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Structural correlation between crystal lattice and lamellar morphology in the ferroelectric phase transition of vinylidene fluoride–trifluoroethylene copolymers as revealed by the simultaneous measurements of wide-angle and small-angle X-ray scatterings

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Abstract

Intimate correlation has been detected between the crystal structure change and the morphological change of stacked lamellae in the ferroelectric phase transition of vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers on the basis of simultaneous measurement of wide-angle (WAXS) and small-angle X-ray scattering (SAXS) patterns in the heating process. The VDF content of copolymers investigated was 65 and 73 mol%. For both of the copolymers, a cold-drawn sample showed the WAXS pattern of the regular low-temperature phase and the four-points SAXS pattern corresponding to the stacking structure of lamellae tilted by about 30° from the draw axis. When the sample was heated above the Curie transition point T_c, the low-temperature phase changed to the conformationally-disordered paraelectric high-temperature phase and the stacked lamellae reoriented into the direction closer to the draw axis. It was also found that the thickness and long period of the lamellae increased remarkably above T_c. These large changes in lamellar stacking mode occurred in parallel with the trans-to-gauche conformational change of the molecular chains in the crystal lattice. In this way, the morphological change was found to relate intimately with the crystal structural change, both of which are considered to be caused commonly as a result of the trans–gauche conformational change and the translational motion of the thermally-activated molecular chains along the chain axis.

Keywords: Vinylidene fluoride–trifluoroethylene copolymers; Wide-angle X-ray scattering; Small-angle X-ray scattering

1. Introduction

Contrast to the case of ionic crystals, ferroelectric phase transition of vinylidene fluoride–trifluroethylene (VDF–TrFE) copolymers is quite unique in such a point that the transition from ferroelectric polar crystal phase to paraelectric non-polar crystal phase is induced through the large and cooperative change in the chain conformation between trans and gauche forms [1,2]. The three types of crystalline phase participate more or less in this transition and they make the transitional phenomena complicated. These three types of crystalline phase are the ferroelectric low-temperature (LT) phase, the paraelectric high-temperature (HT) phase, and the cooled (CL) phase. As shown in Fig. 1(a), the LT phase consists of the regular packing of planar–zigzag chains with the CF_2 dipoles oriented along the *b*-axis [1]. The X-ray diffraction pattern of the uniaxially-oriented LT phase sample is essentially the same as that of poly(vinylidene fluoride) (PVDF) crystal form I. In the HT phase, the conformationally-disordered chains are packed in a hexagonal packing mode and these chains rotate violently around the chain axis, resulting in the non-polar structure. As seen in Fig. 1(c), the X-ray diffraction pattern is characterized by the layer lines corresponding to the 2.3 Å repeating period of $TG\bar{T}\bar{G}$ (or $T_3GT_3\bar{G}$) sequence, similar to those of PVDF forms II and III, although the reflections are more diffuse than the latter two cases. The X-ray diffraction diagram of the CL phase is similar to that of LT phase as shown in Fig. 1(b), but the reflections are shifted upward or downward from the horizontal lines due to the effect of tilting phenomenon of the planar–zigzag chains from the draw direction [1]. The whole X-ray pattern is diffuse because of the structural defect due to the contribution of gauche bonds in

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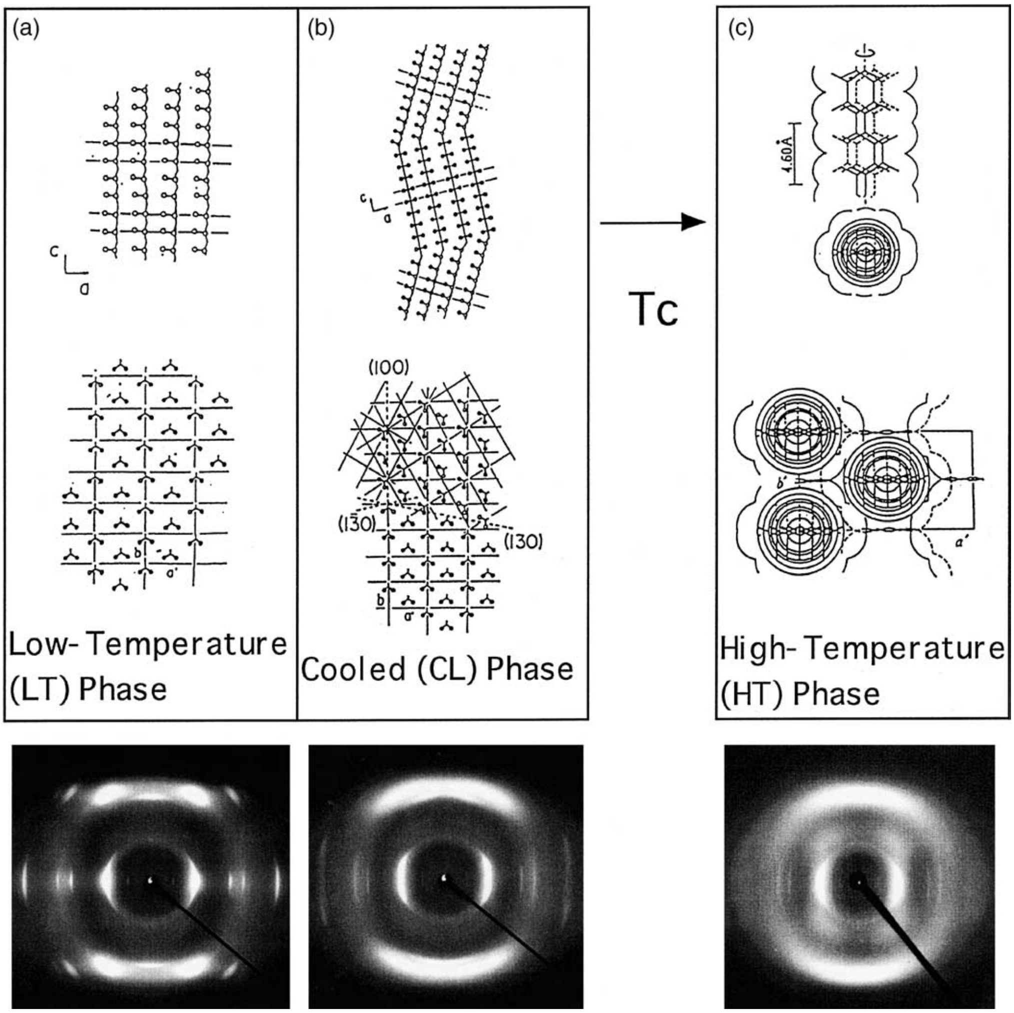

Fig. 1. Crystal structures of vinylidene fluoride–trifluoroethylene copolymer [1]: (a) ferroelectric low-temperature phase, (b) cooled phase, and (c) paraelectric high-temperature phase. The X-ray diffraction diagrams of these phases are also shown, where the vertical axis is parallel to the draw direction.

the trans sequences. These gauche defects cause the tilting of the trans segments and the formation of a superlattice structure consisting of small domains with essentially the same packing structure as that of LT phase. The CF_2 dipoles of individual trans–zigzag chains are oriented along the *b*-axis in each domain, but the total sum of dipole moments or the electric polarization of each domain is oriented along the 60° different directions, as illustrated in Fig. 1(b). When we investigate the X-ray diffraction pattern of the CL phase, we notice the very diffuse scatterings near the positions corresponding to the layer line reflections of 2.3 Å period observed for the HT phase. This is considered to come from the existence of gauche defects.

