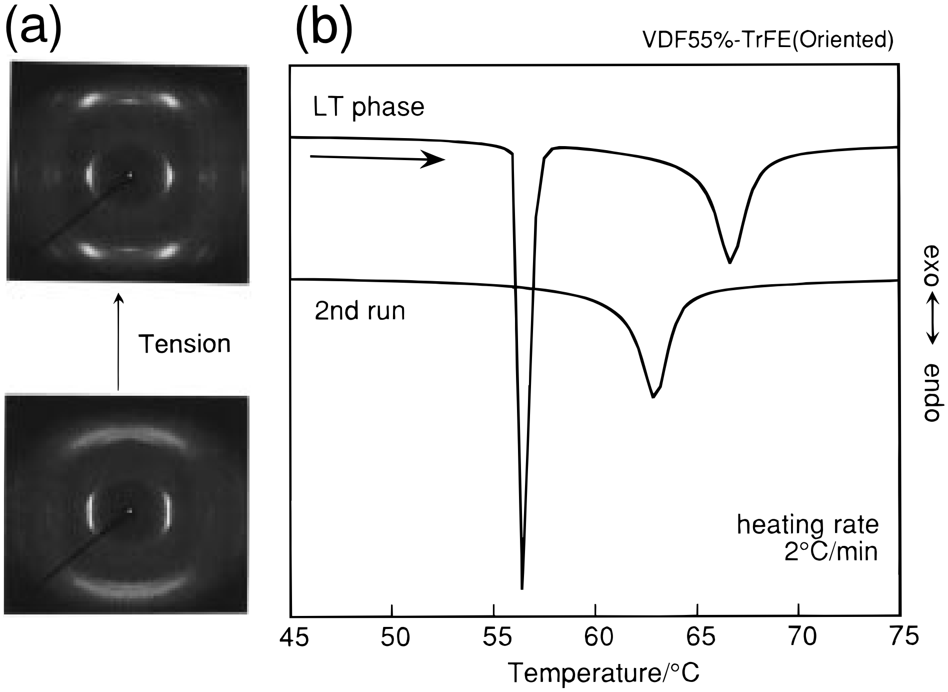

Figure 1. (a) X-ray fiber diagrams of VDF 55% copolymer taken at room temperature. (upper) The low-temperature phase prepared by stretching the uniaxially oriented cooled-phase sample strongly at room temperature by about several percent strain. (lower) The cooled phase which was obtained by annealing the low-temperature phase at 140 °C. (b) DSC thermograms measured for the uniaxially oriented low-temperature phase of the VDF 55% copolymer. (upper) The first run. (lower) The second run which was made after cooling the sample of the first run to room temperature.

enon characteristic of the CL phase. These annealed samples are transferred from the CL phase to the regular LT phase when a tensile stress is applied at room temperature. Actually, as seen in Figure 1a, the uniaxially oriented VDF 55% sample was tensioned at room temperature after annealing at 140 °C (above the transition temperature to the HT phase), giving a clear X-ray fiber pattern of the LT phase. Figure 1b shows the DSC thermograms taken for the uniaxially oriented LT phase of the VDF 55% sample. The heating of this LT phase was found for the first time to give a quite sharp single endothermic peak at about 57 °C, followed by a broad and small endothermic peak around 66 °C. The enthalpy change ΔH at 57 °C was estimated to be 5.7 mJ/mg, and that at 66 °C was 5.7 mJ/mg. After heating to 80 °C, the sample was cooled to room temperature and heated again in the DSC pan. The thermogram during the second run is given in the lower side of Figure 1b, where only a broad and small endothermic peak can be seen. The ΔH of this peak was 5.7 mJ/mg.

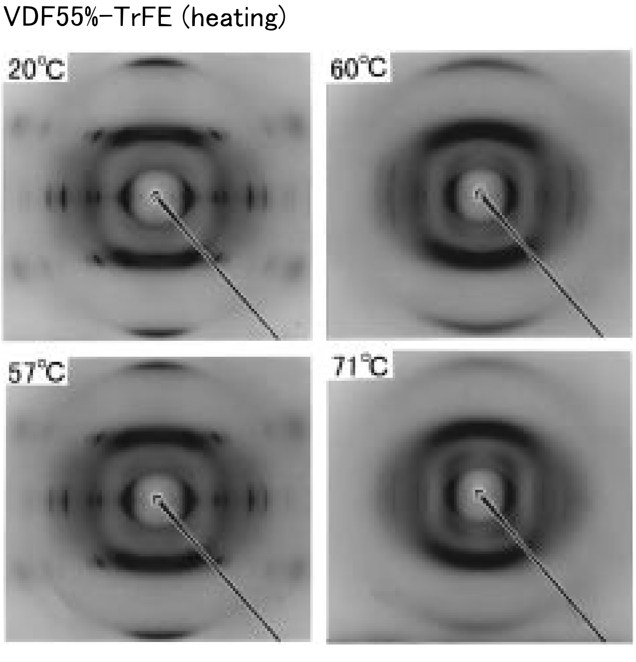

Figure 2. Temperature dependence of the X-ray fiber diagram taken for the uniaxially oriented VDF 55% sample in the heating process. The starting sample was the low-temperature phase.

