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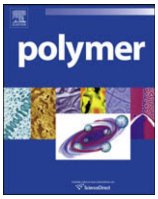

Influence of third monomer on the crystal phase transition behavior of ethylene–tetrafluoroethylene copolymer

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ABSTRACT

Crystal phase transition between the low- and high-temperature phases has been investigated for ethylene (E)–tetrafluoroethylene (TFE) alternating copolymer (ETFE) containing the third monomeric species by the temperature dependent measurements of wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) and differential scanning calorimetry. Nonafluoro-1-hexene (NFH) and hexafluoropropylene (HFP) were chosen as the third monomers, where they are different in the side-branch length, $-(CF_2)_3CF_3$ and $-CF_3$, respectively. In the case of E/TFE/NFH copolymer (ET–C4F9), the crystal phase transition temperature of the original ETFE two-components copolymer was not very much affected by the existence of NFH in the range of NFH content from 0.7 to 3 mol%. Contrarily, the crystal phase transition temperature of E/TFE/HFP copolymer (ET–CF3) was found to decrease drastically with increasing HFP content. The melting temperature and the higher-order structure were also affected sensitively depending on the HFP content. This difference in phase transition behavior between ET–C4F9 and ET–CF3 copolymers is reasonably interpreted as follows: the short side groups ($-CF_3$) of HFP monomeric unit are included in the crystal lattice of E/TFE chains and the unit cell is expanded gradually with an increment of the HFP content, resulting in the decrease in phase transition point because of easier thermal motion of the chains. On the other hand, the long side groups [$-(CF_2)_3CF_3$] of NFH monomeric units are excluded out of the crystal lattice and located on the lamellar surfaces or in the amorphous region and do not affect very much the phase transition temperature even when the NFH content is increased. In association with such a change in crystal structure, the long period of stacked lamellar structure was found to decrease remarkably in the case of NFH, whereas it does not change very much for HFP, consistent with the interpretation of the above-mentioned WAXD data.

1. Introduction

Ethylene (E)–tetrafluoroethylene (TFE) alternating copolymer is one of the melt-processable fluororesins. Because of the excellent thermal and chemical durability and electric property, ETFE copolymer is used for such various industrial applications as chemical equipment materials, wire-coating insulations etc [1]. Recently it is also used as a covering sheet of giant buildings due to the excellent weatherability, transparency and mechanical strength [2]. The various properties are sensitively governed by the structure and properties of the crystal lattice and the higher-order structure composed of crystalline and amorphous regions.

So far the crystal structure and higher-order structure of ETFE copolymer with E/TFE content of about 50/50 molar ratio have been studied mainly on the basis of the X-ray diffraction measurements [3–13]. The crystal structure was assumed tentatively to be an orthorhombic form at low temperature [4,6]. But the detailed investigation required us to reconsider the low-temperature phase as the monoclinic system; the two planar-zigzag chains are packed in a rectangular unit cell of $a = 8.57$ Å, $b = 5.60$ Å, c(fiber axis) $= 5.04$ Å and $\gamma \approx 90°$ in a herring-bone mode similar to that of polyethylene but with lower space group symmetry. This was already pointed out for E/TFE 50/50 copolymer by Wilson and Starkweather [3], and it has been refined by measuring the 2-dimensional X-ray diffraction pattern at such a low temperature as -150 °C [10,13]. In the temperature region around 60 °C it transforms to the pseudo-hexagonal form or the high-temperature phase. The phase transition behavior was reported to be affected sensitively by the E/TFE molar ratio [7,11]. When TFE content is increased, the crystal structure changes from monoclinic (orthorhombic) to pseudo-hexagonal form even at an ambient temperature [7].

In the practical usage, addition of the third component is made because E/TFE two-components copolymers do not show sufficiently good thermal stress crack resistance; when the moldings

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of ETFE copolymer are exposed to a high stress at a high temperature, cracks develop within the moldings. By introducing the third component into ETFE copolymer chains, the thermal stress crack resistance is improved drastically [14]. Therefore, most of the commercially available ETFE copolymers are the three-component copolymers including small amounts of the third or even fourth monomers. The physical properties of these copolymers change sensitively with the type and relative amount of the third (and fourth) monomeric unit as well as the external temperature. Addition of the third monomer component also affects the phase transition of ETFE copolymer [5,11,12]. For example, the crystal structure of the three-components system of E, TFE and perfluoropropylvinylether ($CF_2{=}CFOCF_2CF_2CF_3$) shows the pseudo-hexagonal form even at room temperature, and the crystallinity becomes lower and the crystal size is smaller than those of ETFE two-components system [11].

However, the roles of the third component in the crystalline structure formation and the phase transition phenomenon of ETFE copolymer have not yet been fully clarified. In order to solve these problems, it is needed to know the behavior of the three-components copolymer samples in the heating (and cooling) process. The investigation of a role of the third component on the phase transition behavior of E/TFE copolymer was reported in a few papers [5,11,12]. But the detailed study including the effects of side branching length and monomeric unit content has not yet been clarified.