The transition behavior between these three crystalline phases is changed depending on the VDF content [1,2]. In the case of VDF 50–55% copolymer, the LT phase transforms to the CL phase on the way of heating process to the HT phase above the Curie temperature T_c, being detected clearly as the remarkably large endothermic peak (LT to CL) in the DSC thermogram followed by a smaller endothermic peak (CL to HT) [3]. When the sample is cooled down below T_c, the HT phase does not go back to the original LT phase but the CL phase is stabilized at room temperature. The LT phase can be obtained by stretching the CL phase or by applying the external electric field to it. For VDF 73% copolymer, a clear first-order transition can be observed between the LT and HT phases. The intermediate transition behavior is observed for VDF 65% copolymer, where the LT phase transfers mainly into the HT phase but partly into the CL phase and then to the HT phase.

In this way, the transition behavior is dependent on the VDF content. This comes mainly from the VDF content dependence of the trans–gauche conformational stability and the regularity of CF_2 dipole array in the crystallite, as discussed in a series of papers based on the molecular dynamics calculation [4–8]. The phase transition is also affected sensitively by the heat treatment condition [9–15]. For example, as shown in Fig. 2, the DSC thermogram of VDF 65% copolymer changes systematically and sensitively depending on the annealing temperature [10]. Multiple peaks are observed and the position and relative height of these peaks change remarkably depending on the annealing temperature. Although several papers were reported as for the thermal behavior of the copolymers [11–15], they did not necessarily succeed in the reasonable interpretation of the observed DSC thermograms from the structural point of view. It is important to assign these

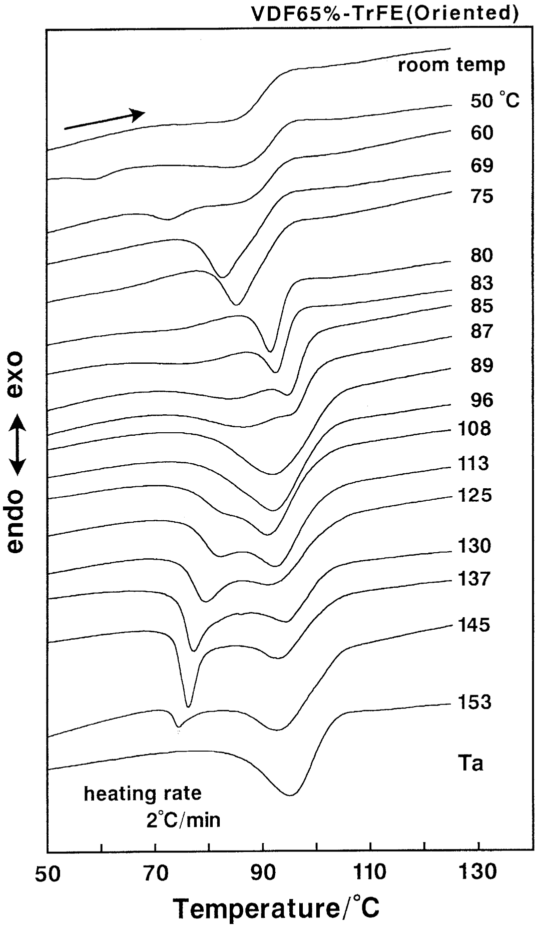

Fig. 2. A series of DSC thermograms taken in the heating process of oriented VDF 65%–TrFE copolymer samples annealed at the various temperatures (T_a).

multiple peaks to the concrete structural changes in order to understand the essential features of the copolymers.

Since the phase transition behavior is affected sensitively by the heat treatment condition, it may be easily speculated that not only the structural changes in the crystal lattice but also the morphological changes in the stacked lamellar structure should occur in the heating process of the bulk samples. In fact, when the SAXS and WAXS patterns were measured at room temperature for the samples annealed at the various temperatures, their patterns were found to change remarkably depending on the annealing temperature. In order to understand the annealing effect on the morphology and crystalline lattice structure, we performed the temperature dependent measurement of WAXS and SAXS patterns in the heating process from room temperature. In the present paper, we will describe the details of this experiment, from which an intimate relation of the structure change between the crystalline lattice and the lamellar stacking mode is discussed. At the same time the physical meanings of the heat treatment procedure viewed from the point of structure is clarified by comparing the X-ray diffraction data collected at room temperature for the annealed samples with those measured at high-temperatures in the heating process.

An organized combination of WAXS and SAXS data has been found to be useful for the structural study of the ferroelectric phase transition of VDF–TrFE copolymers. In particular, it may be valuable to emphasize that the trans–gauche conformational change occurring in the ferroelectric phase transition has been found to be intimately related with the change in the chain packing mode as well as the change in the lamellar stacking structure. The WAXS and SAXS measurements during the slow heating and cooling processes were reported in the literatures [16–18]. In such X-ray experiments, however, it is more useful to take the WAXS and SAXS patterns simultaneously on a single imaging plate detector by adjusting the sample-to-camera distance to a suitable value. This technical idea is practically important because the structural changes viewed at the levels of crystalline lattice (as obtained by WAXS data) and stacked lamellae (by SAXS) should be compared for the data taken under just the same conditions [19].

2. Experimental section

2.1. Samples

VDF–TrFE copolymers used in the present study were VDF 65 and 73 mol% samples which were supplied by Daikin Kogyo Co. Ltd, Japan. These samples were cast from the acetone solutions and stretched by about five times the original length at room temperature. The thus obtained samples were annealed at various temperatures for 2 h under tension and quenched into ice–water bath. The unoriented samples were melted and quenched into ice–water bath, followed by heat treatment at the various temperatures.

2.2. Measurements

WAXS and SAXS patterns of the uniaxially-oriented samples were measured by using a MAC Science DIP 1000 Imaging Plate System with an SRA18X X-ray generator of a rotating anode type. Graphite-monochromatized Cu Kα line was used as an incident X-ray beam. In order to take the two-dimensional WAXS and SAXS patterns simultaneously on a sheet of imaging plate of 20 cm diameter, the sample-to-imaging plate distance was set to 200 mm. The collimator of 0.3 mm diameter was used and the home-made small beam stopper was set above the imaging plate to detect the SAXS pattern up to a maximal repeating spacing of ca. 600 Å. The temperature of the sample was changed by using a home-made heater block, into which the oriented sample was set with a thermocouple contacted directly to the sample. The WAXS profiles were measured also for the unoriented samples in the heating process from room temperature. The X-ray diffraction measurement was made using a Rigaku RAD-ROC diffractometer with graphite–monochromatized Cu Kα radiation equipped with a home-made furnace.

3. Results and discussion

3.1. DSC and WAXS profiles

3.1.1. VDF 65% copolymer

As shown in Fig. 2, the DSC thermogram of the oriented VDF 65% copolymer sample changes remarkably depending on the annealing temperature (T_a). As discussed in the previous paper [10], the DSC thermograms may be classified into four types: (i) the DSC themogram obtained for the samples annealed in a low-temperature region below 70 °C or at the temperature corresponding to an endothermic peak observed for the unannealed as-drawn sample (this peak corresponds to the phase transition, not to the melting point, which appears at about 152 °C). A small subpeak was detected around 50–60 °C for the sample annealed at 50 °C. This peak shifted toward the main peak at 85 °C as the T_a was increased. (ii) The DSC thermogram of the sample annealed in the phase transition region of 70–90 °C. As the T_a was increased, the transition peak shifted toward higher temperature side. At the same time a new but broad peak was detected at a lower temperature and it increased the peak height with increasing T_a. (iii) When the sample was annealed in the region 90–110 °C, apparently single broad peak was detected. (iv) When the heat treatment was made above 110 °C (but below the melting point), a sharp peak was detected as a shoulder of this broad peak and it shifted to lower temperature direction and increased the peak height as the annealing temperature was increased.

