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Structural Study of Phase Transition Behavior of Uniaxially-Oriented Ethylene-Tetrafluoroethylene Alternating Copolymer

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Summary: Crystal modifications and phase transition behavior have been investigated for the uniaxially-oriented ethylene-tetrafluoroethylene alternating copolymer samples of equimolar content by the temperature-dependent X-ray diffraction and Raman spectral measurements. The X-ray fiber diagram measured for the sample drawn at 0 °C has been found to be quite different from that drawn above 100 °C or the normal orthorhombic-type sample. The new X-ray diagram is characterized by the sharpness of the reflections and the positional shift from the horizontal lines, indicating the tilting phenomenon of the crystallites. This sample was found to transform into the hexagonal phase in the temperature region around 110 °C with keeping the tilting phenomenon. The molecular motion of the more or less conformationally disordered chains was enhanced above this transition region as seen from the increase in the half-width of trans bands and the intensity increment of gauche bands in the Raman spectra.

Keywords: crystal modification; ethylene-tetrafluoroethylene copolymer; infrared spectra; phase transition; Raman spectra; X-ray diffraction diagram

Introduction

Ethylene-tetrafluoroethylene alternating copolymer [–(–$CH_2CH_2CF_2CF_2$–)–, ETFE] is one of the industrially most important fluorine polymers. As imagined from the chemical structure, this copolymer may take the characteristic properties originating from polyethylene, polytetrafluoroethylene and poly(vinylidene fluoride). Up to now, this copolymer has been proposed to show two crystalline phases, orthorhombic and hexagonal phases, at low and high temperatures, respectively.[1–3] However, when the X-ray diffraction pattern of the orthorhombic phase is compared between the reports by Tanigami *et al.*[1] and D'Aniello *et al.*,[3] the relative intensity of the two main peaks is quite different. This might be due to such a situation that they used the samples containing various types of crystalline phases at different ratios. Commercial product has been said to contain the third component such as perfluoropropylperfluorovinylether, hexafluoropropylene, or hexafluoroisobutene, affecting significantly the stability of crystal modifications and the phase transition behavior.[3,4] Depending on the orientation of crystallites, the relative intensity of X-ray reflections may be also affected to some extent. We have many essentially important but not-yet-solved problems about the crystal structure and phase transition behavior of this copolymer. In order to clean up the controversial interpretation of the crystal modifications, the phase transition behavior, and the effect of third component, we have investigated the ETFE species consisting of

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only two components, ethylene and tetrafluoroethylene, with equimolar ratio by measuring the X-ray diffraction and IR/Raman spectra for the uniaxially oriented samples.

Crystal Modifications of ETFE

Uniaxially oriented samples were prepared by drawing at various temperatures after melt-quenching in ice-water. Figure 1 shows the X-ray fiber diagrams of these ETFE samples. When the sample was stretched at a temperature higher than 100 °C, the X-ray diffraction pattern was obtained which was similar to that reported by Tanigami *et al.*[1]. The crystal form giving this X-ray diffraction pattern is called here the α form. On the other hand, the sample drawn at 0 °C was found to give the new X-ray fiber diagram which had never been reported so far. We call it the β form. When the drawing temperature is increased, the X-ray pattern changes from the pattern of the β form to that of the α form. Figure 2 shows the X-ray fiber diagrams of the α and β forms taken at room temperature. The characteristic features of the X-ray diffraction pattern of the β form are as follows: (1) the reflections are relatively sharp compared with those of the α form; (2) there are some specific reflections which have never been found for the α form; and (3) many reflections are shifted upward and downward from the equatorial line, so-called tilting phenomenon. That is to say, the crystalline lamellae are tilted by some degrees from the drawing direction. We are now analyzing the X-ray diagram by taking this tilting phenomenon into account.

The polarized infrared spectra of the α and β forms are shown in Figure 3 (a). The dichroic ratio between the parallel and perpendicular band intensities is apparently lower for the β form than the α form due to the tilting phenomenon of the former sample. Although the relative intensities of various peaks are different from each other in this way, the spectral profiles are essentially the same, suggesting that the molecular chain takes commonly the planarzigzag conformation. The similar situation can be observed also for the polarized Raman spectra shown in Figure 3 (b).

Phase Transition Behavior

In order to clarify the phase transition behavior of the α and β forms, the temperature dependence of WAXD was measured. Figure 4 shows a series of X-ray fiber diagrams of the α form measured in the

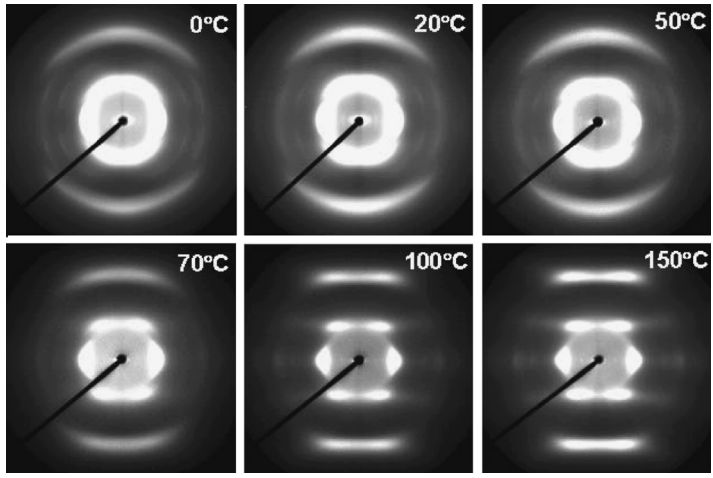

Figure 1.
X-ray fiber diagrams of ETFE drawn at various temperatures.