Our research purpose is to clarify this effect of the third component on the crystal structure and phase transition behavior of the original two-components E/TFE copolymer. We describe the details of the phase transition behavior of ETFE copolymer containing the 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene ($CH_2{=}CHCF_2CF_2CF_2CF_3$ NFH) or hexafluoropropylene ($CF_2{=}CFCF_3$ HFP) as the third component. These two types of monomers are different in the length of side chains: $-CF_3$ of HFP and $-CF_2CF_2CF_2CF_3$ of NFH. Therefore it may be possible to clarify the effect of the side chain length on the phase transition behavior as well as the effect of the content of the third component. At the same time the investigation of the influence of the third component on the higher-order structure is also important to understand the bulk properties of these materials. Therefore the measurement of small-anlge X-ray scattering (SAXS) was performed as well as the WAXD experiments.

2. Experimental

2.1. Samples

Copolymers consisting of E, TFE and the third monomers were synthesized by means of solution polymerization method using fluorinated hydrocarbon as a solvent [15]. The chemical compositions were analyzed by performing the molten-state ^{19}F NMR measurement and fluorine ultimate element analysis. The compositions of the synthesized copolymers are listed in Table 1. Hereafter these two polymers are named ET–CF3(*) and ET–C4F9(*) where * is molar % of the third unit.

The samples for wide-angle X-ray diffraction (WAXD) measurement were prepared by melting the copolymers followed by rapid cooling to room temperature. The samples for the DSC measurement were prepared by cutting small pieces from the strands. The sample sheets for the SAXS measurements were prepared by compression molding the melt followed by cooling to room temperature with circulating cold water around the metal holders.

Table 1
Compositions of the two- and three-components ETFE copolymers.

Sample	Composition/mol%			
	E	TFE	NFH	HFP
ET	46.0	54.0	–	–
ET–C4F9(0.8%)	45.7	53.6	0.8	–
ET–C4F9(1.5%)	45.4	53.2	1.5	–
ET–C4F9(3.3%)	38.6	58.1	3.3	–
ET–CF3(2.7%)	43.8	53.5	–	2.7
ET–CF3(4.6%)	42.0	53.4	–	4.6

E: ethylene, TFE: tetrafluoroethylene, NFH: 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene $CH_2{=}CH(CF_2)_3CF_3$, HFP: hexafluoropropylene $CF_2{=}CFCF_3$.

2.2. Measurements

Temperature dependence of WAXD profiles was measured using an X-ray diffractometer Rigaku RINT-TTR3 thermo plus with a graphite-monochromatized Cu Kα line ($\lambda = 1.5418$ Å) as an incident X-ray beam. The sample was heated up to the molten state above 300 °C, and cooled to −40 °C at the rate of 2 °C/min. The thus-obtained samples were supplied to the measurements in the heating process at 2 °C/min. The DSC curves were obtained using a DSC Q1000 (TA Instrument) at the heating rate 10 °C/min in the range of −50 to 300 °C. The heating and cooling rates in the DSC measurements were different from those set in the WAXD/DSC simultaneous measurement. In the latter case a good balance was needed between the scanning rate of the X-ray diffractometer and the heating rate of DSC to obtain as many X-ray diffraction profiles as possible. In the DSC measurement the heating (and cooling) rate was increased to detect the phase transition peak with quite small enthalpy change. The difference in melting point estimated from these two experiments was negligibly small and does not affect seriously the content of the discussion. The SAXS patterns were measured at room temperature using an X-ray diffractometer Rigaku NANO-Viewer with the X-ray beam (Cu Kα) finely focused by a confocal mirror. The imaging plate was used as a 2D detector with the camera-to-detector distance of 700 mm.

3. Results and discussion

The temperature dependence of WAXD profile of ETFE two-components sample with 46 mol% E content is shown in Fig. 1. At temperatures higher than 100 °C, only one peak was observed at about $2\theta = 19°$. This peak corresponds to the 100 reflection of the pseudo-hexagonal form [4]. With cooling the sample, as shown in Fig. 1 (a), the peak position shifted to higher-angle side because of the thermal contraction of the lattice spacing. Further cooling made the peak broader and split into two. The two peaks are tentatively indexed as 120 and 200 of the “orthorhombic” (or monoclinic) form [4,6]. The changes in X-ray diffraction profile occurs almost reversibly in the heating process [Fig. 1 (b)]. The lattice spacings of these reflections are plotted against temperature as shown in Fig. 2. The transition occurs at around 50–70 °C between the low- and high-temperature phases. The thermal hysteresis of about 20 °C is detected between the heating and cooling processes. Apparently the transition looks to occur continuously as long as only these main two peaks are focused on. But the detailed investigation of the higher-angle reflections revealed that this transition should be of the discontinuous first-order type between the low-temperature and high-temperature phases with a thermal hysteresis [13].