In this way, the DSC thermograms of the VDF 65% samples exhibits a remarkable change depending on the heat treatment temperature. What kind of structural change occurs in these peak temperatures? In order to assign them, we performed the temperature dependent measurement of WAXS pattern for the various kinds of unoriented VDF 65% sample (we used here the unoriented samples because the CL phase give the tilting phenomenon and the equatorial reflections shifted from the horizontal line, making it difficult to estimate the integrated intensity of the reflection components exactly. But it should be noted that the DSC thermograms taken for the unoriented samples were essentially the same as those of the oriented samples). It should be noted here that the heating rate in the DSC measurement (2 °C/min) is rather higher than that in the X-ray diffraction measurement. This difference might cause the difference in the structural formation process during the phase transition. Therefore, strictly speaking, the direct comparison between the DSC thermogram and the X-ray diffraction data might be difficult more or less. But, such a kinetic effect on the phase transition and crystallization phenomena has not yet been perfectly understood for this VDF–TrFE copolymer, although we reported the time-resolved X-ray diffraction measurements in the isothermal crystallization and ferroelectric phase transition phenomena [20]. In the present paper, we will compare the DSC and X-ray results by neglecting this kinetic effect as an approximation. Fig. 3 shows an example for the VDF 65% sample annealed at 140 °C. As the temperature was increased from 30 °C, a broad X-ray peak of the LT phase at about 20° decreased in intensity and a new peak began to appear around 18.5°, which corresponds to the peak of the HT phase. This new peak increased in intensity with increasing temperature and became sharper. On the way of heating, the reflections of the CL phase were also detected at the positions between the LT and HT phase reflections. As shown in Fig. 3(c), the X-ray profile was separated into the components of LT, CL (2 peaks of CL_1 and CL_2, corresponding to (110) and (1$\bar{1}$0/200) reflections, respectively [1]), and HT phases, and the position (2θ) and integrated intensity of each reflection were evaluated. In this curve fitting process, we referred to the information about the peak positions of each phase reported in the literature [1]. Fig. 4 shows the thus obtained result. The CL phase, which existed already at the starting point (observed as a broad

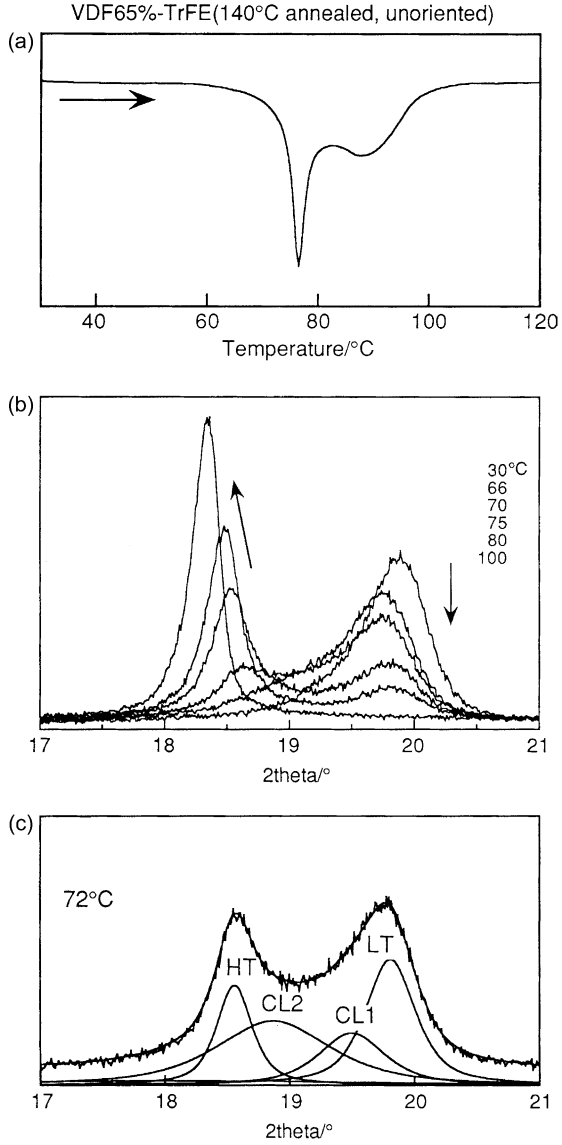

Fig. 3. Temperature dependence of X-ray diffraction profile (b) measured in the heating process of unoriented VDF 65%–TrFE copolymer sample annealed at 140 °C in comparison with the corresponding DSC thermogram (a). Curve separation of X-ray diffraction profile is illustrated in (c), where LT, HT and CL are the reflection components of the low-temperature phase, the high-temperature phase, and the cooled phase, respectively.

shoulder of the LT phase reflection), increased slightly in the reflection intensity in the temperature region of 50–70 °C, suggesting a partial transition from the LT phase to the CL phase. The reflections of the CL phase decreased in intensity remarkably in the temperature region of 70–80 °C, where the reflections of the HT phase increased instead. The reflection of the original LT phase decreased also in almost the same temperature region, but it did not disappear completely but continued to be observed even above 83 °C or the end of the sharp DSC peak. The reflection of the LT phase disappeared for the first time around 100 °C. By comparing this X-ray result with the DSC thermogram given in Fig. 4(a), we could assign the DSC peaks to the concrete phase transitions. In the temperature region of a sharp DSC peak, the transition from the CL to HT phase occurs mainly. Minor part of the LT phase transforms to the CL phase in such a low-temperature region as 50–60 °C. Most of the LT phase shows the transition to the HT phase in a wider temperature region of 65–95 °C.

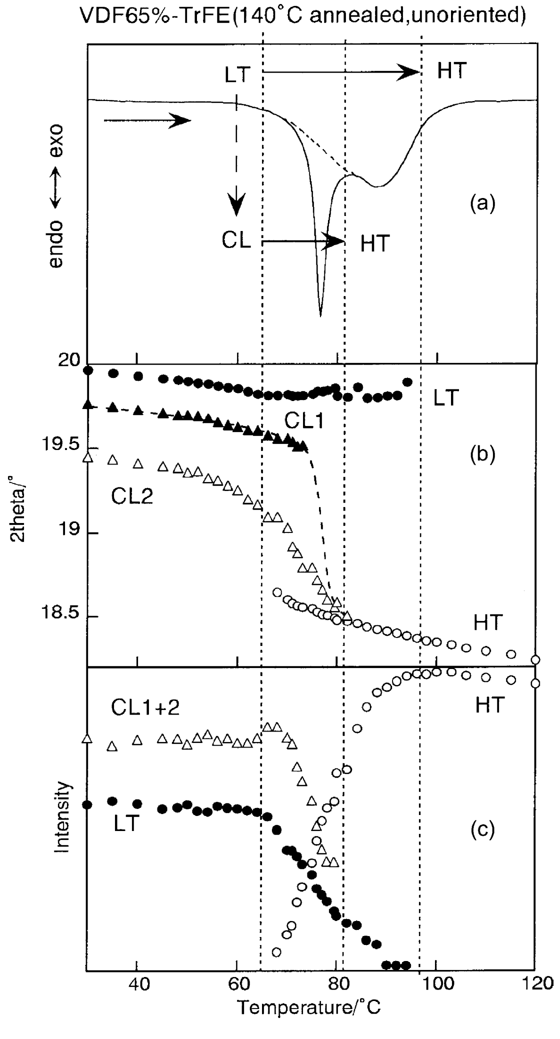

Fig. 4. Temperature dependence of (b) peak position and (c) integrated intensity evaluated for X-ray reflections of LT (low-temperature), HT (high-temperature) and CL (cooled) phases in the heating process along the DSC thermogram shown in (a). The sample was the unoriented VDF 65%–TrFE copolymer annealed at 140 °C (refer to Fig. 3).

