Correlated Changes in Meso- and Nano-Scale Hierarchical Structure of Vinylidene Fluoride-Trifluoroethylene Random Copolymers Investigated by Simultaneous Measurements of DSC and SAXS/WAXD Utilizing Synchrotron Radiation

H Masunaga¹,*, S Sasaki¹, M Takata¹,²,³, M Hanesaka⁴, K Tashiro⁴

¹Japan Synchrotron Radiation Research Institute (JASRI) / SPring-8, Sayo, Hyogo 679-5198, Japan;
²The RIKEN Harima Institute / SPring-8, Sayo, Hyogo 679-5198, Japan;
³Graduate School of Frontier Science, The University of Tokyo, Chiba 277- 8561, Japan;
⁴Department of Future Industry-oriented Basic Science and Materials, Graduate School of Engineering Toyota Technological Institute, Tempaku Nagoya 468-8511, Japan.
E-mail: masunaga@spring8.or.jp

ABSTRACT. Hierarchical structural features of Vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymers during the phase transition have been successfully investigated in detail by in-situ simultaneous measurements of DSC and SAXS/WAXD utilizing synchrotron radiation. In a heating process at a constant rate of 1 °C /min, a broad endothermic peak was measured for a VDF-TrFE copolymer from ca. 75 °C to ca. 135 °C. On the other hand, WAXD data indicated that the phase transition from the crystal form II to the high-temperature (HT) phase began to occur at ca. 105 °C. With an increase in temperature from ca. 75 °C to ca. 105 °C (temperature region A), lamellar staking distance (long period) and lamellar thickness evaluated in SAXS data analyses slightly increased though the crystallite size (the lateral dimension of the lamellae) was almost constant. The (110) reflections of the crystal form II gradually decreased in integrated intensity and scattering from the amorphous region increased instead, which implied that lamellae in crystal form II became partially disordered before the phase transition.

1. Introduction
A part of vinylidene fluoride-trifluoroethylene (VDF-TrFE) random copolymers exhibits the phase transition between the crystal form II and the high-temperature (HT) phase at Curie transition temperature.¹⁻³ The crystal form II consists of the packing in which chain conformation is the trans-gauche(+) -trans-gauche(-). The HT phase consists of the molecular chains with statistical distribution of trans and gauche bonds along the chain axis, and these chains rotate violently around the chain axis due to the thermally activated motions. In the phase transition temperature region where the trans-to-gauche conformational change of chains occurs in the crystalline lattice, the thickness of stacked lamellae drastically increased. However, the relationship between the nano- and meso-scale structural changes has not been revealed in detail.
The purpose of this study is to clarify the hierarchal structure change connected with so-called crystallographic phase transition of a VDF-TrFE random copolymer. Differential scanning calorimetry (DSC) can confirm temperature ranges of phase transitions. By small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements utilizing synchrotron radiation, lamellar and crystal structures can be investigated in the in-situ heating process, respectively. Therefore, DSC/SAXS/WAXD simultaneous measurements were efficient for clarifying the entire structural change from the nano scale to the meso scale in the so-called phase transition correlation between a hierarchal structure change and a heat flow. It is necessary to utilize synchrotron radiation for tracing the details of structural changes. In the present paper we will report the experimental results on the melt-quenched sample of VDF 82% copolymer. We paid attention to slight changes on each hierarchal structure scale in the beginning of the first endothermic peak in a heating process, and considered the phenomenon to relate with chain activation.

2. Experimental Section

2.1. Sample:
Vinylidene fluoride–trifluoroethylene random copolymer of VDF 82 molar % used as a sample. The sample was supplied by Daikin Kogyo Co., Japan. The sample was melted at 200°C and rapidly quenched into liquid nitrogen, which contained mostly the crystal form II. The thus melt-quenched VDF 82% was used for measurements.