As examples, the temperature dependent WAXD profiles of ET–C4F9 polymers, whose NFH contents are 0.8 and 3.3 mol%, are shown in Figs. 3 and 4, respectively. All these polymers show essentially the similar behavior each other. At a low temperature we observed two broad peaks (120 and 200) assigned to the low-temperature phase. In a high-temperature region, they merged into a relatively sharp peak, 100 of the pseudo-hexagonal phase at $2\theta \approx 19°$. Compared with the case of ET, the two peaks of the low-

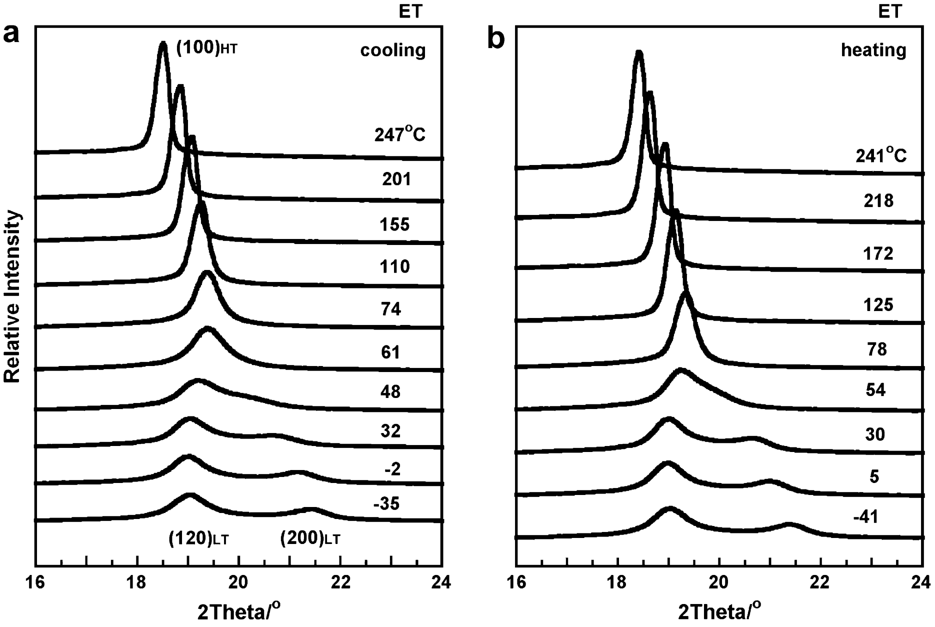

Fig. 1. Temperature dependence of WAXD profile of ET two-components copolymer, (a) cooling process (2 °C/min), (b) heating process (2 °C/min).

temperature phase were broader as the NFH content was higher, indicating more highly disordered crystal structure or smaller domain size of the crystallites. Fig. 5 shows the temperature dependence of the lattice spacings measured for ET–C4F9(0.8%), ET–C4F9(1.5%) and ET–C4F9(3.3%). The phase transition occurred in the temperature range of 20–50 °C. The transition point is slightly lower than that of ET two-components polymer, but it is not very strongly affected by the content of NFH unit. The lattice spacings are slightly longer for ET–C4F9(3.3%) than those of ET–C4F9(0.8%) and ET–C4F9(1.5%) due to higher TFE content in the former case. The thermal hysteresis between the heating and cooling processes became smaller for the copolymer with higher NFH content.

Figs. 6 and 7 show the temperature dependences of the WAXD profiles measured for ET–CF3 copolymers with 2.7 and 4.6 mol% HFP unit, respectively. In these cases, only one peak was observed in a wide temperature range from 0 °C to 250 °C, corresponding to the 100 reflection of the pseudo-hexagonal phase. In the case of ET–CF3(2.7%), the peak was broader and split into two at low temperature, though the deconvolution of the overlapped

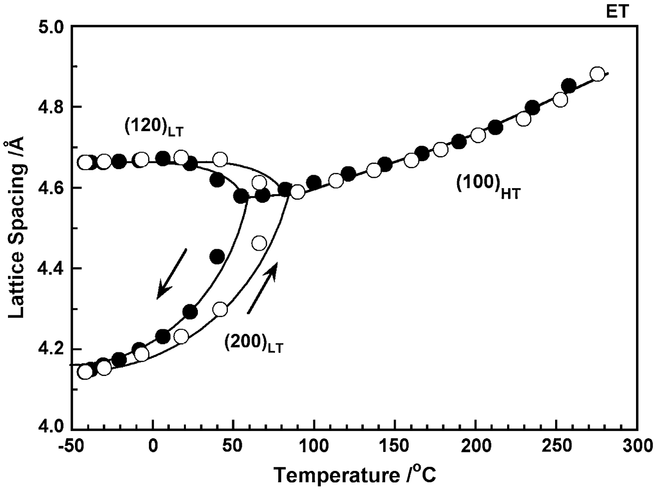

Fig. 2. Temperature dependence of the lattice spacing of orthorhombic (monoclinic) 120 and 200 reflections and pseudo-hexagonal 100 reflection measured for the ET two-components copolymer in the cooling (●) and heating (○) processes at 2 °C/min.