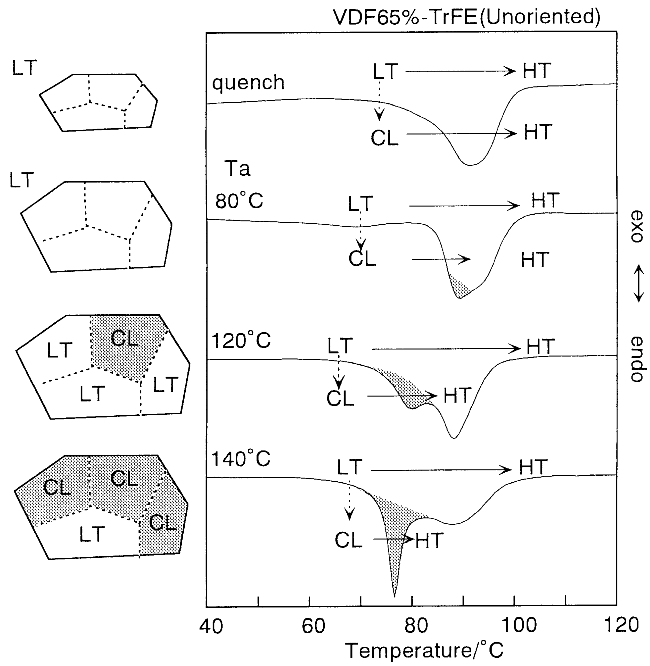

Fig. 5. Assignment of peaks in DSC thermograms measured for the VDF 65%–TrFE copolymer samples annealed at the various temperatures (T_a). LT, HT, and CL denote, respectively, the low-temperature phase, the high-temperature phase, and the cooled phase. In the left part of this figure are shown the illustrations of domain structures at room temperature, estimated for the samples annealed at the corresponding temperatures.

The similar investigation was made for the VDF 65% samples annealed at the various temperatures. The assignment of the DSC peaks to the various transitions is shown in Fig. 5. For the unannealed sample, the CL-to-HT phase transition peak is difficult to detect. The transition from the LT phase to the HT phase occurs in a wide temperature region. For the sample annealed at 80 °C, the LT-to-CL phase transition is observed around 70 °C and the transition from the CL phase to the HT phase occurs at the shoulder of the main endothermic peak detected around 90 °C. The transition from the LT to HT phase occurs in a wide region of 80–100 °C. For the sample annealed at higher temperature, the transitions of CL-to-HT and LT-to-HT phases are observed more clearly in the separated temperature regions.

Here, we need to consider the reason why the CL-to-HT phase transition occurs in a narrower and lower temperature region. By comparing the relative X-ray intensity of each crystalline phase taken at room temperature among the samples annealed at various temperatures, we can say that the sample annealed at higher temperature shows higher contribution of the CL phase at room temperature, as illustrated in the left side of Fig. 5. The larger DSC endothermic peak observed for the sample annealed at higher temperature corresponds well to this higher contribution of the CL phase at the starting temperature. As mentioned in an introductory section, the CL phase is a disordered phase characterized by the tilting phenomenon of the zigzag chain segments from the draw axis. The tilted trans segments are linked together through conformationally irregular trans–gauche defects. The existence of these gauche defects is speculated to accelerate the trans-to-gauche transition in the trans–zigzag sequences. Besides, the trans–zigzag chain segments are separated into the domains with different polarization axes (Fig. 1(b)). The trans-to-gauche conformational change occurs at lower temperature when such domains are contacted side by side as already clarified by a molecular dynamics calculation [8]. That is to say, the conformational transition occurs at lower temperature for the multi-domain structure. These factors, i.e. the contribution of gauche bonds in the trans–zigzag segments and the irregular packing of the polar domains are considered to cause the CL-to-HT phase more easily in a relatively lower temperature region.

3.1.2. VDF 73% copolymer

In the case of VDF 73% copolymer sample, the DSC thermogram can be interpreted relatively easily. As reproduced in Fig. 6, a small subpeak was observed for the samples annealed below T_c and it shifted toward the main peak of the LT-to-HT phase transition located at 110–130 °C (A larger peak at 147 °C is the melting peak.). The subpeak is considered to come from the phase transition occurring in the small crystallites created at the corresponding annealing temperature. As the annealing temperature became closer to the main transition point, the subpeak approached the main peak and fused into one. The heat treatment above T_c increased the DSC peak height and the T_c shifted toward a lower temperature direction, probably due to small contribution of the CL phase, just like the case of VDF 65% sample. Anyway, however, the DSC peaks detected in VDF 73% samples correspond mainly to the transition of LT-to-HT phase, which may occur at a lower temperature in the small crystallites and at a higher temperature in the large crystallites.

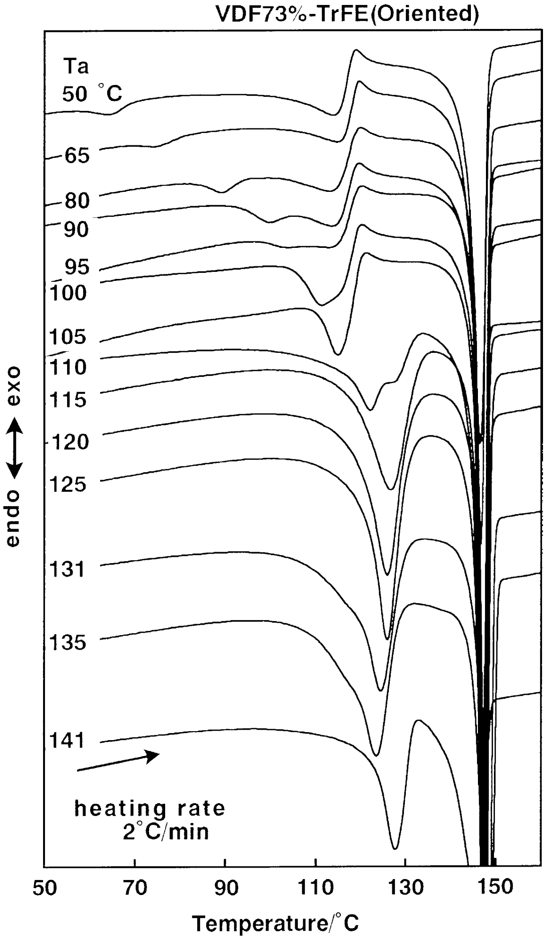

Fig. 6. A series of DSC thermograms taken in the heating process of VDF 73%–TrFE copolymer samples annealed at the various temperatures (T_a).

We notice one point in the interpretation of the DSC thermogram, that is, an exothermal peak detected just above the main transition peak. This peak is detected for both of VDF 65 and 73% samples annealed in the temperature region of the broad endothermic peak. One possible interpretation of this endothermic peak is that it might correspond to the morphological change or the further growth of crystalline lamellae or the increase of the crystallinity [16,21–23]. In fact, as will be discussed in a later section, the lamellar thickness is remarkably increased in this temperature region and the tilting angle of these lamellae is also largely changed.

3.2. Correlation of WAXS and SAXS profiles

In the aforementioned section, we investigated the phase transition behavior in the heating process for the samples annealed at the various temperatures. In order to know the correlation between the structural change in the crystal lattice and the morphological change of stacked lamellae, we measured the temperature dependence of WAXS and SAXS profiles for the as-drawn unannealed sample. We used here the unannealed samples because they were considered to give us the details about the concrete structural changes occurring in the heat treatment process. The two-dimensional WAXS and SAXS patterns were recorded simultaneously on a single imaging plate so that the structural changes viewed from the crystalline lamellar levels could be traced under strictly the same condition.