To clarify the structural change occurring during these endothermic peaks, the temperature dependence of the X-ray fiber pattern was measured as reproduced in Figure 2. The starting sample was the LT phase at 20 °C. Heating to 57 °C still gave the LT phase, while it changed drastically to the pattern of the CL phase at 60 °C, where the fiber pattern showed the tilting phenomenon with the shift of the equatorial and the layer line reflections upward and downward from the original horizontal lines. Heating to 71 °C gave the fiber pattern of the HT phase with the tilting phenomenon still kept to some extent. Figure 3a shows the change of the equatorial profile taken from the fiber diagram of Figure 2. The temperature dependence of the peak position of the equatorial (200, 110) reflection is shown in Figure 3b in comparison with the observed DSC curve. A more detailed description of the X-ray diffraction data is made in Figure 4, where the temperature dependence of the integrated intensity, half-width, and lattice (or *d*) spacing is shown. In the temperature region of the quite sharp endothermic peak around 57 °C, the reflection of the LT phase changes discontinuously into that of the CL phase, just when the intensity, half-width, and *d* spacing increase drastically. The CL phase reflection shifts continuously toward the HT phase reflection in the region of the broad DSC peak

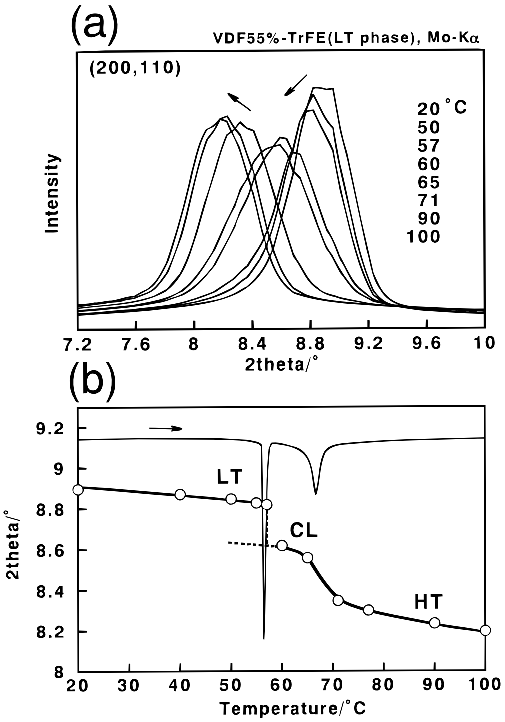

Figure 3. (a) Temperature dependence of the (200, 110) X-ray reflection profile measured for the uniaxially oriented low-temperature phase of VDF 55% copolymer sample. (b) Temperature dependence of the scattering angle estimated for the (200,110) reflection in comparison with the DSC thermogram (the heating process).

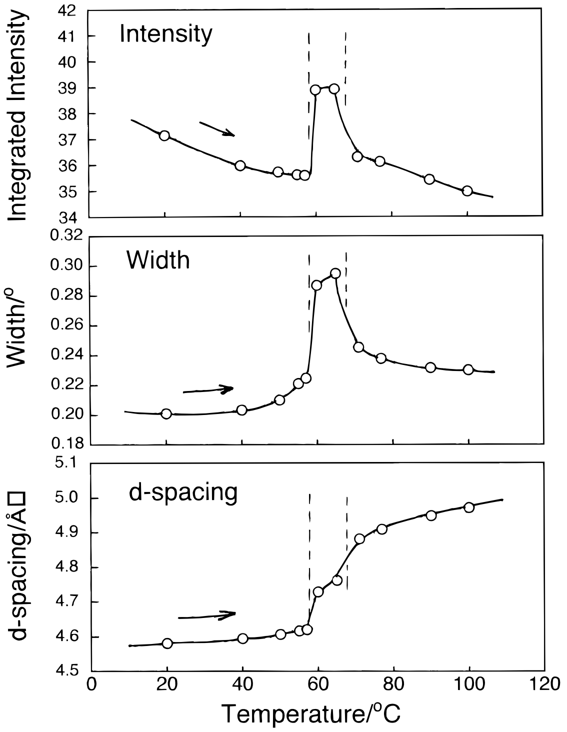

Figure 4. Temperature dependence of the integrated intensity, half-width, and *d* spacing evaluated from Figure 3a for the VDF 55% copolymer sample.