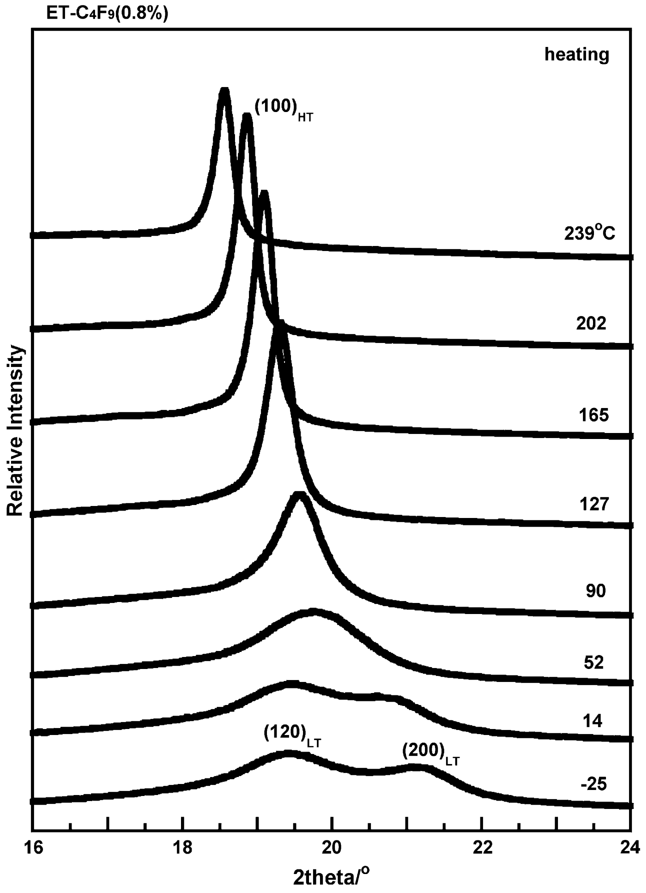

Fig. 3. Temperature dependence of WAXD profile measured for ET–C4F9(0.8%) copolymer in the heating process at 2 °C/min.

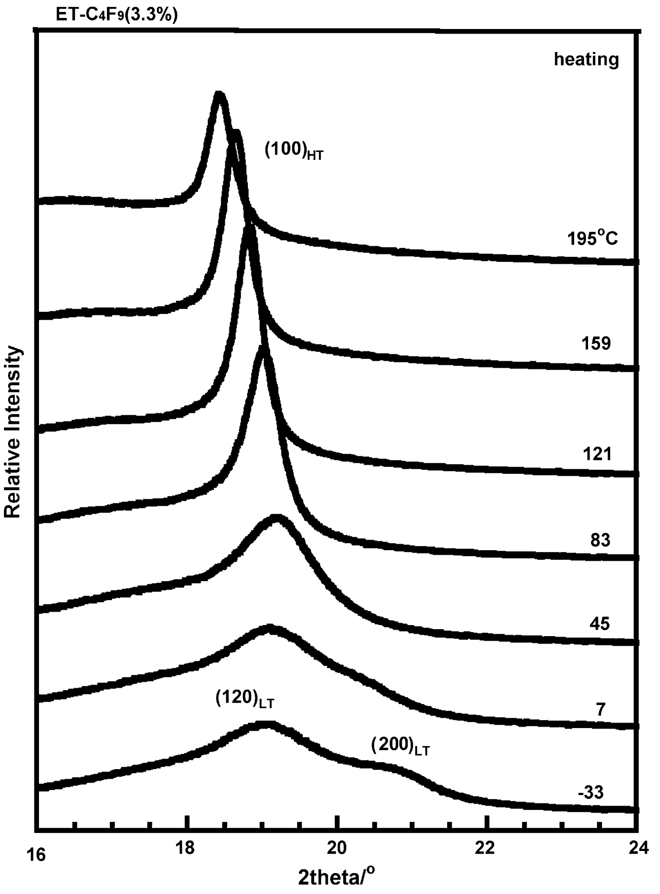

Fig. 4. Temperature dependence of WAXD profile measured for ET–C4F9(3.3%) copolymer in the heating process at 2 °C/min.

reflections is difficult. For sample ET–CF3(4.6%), the peak separation was not still observed even at the lowest temperature of this study as seen in Fig. 8, where the lattice spacings are plotted against temperature.

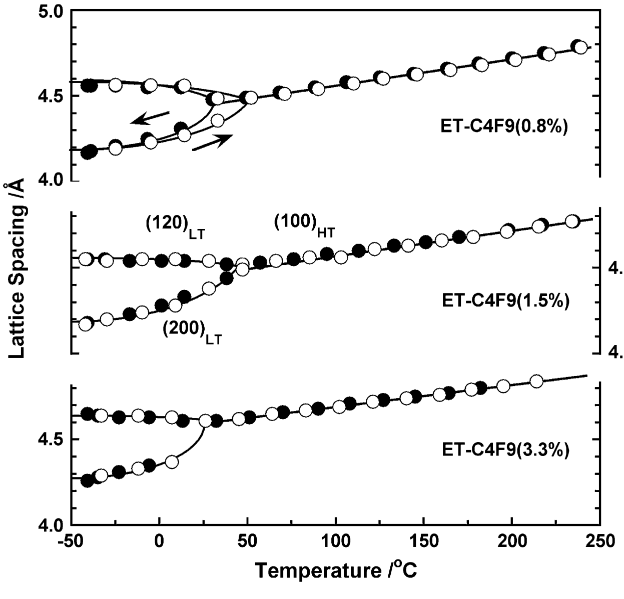

Fig. 5. Temperature dependence of the lattice spacing of the 120 and 200 reflections of the low-temperature phase and the pseudo-hexagonal 100 reflection measured for ET–C4F9 (0.8%), (1.5%) and (3.3%) copolymers in the cooling (●) and heating (○) processes.