2.2. DSC/SAXS/WAXD Measurements:
DSC, SAXD and WAXS measurements were performed simultaneously at BL40B2 beamline in SPring-8, Japan. The wavelength of incident X-ray beam used in this study was 1.5 Å. The 2D-WAXD pattern was taken with a BAS-MS2025 imaging plate (IP, FUJIFILM Corp., Japan) set into an original IP holder. The 2D-SAXS signal from the sample passed through a hole with an 8 mm diameter, which was opened at the center of IP for WAXD, and it was detected with an IP installed in an R-AXIS IV++ IP System (Rigaku Co., Japan). An FP84HT hot stage where the detector-side window of the hot stage was customized in opening an angle for measuring the X-ray scattering up to the scattering angle 2θ and an FP90 control unit (Mettler-Toledo International Inc., U.S.A.) were utilized for DSC measurements. The DSC/WAXD/SAXS simultaneous measurement was performed for every 5 min at a temperature increased by 5°C step in the heating process. The DSC thermogram was started to be recorded at a heating rate of 1°C/min from ca. 30°C.

The SAXS data were analyzed on the basis of the two-phase model consisting of crystal and amorphous phases using the one-dimensional electron density correlation function of the SAXS data. A long period which is a lamination interval of lamellar crystals and a crystal thickness estimated here were defined L and dc, respectively. The crystallite size was estimated from the reflection width on the basis of Scherrer’s equation, where the instrumental line width was estimated on the basis of the diffraction data of CeO2 powder (NIST standard sample).

3. Results and Discussion

The change in the lamellar morphology was monitored by the SAXS measurements. The temperature dependence of the SAXS profiles corrected for the Lorentz factor (I(q)q²) at 40.5, 105.5, 125.5, 145.5, 155.5°C is shown in Figure 1. Here, q is the magnitude of the scattering vector, and q = 4πsinθ/λ, where 2θ is a scattering angle, and λ is a wavelength. The peak observed at about q=0.2 nm⁻¹ corresponds to a long period. The peak position was sift slightly to a lower angle and the intensity increased under 145.5°C. The peak position largely shifted to a low angle upper 145.5°C, and the peak disappeared at 155.5°C. It is shown that a long period spread gradually under 145.5°C and spread rapidly near 155.5°C.

Figure 2 shows that the WAXD profiles measured for the sample in the heating process. The peaks about 2θ=16, 17, 18, 25, 25.5° are assigned to the reflections of (010)II, (200)II, (110)II, (201)II.
As the temperature is increased, the intensity for the reflections of (110)$_{II}$ and (201)$_{II}$ decreased remarkably at about 125.5°C. The peak near $2\theta = 17^\circ$ shifted to lower angle side with slight change in intensity. In higher temperature range only this peak was observed and disappeared above the melting point. As the temperature is increased, the integral peak intensity near $2\theta = 18^\circ$ became small. This indicates that the crystal form II transforms to the HT phase near 125.5°C before melting. At the DSC thermogram taken at the same time, an endothermic peak observed in a wide temperature range from 75°C to 135°C is assigned to the crystalline phase transition from the crystal form II to the HT phase, while the sharp endothermic peak at 151°C corresponds to the melting point. The transition occurs in a wide temperature range with a relatively large enthalpy change. Here, the temperature range from 105°C to 135°C is defined as a temperature region B, the temperature upper 135°C is defined a temperature region C. Respectively, they are the temperature before the HT phase appears, the temperature range in which the HT phase increases, and the temperature which a crystals are melting. The endotherm is slightly observed between 75°C - 105°C, and this temperature range is defined as a temperature region A.