Fig. 7 shows the experimental result for the as-drawn unannealed VDF 73% copolymer sample in the heating process from room temperature. The two-dimensional WAXS pattern at room temperature showed clearly the (200/110) reflection of the LT phase. The SAXS pattern showed the four-points pattern, indicating a tilt of stacked lamellae from the draw axis. As the temperature was increased and approached the transition point, the (100) reflection intrinsic of the HT phase began to appear at lower scattering angle and increased in intensity. This (100) reflection became much sharper at a higher temperature. This drastic change in the reflection width can be interpreted reasonably by considering a change in the domain size [9]. As mentioned above, the crystalline lamellae of the LT phase consist of the small domains and the electric polarization of each domain is oriented in the different direction, forming a so-called multi-domain structure (Fig. 8). By increasing temperature, the trans–zigzag chains change the conformation to the gauche form and they rotate violently around the chain axes, resulting in the non-polar structure. As a result the structural difference between the neighboring domains disappears and the multi-domain

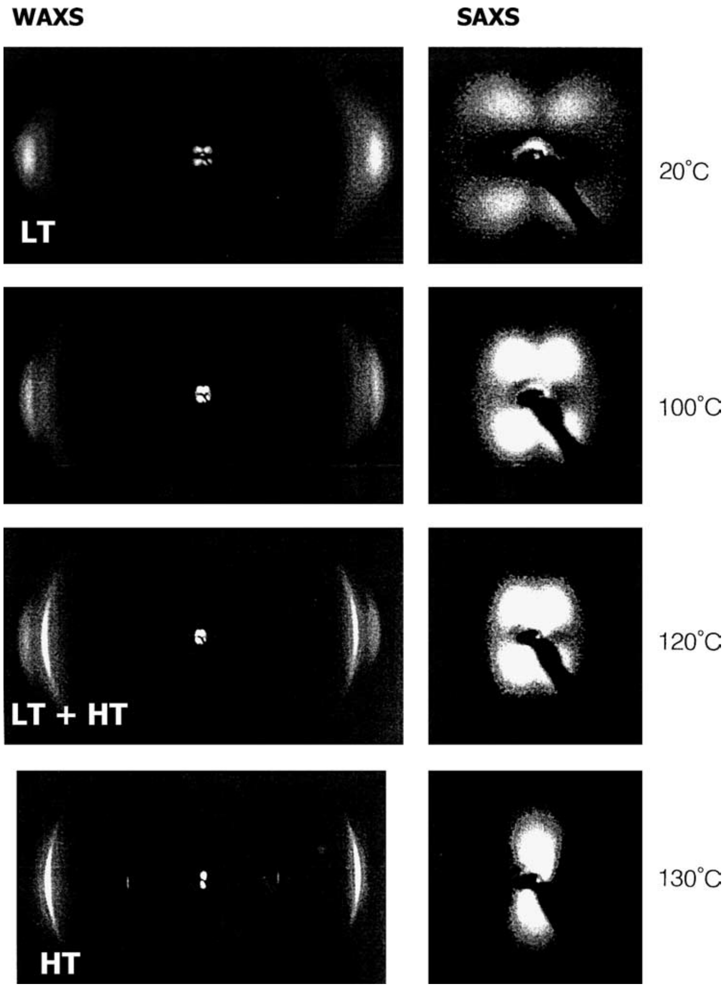

Fig. 7. Temperature dependence of WAXS and SAXS patterns simultaneously measured for the as-drawn unannealed VDF 73%–TrFE copolymer sample in the heating process from room temperature.

structure changes to the single domain structure with larger size. Because of such an increment in the domain size the half-width of the equatorial reflections becomes sharper. Not only the WAXS pattern but also the SAXS pattern was found to change remarkably. As seen in Fig. 7, the scattering peaks became closer to each other and shifted toward the meridional direction as the temperature approached the transition point.

The similar phenomenon was observed also for VDF 65% copolymer sample. As shown in Fig. 9, the SAXS pattern changed from the four-points pattern to the almost two points pattern above the transition temperature. The WAXS pattern showed a little different behavior from the case of VDF 73% sample. In the latter case, the WAXS pattern changed almost between the LT and HT phases, and the contribution of the CL phase was negligibly small. But, in the case of VDF 65% sample, the contribution of the CL phase cannot be ignored, as already mentioned in Section 3.1.1. When we see the WAXS pattern given in Fig. 9, the reflection of the CL phase is observed at 76 °C, for example, in addition to the reflection of the LT phase: the reflection of the CL phase splits into two from the equatorial line, corresponding to a tilting phenomenon. As the temperature increased furthermore, the reflections of the CL phase transferred continuously to those of the HT phase. The profiles of reflections on the equatorial line were extracted from the two-dimensional WAXS patterns and the peak position, integrated intensity, and half-width of the LT (110/200) reflection, the CL (110) reflection and the HT (100) reflection were plotted against temperature as shown in Fig. 10. Similarly to the result observed for the unoriented sample, the CL phase began to increase around 50 °C and it transferred continuously to the HT phase in the temperature region around 80 °C. The LT phase disappeared above 100 °C. The half-width of the HT phase reflection decreased drastically. As known from the comparison between DSC thermogram and the WAXS data, the crystalline region was almost occupied by the HT phase in the temperature region of exothermaic peak around 95 °C. This exothermic peak is considered to relate rather with the change in the SAXS profile or the morphological change, as already pointed out before.

The SAXS patterns observed for VDF 65 and 73% samples were analyzed quantitatively as illustrated in Fig. 11. From the peak position of the profile taken along the line connecting the scattering peak and the central point, the distance L' between the adjacent lamellae can be estimated. The profile traced along the azimuthal direction gives the tilting angle ϕ of the lamellar normal from the draw axis. The long period L

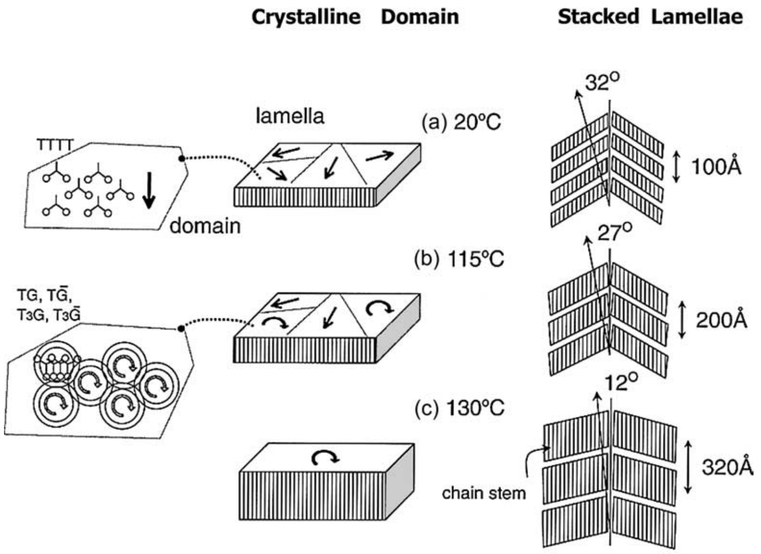

Fig. 8. Illustrated domain structure and stacked lamellar structure in the heating process of as-drawn VDF 73%–TrFE copolymer sample. (a) 20 °C: a crystalline lamella consists of multiple domains, in which the planar–zigzag chain stems are packed in parallel to form a polar crystal domain. These lamellae are stacked together with the normals tilted by about 32° from the draw axis. Exactly speaking, the zigzag chain stems in a crystalline lamella, shown in a central part, should be tilted from the normal by 32° so that the chain axis is parallel to the draw direction. (b) 115 °C: some domains are occupied by conformationally-disordered TG chains which rotate violently around the chain axis. The tilting angle of stacked lamellae is smaller, 27°, and the long spacing is increased. (c) 130 °C: a crystalline lamella becomes a single domain consisting of thermally active gauche-type chains, and these lamellae are stacked with the normals almost parallel to the draw direction. The long spacing is longer than 300 Å.