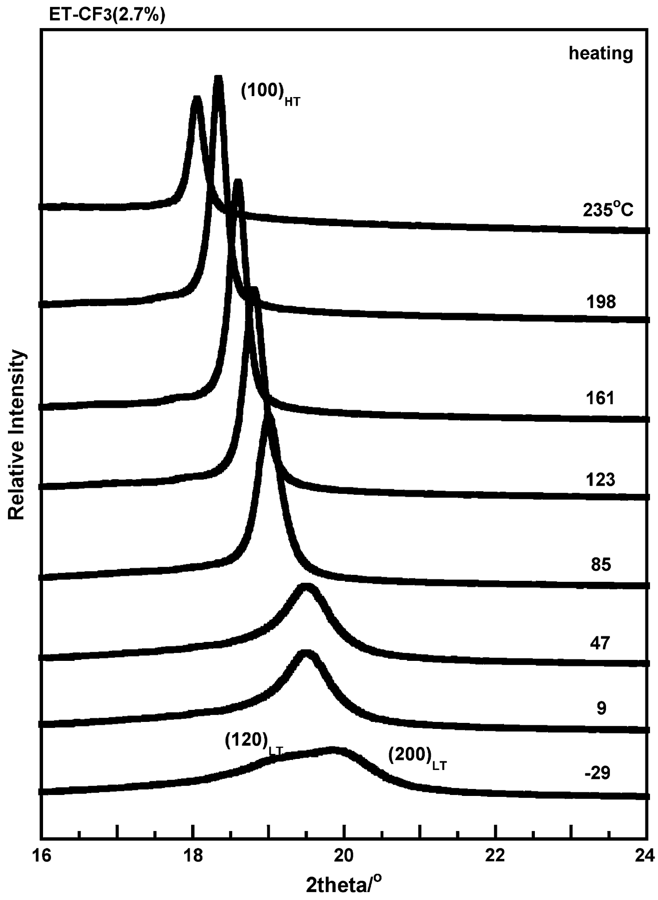

Fig. 6. Temperature dependence of WAXD profile measured for ET–CF3(2.7%) copolymer in the heating process at 2 °C/min.

These X-ray diffraction data allow us to interpret the DSC thermograms measured for all the copolymer samples mentioned in the present paper. For example, Fig. 9 shows the DSC thermograms measured for ET two-components sample in the heating and cooling processes. The small endo- and exothermic peaks are detected at about 60 and 50 °C in the heating and cooling processes, respectively. They correspond well to the phase transition points between the low- and high-temperature phases. Fig. 10 shows the case of ET–CF3(2.7%). The endo- and exothermic peaks corresponding to the phase transition points are difficult to detect.

The melting and phase transition points detected by DSC and WAXD measurements are plotted in Fig. 11. The melting temperature decreases rapidly with an increase in NFH (–C_4F_9) content. This melting point depression is smaller for ET–CF3 copolymer. The phase transition point decreases also with increasing the third monomer content. The degree is smaller for ET–C4F9 but more remarkable for ET–CF3.

Fig. 12 shows the SAXS profiles measured at room temperature for ET, ET–4F9 and ET–CF3 samples. In the case of ET, an intense peak is observed at about $2\theta = 0.28°$, corresponding to the long period of 260 Å. The peak becomes broader by introducing the third monomeric unit. As plotted in Fig. 13, the long period becomes shorter for the copolymer with higher content of the third monomer unit. In particular, the long period decreases more remarkably for ET–C4F9 copolymer.

In this way the thermal properties and phase transition behavior have been found to be affected remarkably by the difference in content and side chain length of the third monomeric unit. The effect is more remarkable for the samples with HFP unit (–CF_3). These phenomena may be reasonably interpreted