In Figure 3, the temperature dependences of the $L$, $d_c$, the size of the diagonal direction of a crystal lattice of a crystal form II and a HT phase in the lateral dimension of lamellae, integrated peak intensities of (110)$_{II}$, (100)$_{HT}$, and amorphous halo evaluated from WAXD and SAXS data are compared with the DSC thermogram taken simultaneously. In the temperature region A, the crystallite sizes corresponding to the lateral dimension of lamellae were almost constant, the $d_c$ increased slightly, the integrated intensity of the crystal form II gradually decreased, the endotherm observed above 75°C slightly. In the temperature region B, the $d_c$ increased remarkably, the crystallite size of the crystal form II decreased, and the decrease in the integral intensity of the crystal form II and increase of the HT phase and the endotherm corresponding to them are observed. In the region C, the drastic structural change was observed before or after a melting temperature. The $L$ increases, the crystallite size of the crystal form II decreased, the integral intensity of the HT phase decreased, and the intensity of amorphous halo increased drastically.

The phenomenon in the temperature region A was considered as follows; the intermediate phase among the crystal form II and the amorphous phase changes to the amorphous at lower temperature in which the HT phases appeared. In the temperature region B, chains near the surface of lamellae would order and a part of lamellae change into amorphous due to the activated thermal motion of the molecular chains along the chain axis. In the temperature region C in which the thermal motion of the molecular chains is activated along the chain axis, nano-scale crystals would be melting and meso-scale lamellar morphology would change.

4. Conclusions
In the present paper we have described the relationship between morphological change and crystal structure change occurring during the heating process of melt-quenched VDF 82% copolymer sample by using the newly-built-up DSC/WAXD/SAXS simultaneous system with highly brilliant synchrotron X-ray beam of SPring-8. In the temperature from ca. 75°C to ca. 105°C (temperature region A), lamellar staking distance and lamellar thickness evaluated in SAXS data analyses slightly increased though the crystallite size was almost constant. The integrated peak intensities of (110) reflections for crystal form II gradually decreased and scattering from the amorphous region increased instead, which suggested that lamellae in crystal form II became partially disordered before the phase transition.

Acknowledgements. The authors thank Dr. Ohta, Dr. Inoue and Dr. Yagi, Japan Synchrotron Radiation Institute/SPring-8 for their helpful discussion about the DSC measurements. The DSC/WAXD/SAXS simultaneous measurements were performed at a synchrotron radiation system SPring-8 with approved numbers 2006A1128 and 2006B1100. They thank also Daikin Kogyo Co. Ltd., Japan for their kind supply of VDF 82% sample.
Figure 1. Temperature dependence of SAXS profiles corrected for the Lorentz factor measured for the melt-quenched VDF 82% sample.

Figure 2. Temperature dependence of WAXD profiles measured for VDF 82% sample. The reflections (010)_{II}, (200)_{II}, (110)_{II}, (201)_{II}, (111)_{II} are for the crystal form II. A peak observed near 17° observed at 145°C is the reflection (100) of the HT phase.

Figure 3. Temperature dependences of $L$ and $d_c$ estimated from the SAXS data, the crystallite size estimated from (110)_{II}, (100)_{HT}, WAXD integrated intensities of (110)_{II}, (100)_{HT} and amorphous halo, and DSC thermogram measured for VDF 82% sample in the heating process.

References
[1] Tashiro K, In Nalwa, HS editor, 1995 Ferroelectric polymers New York: Marcel Dekker: chapter 2
[2] Lovinger A J 1985 Jpn. J. Appl. Phys. Suppl. 24 18
[3] Tashiro M, Kobayashi M 1985 Polymer Prepr. Jpn. 34 2241
[4] Masunaga H, Sasaki S, Tashiro K, Hanesaka M, Takata M, Inoue K, Ohta N, and Yagi 1997 Polym. J. 39 1281
[5] Stroble, G. 1996 The Physics of Polymers, Springer 408
[6] Hasegawa R, Takahashi Y, Chatani Y, Tadokoro H 1972 Polymer J. 3 600
[7] Tashiro K, Takano K, Kobayashi M, Chatani Y, Tadokoro H 1984 Polymer 25 195
[8] Tashiro K, Tanaka R 2006 Polymer 47 5433