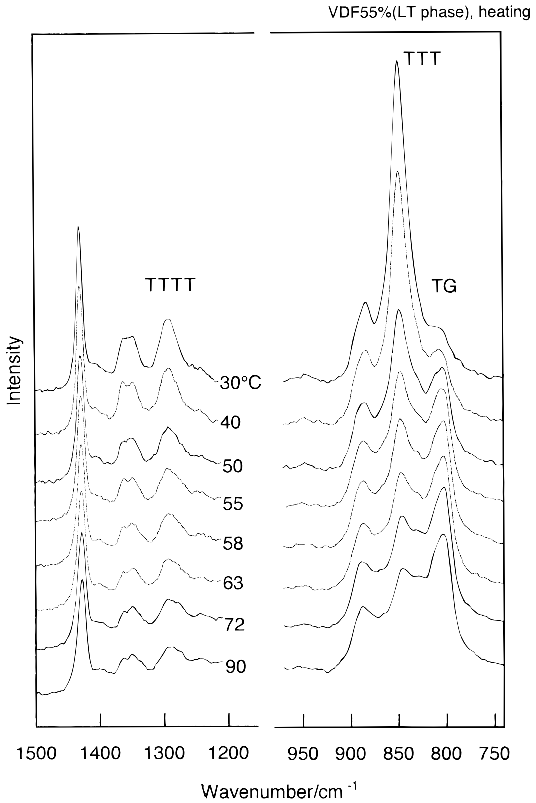

Figure 5. Temperature dependence of the FT-Raman spectra measured for the VDF 55% copolymer sample starting from the LT phase.

around 66 °C. The half-width decreases simultaneously, suggesting a change in the size of the X-ray coherent domain or a change in the structural disorder as already reported.[11] In the second heating process after cooling from the HT phase, the X-ray pattern changed from that of the CL phase to that of the HT phase. The enthalpy change ΔH observed around 66 °C, 5.7 mJ/mg, was essentially the same between the first and the second runs, supporting an occurrence of the same kind of phase transition from the CL to the HT phase. The enthalpy change between the LT and CL phases at 57 °C is accidentally the same as that between the CL and HT phases. At the present stage it is difficult to interpret this ΔH from the viewpoint of structural change.

In parallel to these thermal and X-ray diffraction experiments, we performed the measurement of the FT-Raman spectra as a function of temperature. The band assignment had been established based on the vibrational analysis made for the various types of crystalline forms of PVDF homopolymer.[1] For example, the band at 1293 cm^{-1} is the CF$_2$ stretching of the long trans-zigzag sequence of the VDF segments. The band at 849 cm^{-1} is that of the short trans-zigzag sequence of the VDF segments. The 801 cm^{-1} band originates from the gauche form. Figure 5 shows the temperature dependence of the thus assigned Raman bands measured for the LT phase of the VDF 55% copolymer sample. In Figure 6 is compared the temperature dependence of the integrated intensities of these Raman bands with the DSC thermogram. The trans-zigzag bands decreased the intensity largely around the sharp peak of the DSC thermogram. The gauche band at 801 cm^{-1} increased the intensity. As the temperature was increased further, the trans bands decreased their intensities gradually and the gauche band increased in parallel. Combination of these spectral data with the X-ray diffraction data allows us to realize that the phase transition from the LT phase to the CL phase is accompanied by the partially occurring trans-to-gauche conformational change. In other words, the CL phase is generated by

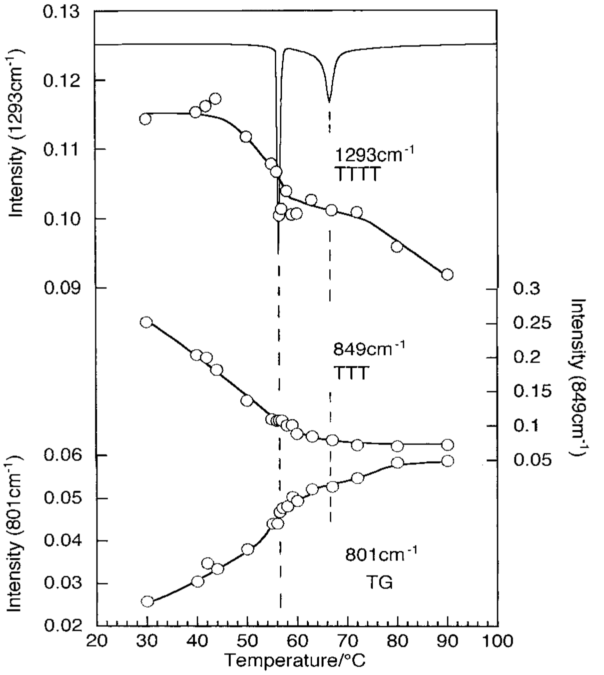

Figure 6. Comparison of the temperature dependence of the integrated intensities of the Raman bands shown in Figure 5 with the DSC thermogram of the VDF 55% copolymer sample.

introducing the gauche bonds into the regular all-trans-chain crystals of the LT phase; i.e., the CL phase has a crystal structure essentially similar to that of the LT phase but contains some gauche bonds, being probably also the origin of the tilting phenomenon of the zigzag chains.

In this way the sharp endothermic peak in the DSC thermogram and the generation of gauche bonds in the Raman spectra seem consistent with the structural image of the CL phase. But these data might be interpreted also on the basis of the structural model proposed by other groups:[3-6] the all-trans-zigzag chain transfers discontinuously to the chain conformation consisting of the trans-zigzag sequence and the disordered gauche sequence, and then this conformationally disordered chain transfers to the HT phase. From the point of view of the conformationally disordered chain conformation, these two structural images about the CL phase might be essentially the same. Anyway, however, more quantitative analysis of the X-ray diffraction data may be required to establish the crystal structure of the CL phase.

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