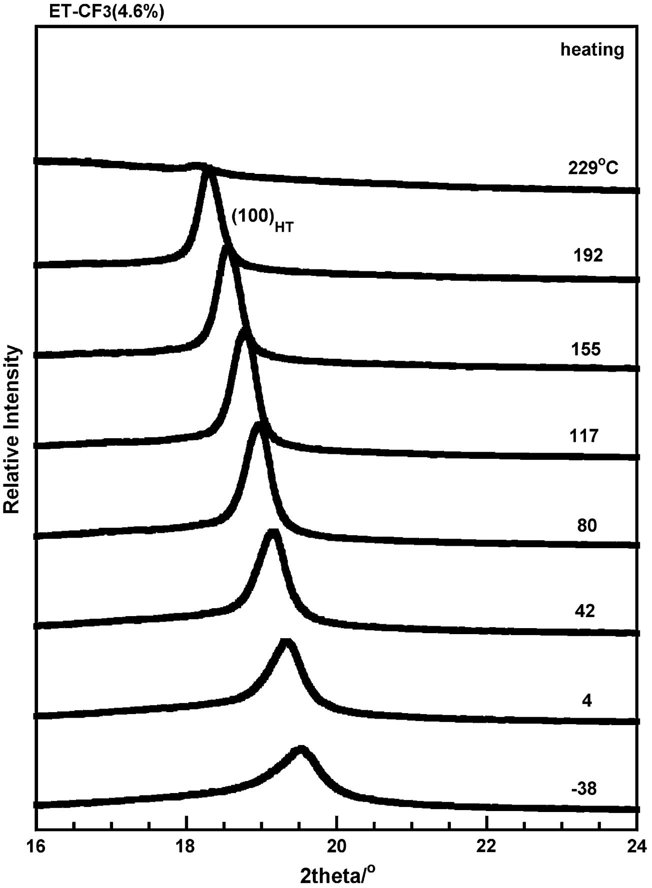

Fig. 7. Temperature dependence of WAXD profile measured for ET–CF3(4.6%) copolymer in the heating process at 2 °C/min.

by assuming an incorporation of the side chain groups of the third component into the crystal lattice. The CF_3 side group is short and can be included into the crystal lattice and expand the lattice. The C_4F_9 side chain is long and excluded from the crystal lattice, and it gives almost no influence on the crystal structure. The cell expansion means the looser packing of the copolymer chains, resulting in easier occurrence of the transition between the low- and high-temperature phases at a lower temperature. On the other hand, the long period is reduced remarkably by introducing the C_4F_9 side groups. This is consistent with the above-mentioned spatial distribution of side groups. The long side groups are excluded from the crystal lattice and existent on the lamellar surface or in the amorphous region, and therefore the lamellar thickness becomes thinner since only the parts of straight stems without long side groups are included in the lamellae. The CF_3 side groups are included in the crystal lattice and the lamellar thickness (and the long period) becomes only gradually thinner as illustrated in Fig. 14.

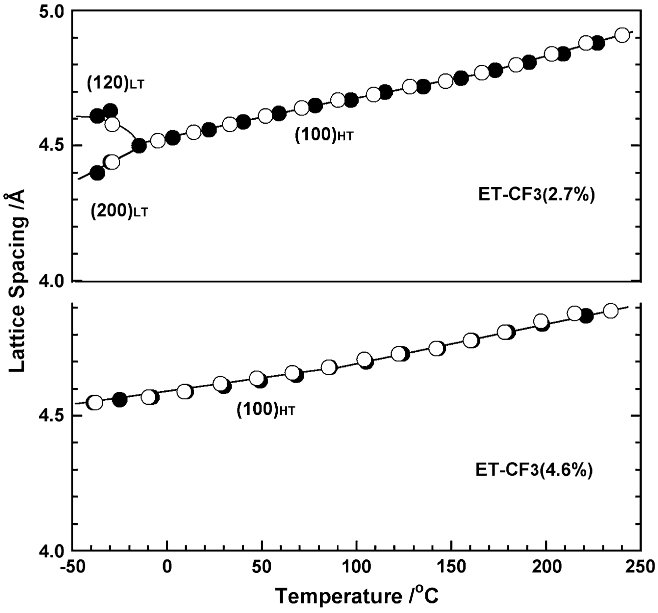

Fig. 8. Temperature dependence of the lattice spacing of the low-temperature 120 and 200 reflections and pseudo-hexagonal 100 reflection measured for ET–CF3(2.7%) and (4.6%) copolymers in the cooling (●) and heating (○) processes at 2 °C/min.

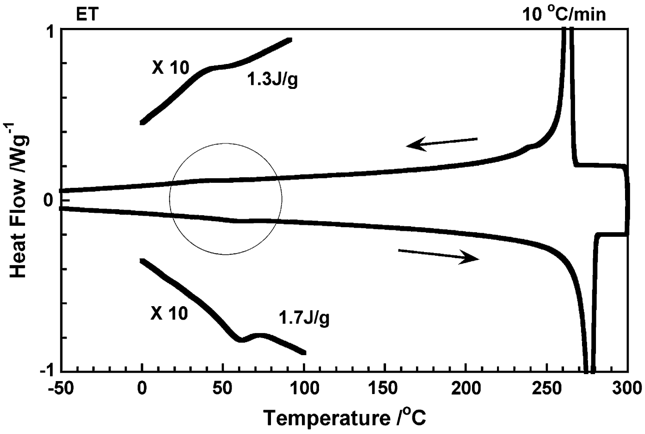

Fig. 9. DSC thermograms of ET two-components copolymer measured in the heating and cooling processes at 10 °C/min.