along the draw axis and the distance L' between the adjacent lamellae are related by the equation $L' = L\cos\phi$. Fig. 12 shows the temperature dependence of L' and ϕ evaluated for VDF 65% copolymer sample as an example. In this figure, the DSC thermogram of the as-drawn and unannealed sample is reproduced as a reference. The two endothermic peaks are observed in DSC thermogram. At a low endothermic peak around 50 °C, the tilting angle ϕ decreased from 28° at room temperature to 26° at 60 °C. As the temperature approached the main endothermic peak of 80 °C corresponding to the

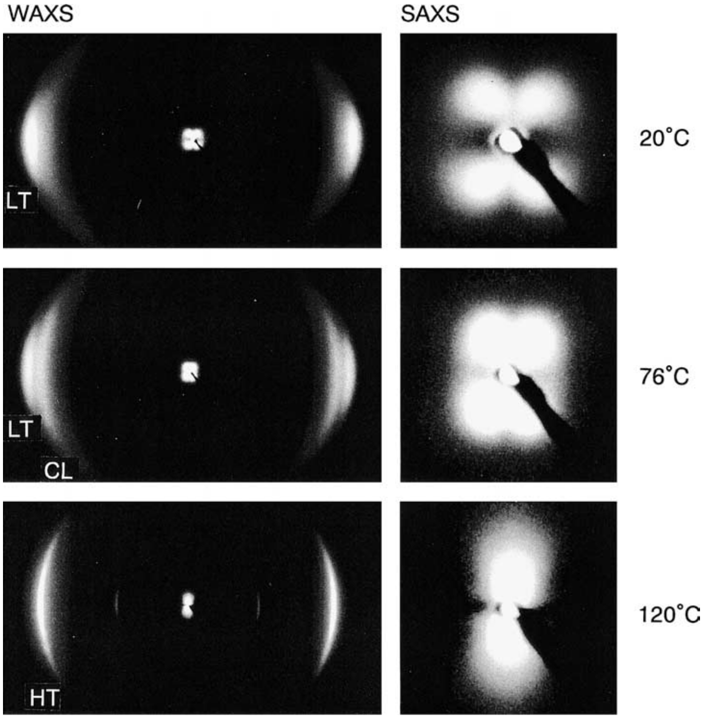

Fig. 9. Temperature dependence of WAXS and SAXS patterns simultaneously measured for the as-drawn unannealed VDF 65%–TrFE copolymer sample in the heating process from room temperature.

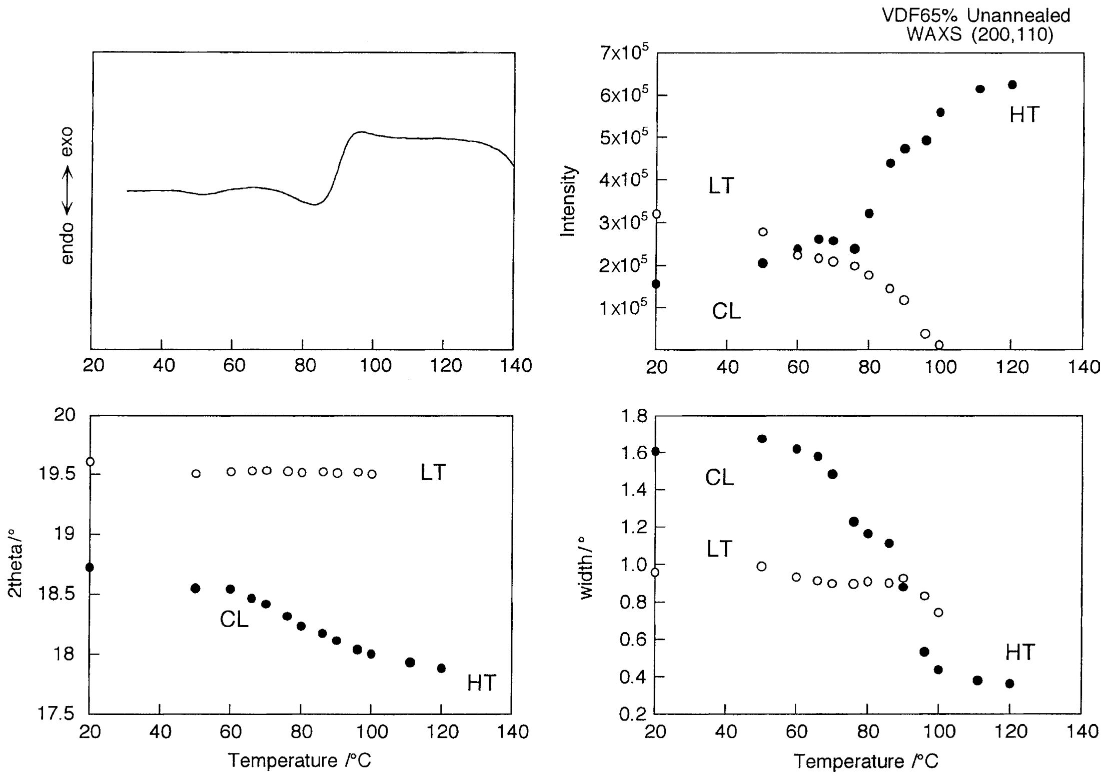

Fig. 10. Temperature dependence of peak position (scattering angle, 2θ), integrated intensity and half-width of the X-ray reflections estimated for LT, HT and CL phases of as-drawn unannealed VDF 65%–TrFE copolymer sample. A corresponding DSC thermogram is shown for reference.

transition point, the tilting angle ϕ decreased gradually down to 22° and the L' increased to 200 Å. In the exothermic peak region, the ϕ decreased remarkably to 12° and the L' increased to 250–300 Å. The similar phenomenon was observed also for VDF 73% sample as shown in Fig. 13. In the temperature region of small endothermic peak at 60 °C, the tilting angle changed only slightly, and then the angle ϕ was kept almost unchanged in the main transition region. The long period L increased gradually in this temperature region. In the region of the DSC exothermic peak, the ϕ value decreased largely to

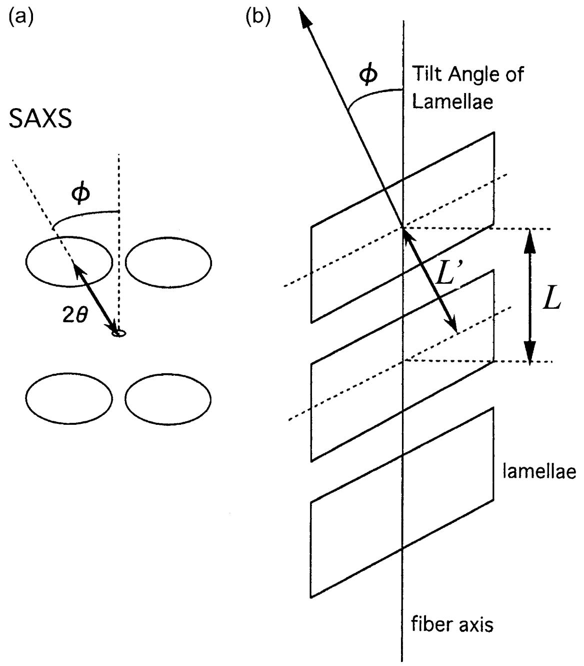

Fig. 11. (a) An illustration of SAXS pattern and (b) the related parameters of stacked lamellar structure.