As additional discussion we need to consider the thermal hysteresis of the phase transition phenomenon. When we compare the transition behavior of ETFE copolymer containing third monomer component (Figs. 5 and 8) with that of the two-component copolymer (Fig. 2), we notice that the thermal hysteresis between the heating and cooling processes gradually disappears for the copolymer with higher content of the third component. The thermal hysteresis is considered to come from the existence of energy barrier between the low- and high-temperature phases which may be different depending on the route. Introduction of the third monomeric unit seems to reduce these

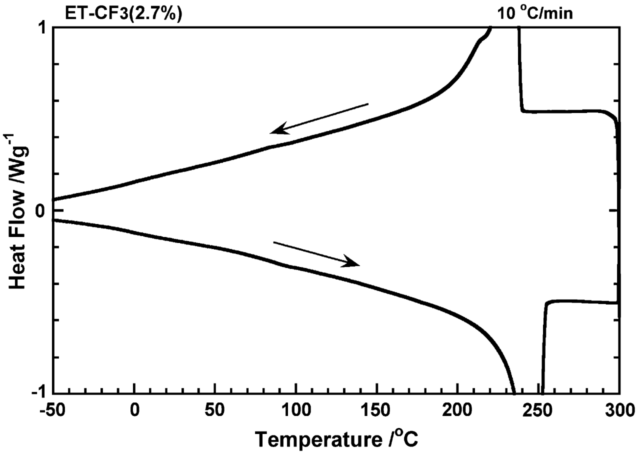

Fig. 10. DSC thermograms of ET–CF3(2.7%) copolymer measured in the heating and cooling processes at 10 °C/min.

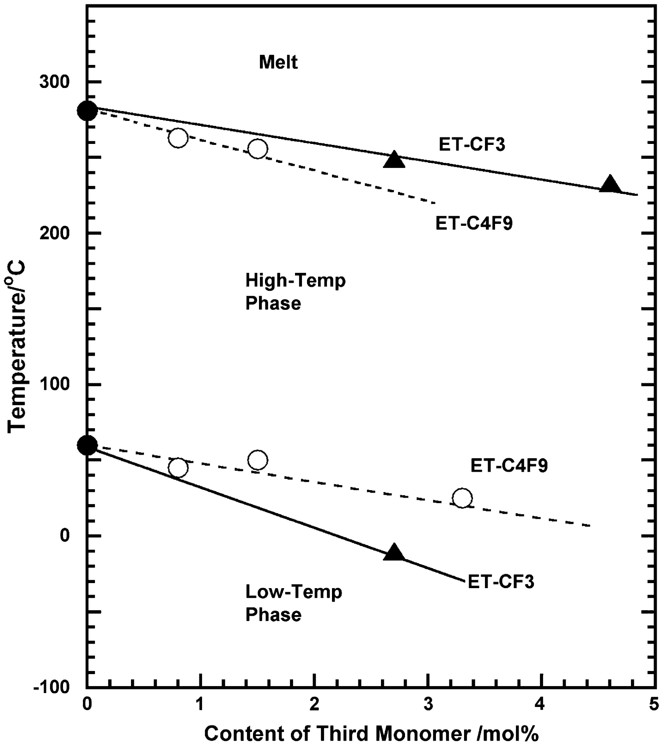

Fig. 11. Dependence of melting and phase transition temperatures on the third monomer content obtained for E/TFE (●), ET–C4F9 (○) and ET–CF3 (▲) copolymers.

energy barriers due to some expansion of the unit cell size, resulting in almost negligibly small hysteresis. The unit cell expansion is considered to reflect also on the shift of phase transition temperature itself as seen clearly for the case of side group of CF_3. In this way the introduction of the third monomeric unit causes the easier transition between the low- and high-temperature phases with smaller thermal hysteresis.

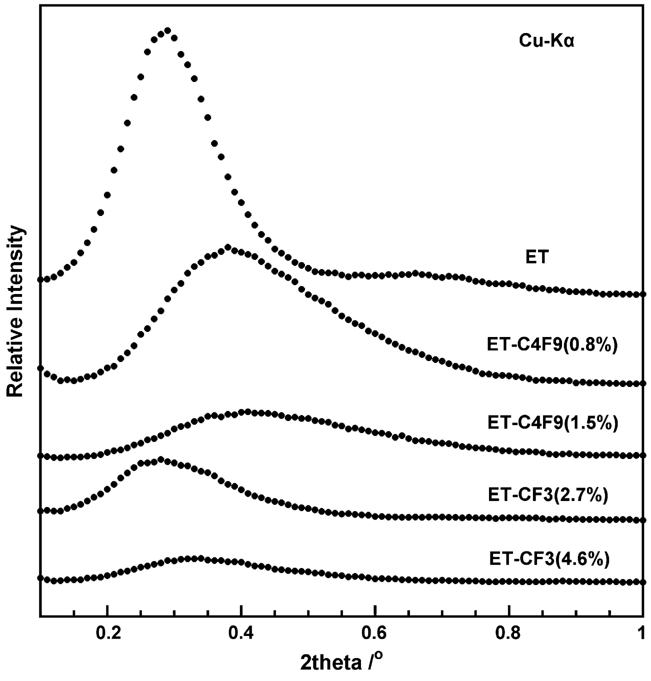

Fig. 12. SAXS profiles of ET, ET–C4F9 and ET–CF3 measured at room temperature.

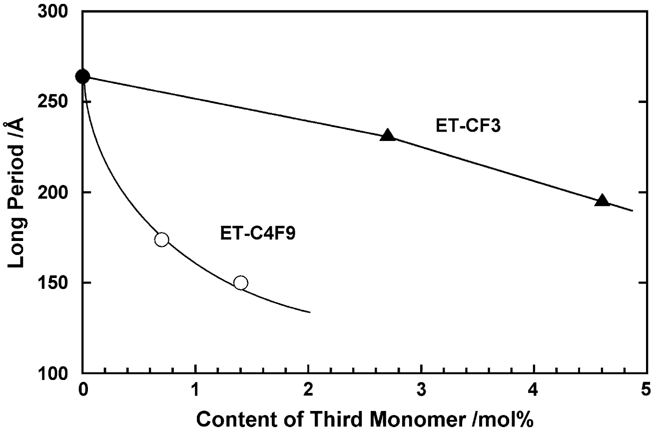

Fig. 13. The dependence of long period on the third monomer content estimated for ET (●), ET–C4F9 (○) and ET–CF3 (▲) copolymers.

As shown in Fig. 11, the melting and phase transition points are found to be reduced also to some extent by introduction of the third component. The effect on the melting point depression is more remarkable for the case of C_4F_9 case, while the effect on the phase transition point depression is larger for the case of CF_3 groups. The structural disordering on the lamellar surface and the smaller lamellar thickness may be caused by the existence of side groups, which result in the energetic instability of the crystal lattice. The unit cell size is also affected sensitively by the existence of side groups. The degree of transition point depression is considered to come from the sensitive balance between the factors of small lamellar thickness, surface disordering, unit cell expansion etc. Remarkable shift of phase transition point seen for CF_3 side group might come from the larger contribution of the factor of the unit cell expansion due to the coexistence of CF_3 groups in the ETFE unit cell. Remarkable shift of melting point for C_4F_9 groups may be due to the effect of structural disordering on the lamellar surface which may make the surface melting easier. For more detailed interpretation the molecular dynamics

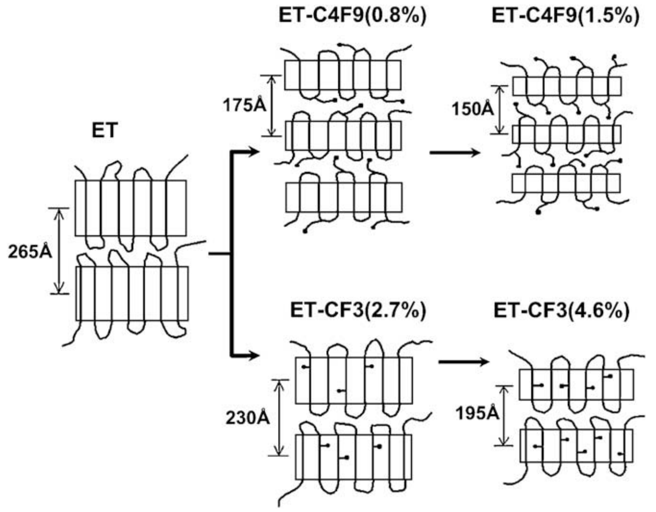

Fig. 14. Schematic illustration of stacked lamellae of ETFE copolymers including the third monomer content. In the case of ET–CF3, the CF_3 groups are included in the crystal lattice and the lattice is expanded, while the long period of lamellae is not affected very much. In the case of C_4F_9 groups, the long side chains are excluded from the crystal lattice, and the lattice is not very much expanded. The long period or the lamellar thickness becomes thinner with an increase in C_4F_9 content.

calculation, for example, may be needed for the concrete structural models of these fluorine copolymers.

4. Conclusions

The crystal phase transition of ethylene–tetrafluoroethylene alternating copolymer (ETFE) containing the third monomer has been investigated by the measurements of temperature dependent WAXD, SAXS and DSC. NFH (C_4F_9) and HFP (CF_3) were chosen as the third monomers. In the case of ETFE copolymer containing NFH, the crystal phase transition temperatures were almost the same among the samples whose NFH contents were 0.7–3.3 mol%. In the case of ETFE copolymer containing HFP, the crystal phase transition temperature drastically decreases with an increase of HFP content. These phenomena were reasonably interpreted by assuming that the short side chains (CF_3) are included in the crystal lattices, whereas the long side chains (C_4F_9) are excluded from the crystal lattices. As the results, the lattice is expanded by the CF_3 group inclusion, reducing the phase transition point as seen in Fig. 11. The difference in side chain length may be one of the most significant causes of these phenomena. This idea was also supported by the results of SAXS and DSC measurements.

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