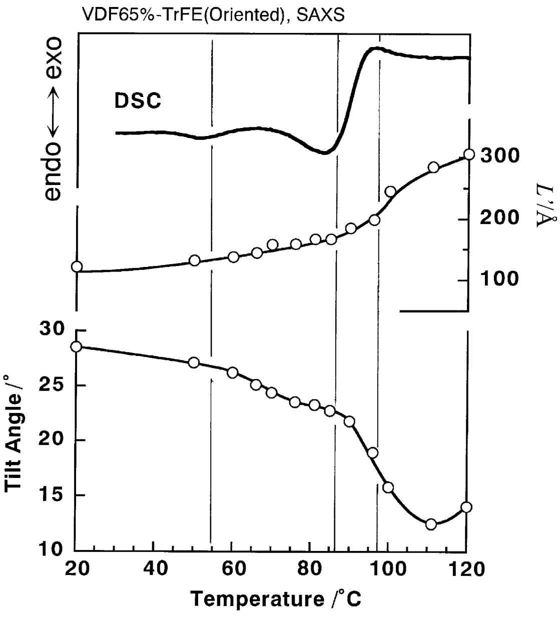

Fig. 12. Temperature dependence of long period (L') and tilting angle estimated in the heating process of the as-drawn unannealed VDF 65% sample in comparison with the corresponding DSC thermogram.

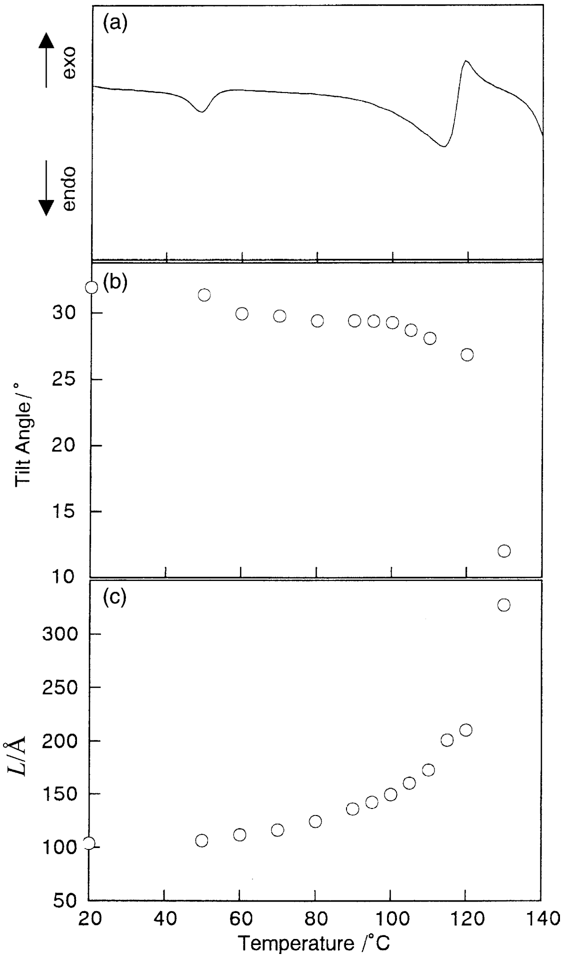

Fig. 13. Temperature dependence of long period (*L*) and tilting angle estimated in the heating process of the as-drawn unannealed VDF 73% sample in comparison with the corresponding DSC thermogram.

12°. The long period *L* increased also remarkably to 320 Å in this temperature region.

The structural change in the crystalline lattice and the change of the lamellar stacking mode are illustrated as shown in Fig. 8, where the case of VDF 73% sample is given as an example. The starting sample consists of the LT phase. As discussed above, the lamella takes a multi-domain structure. As known from the SAXS pattern, the lamellae are tilted by ca. 30° from the draw axis. The long period is about 120 Å. When the sample is heated up to the transition temperature region of LT-to-HT phase, the multi-domain structure of a crystallite changes to a single domain, and the crystallite is occupied by the HT phase, in which the gauche-type chains are rotated around the chain axis. In the case of VDF 65% sample, the CL phase also participates in the transition. As the temperature is raised furthermore, the lamellar thickness increases remarkably and the long period reaches ca. 300 Å. The tilting angle of the lamellae is also drastically reduced down to ca. 12°. In this way, we can find a common phenomenon about the lamellar stacking structure change between these two kinds of copolymers, VDF 65 and 73% samples, although some details are different from each other. Besides, the morphological change is found to relate with the phase transition between the LT (and CL) and HT phases or with the trans–gauche conformational change. It is important to notice that the trans–gauche conformational change affects not only the inner structure of the crystallite but also the lamellar stacking structure of the whole sample. The molecular chains in the HT phase experience active thermal motion; a translational motion along the chain axis and a rotational motion around the chain axis. These molecular motions are strongly related with the trans–gauche conformational change of the chains: trans–gauche exchange occurs in the chains, which cause the translational and rotational motion of the whole chains, as revealed by the NMR experiments [24–30] and molecular dynamics calculation [4–8]. Another important point is a remarkable increment of lamellar thickness and a drastic reduction of lamellar tilting angle in the temperature region where the crystalline phase has changed mostly to the HT phase. The conformationally-disordered chains of the HT phase are considered to move easily along the chain axis and induce the remarkable increment of the lamellar thickness and reduction of the tilting angle [31]. This large morphological change and the increase in crystallinity are detected as an exothermic peak of the DSC thermogram of the unannealed sample, indicating an energetic stabilization of lamellar stacking structure.

3.3. Structural meaning of heat treatment

Fig. 14 shows the SAXS patterns taken at room temperature for the VDF 65 samples annealed at the various temperatures. The change of these patterns is quite similar to the change observed in the heating process (Fig. 9). The SAXS pattern measured at a high temperature is almost preserved even after the sample is cooled to the room temperature. In Fig. 15, we compare the long period measured for the as-drawn VDF 65% sample at the various temperatures and those measured at room temperature for the samples annealed at the corresponding temperatures. Although the long period is longer for the annealed sample because of the further growth of lamellae in the cooling process, the tendency is essentially the same between these two cases (at 120 °C the long period observed for the annealed sample is much longer than that of the sample being heated at the same temperature. This remarkable increase of long period of the annealed sample might be related with the growth of crystallites along the chain axis, which is more remarkable in the cooling process from the HT phase with active molecular motion [1]). In the case of VDF 73% sample also the similar relation is observed. As shown in Fig. 16, where the VDF 65 and 73% cases are compared as for the L' and ϕ values, the long period increased dramatically from 120 to 700 Å when the as-drawn sample was annealed in the temperature region of DSC exothermic peak. In this way, the growth of stacked lamellar structure is accelerated at a higher temperature and it is frozen by cooling down to the ambient temperature (strictly speaking the structure is grown furthermore in the cooling process). On the other hand, as seen in the WAXS pattern change, the gauche-to-trans conformational change can occur in the cooling process and the molecular chains go back to the original LT phase (for VDF 73% sample) or more preferable CL phase (for VDF 65% sample).

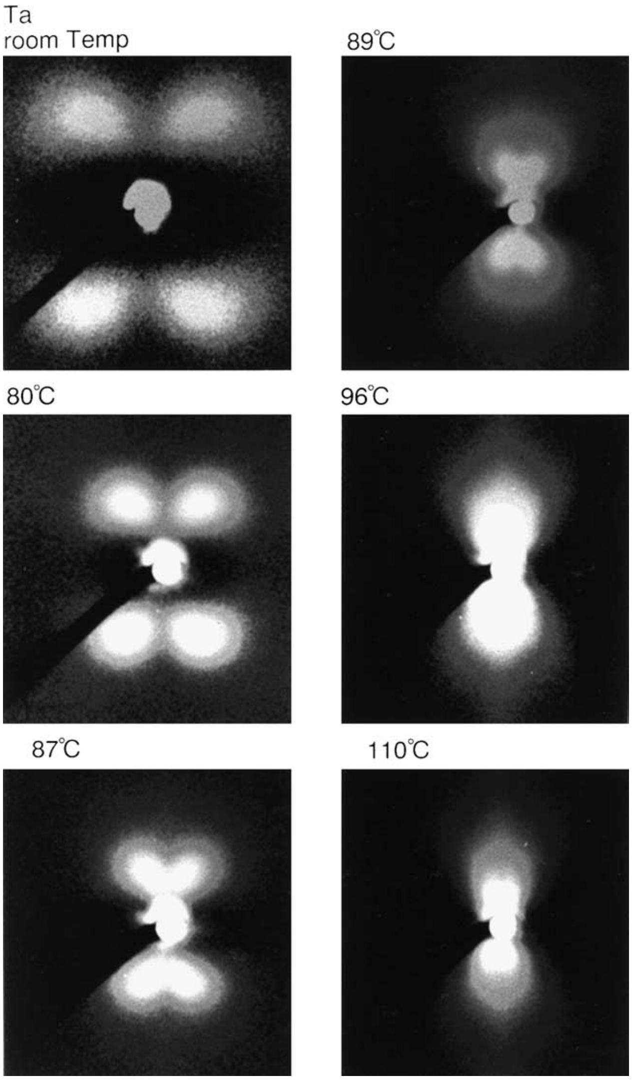

Fig. 14. The SAXS patterns measured at room temperature for the oriented VDF 65% sample annealed at the various temperatures (T_a).

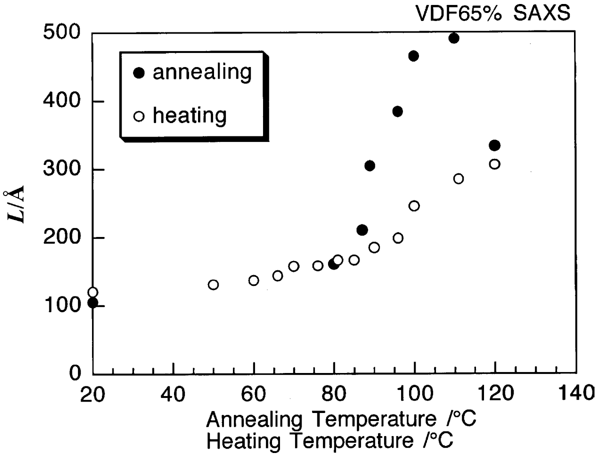

Fig. 15. Comparison between the long period estimated at room temperature for VDF 65% sample annealed at the various temperatures and the long period estimated for the as-drawn VDF 65% sample in the heating process.

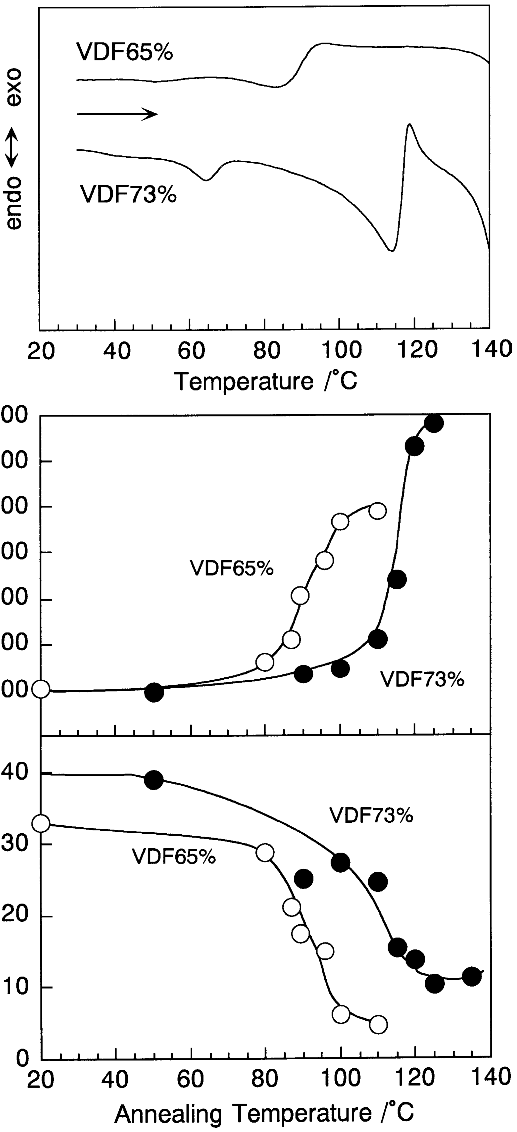

Fig. 16. Comparison in the annealing temperature dependence of long period and tilting angle estimated from the SAXS data taken at room temperature between VDF 65 and 73% copolymer samples. The DSC thermograms of the as-drawn unannealed samples are also shown for comparison.

Figs. 15 and 16 tell us important and sophisticated points about the formation of higher-order structure or stacked lamellar morphology and also about the physical meaning of heat treatment at high temperature. Heating of the sample activates the trans-to-gauche conformational exchange and the phase transition occurs from the LT (or CL) to HT phase. Because the thermal motion of the whole chain is activated through such a trans–gauche exchange phenomenon, the thickness and shape of the lamellae are changed remarkably. Once the phase transition is completed and the pure HT phase is created, the molecular motion is more enhanced, because the long trans segments disappear which are speculated to disturb the smooth translational motion of the whole chain along the chain axis coupled with the trans–gauche exchange. As a result of such a smooth translational motion along the chain axis the lamellar thickness is increased dramatically in the temperature region of the pure HT phase. When the sample is cooled from these situations, the whole molecular motion is ceased but the chain conformation is still changed through the relatively easy gauche-to-trans exchange motion even at a low temperature. As a result the HT phase transfers to the LT (or CL) phase. The lamellar thickness attained at high temperature is preserved or becomes rather larger because the violent chain motion is ceased at low temperature and the chains tend to stretch along the chain axis.

4. Conclusions

In the present paper, we showed the changes of WAXS and SAXS patterns by the heat treatment of VDF 65 and 73% samples and also the changes induced by heating them. The measurement of WAXS profile in the heating process allowed us to assign the endothermic peaks of the DSC thermograms to the phase transitions of LT-to-HT or LT-to-CL-to-HT. The two-dimensional WAXS and SAXS patterns, which were measured simultaneously for the uniaxially oriented samples, were found to change remarkably in the heating process, and the quantitative analysis revealed the complicated structure changes occurring in the crystalline region and in the stacked lamellar structure. The as-drawn and unannealed sample takes the stacked lamellar morphology of relatively thin thickness. The lamellae are tilted by ca. 30^{o} from the draw axis, being observed as the four-points SAXS pattern. When the sample is heated above the transition temperature, the crystalline phase changes from the LT phase to the HT phase (via CL phase in the case of VDF 65% sample), and the multi-domain structure changes to the single domain consisting of the trans–gauche-type chains with violent thermal motions. In the temperature region of pure HT phase, the tilting of the lamellae is reduced and the long period (and so the lamellar thickness) increases remarkably. In particular, in the temperature region where the long trans segments disappear and so the molecular chains can move more smoothly through the trans–gauche exchange motion, the lamellar thickness was found to increase dramatically. In this way, the structural changes in the crystalline region are intimately related with the changes in the lamellar stacking mode. This intimate relationship is originated from the conformational changes between trans and gauche bonds and the associated molecular motions of the chains. In other words, the molecular motion enhanced in the high-temperature region gives the drastic growth of lamellar thickness. Once the thus heated up sample is cooled to lower temperature, the local conformational change can still occur and the HT-to-LT (or CL) transition is induced, but the lamellar thickness is preserved because of the low thermal mobility of the whole chains. Here, we can know the physical meaning of the heat treatment. This concept of heat treatment has been imagined already for a long time, but the present study can present the concrete experimental evidence for the structural meaning of the heat treatment by measuring the DSC thermogram and WAXS and SAXS patterns in the heating process of VDF copolymer samples.

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