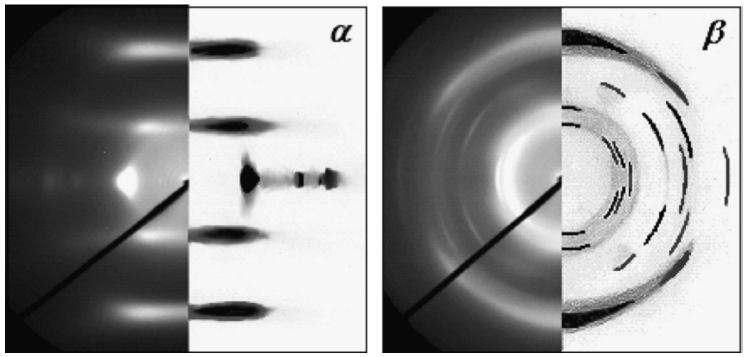

Figure 2.
X-ray fiber diagrams and their illustrations of the α and β forms, where the stretching directions are vertical.

heating process. The essential feature of the pattern does not change significantly but the sharpness and peak position of the innermost reflection on the equatorial line, for example, are found to change gradually with increasing temperature as plotted in Figure 5. When the temperature is increased, the lattice spacing of this reflection becomes larger, reflecting the thermal expansion of the unit cell. The half-width is found to decrease with increasing temperature. In general, the half-width corresponds to the size of the X-ray coherent crystalline region in an inversed relation.[5] As discussed previously,[6] if a crystallite is assumed to consist of many domains, when the temperature increases, the domains are fused into one larger domain because the large-amplitude rotation of the chains erases the difference between the domains. In this way, the decrease in half-width is considered to come from the increase in the

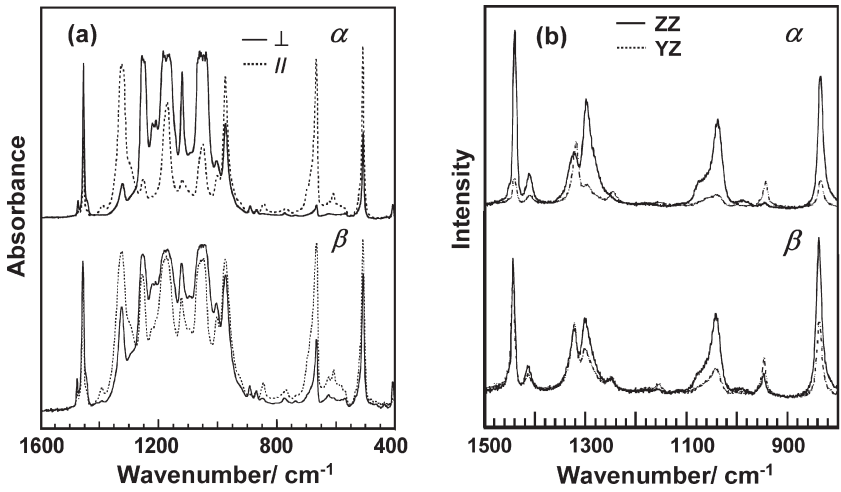

Figure 3.
(a) Polarized IR spectra and (b) polarized Raman spectra of the α and β forms. In (a), the solid and broken lines represent respectively the absorption taken by the infrared beam with the electric vectors perpendicular and parallel to the orientation direction. In (b), the solid and broken lines represent respectively the Raman components taken with the ZZ and YZ polarization geometry where the X, Y, and Z are the Cartesian coordinates system fixed on the sample and the Z is along the draw axis.

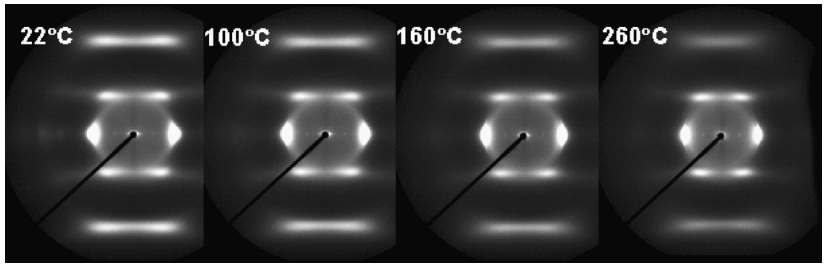

Figure 4.
X-ray fiber diagrams of the α form taken at the various temperatures in the heating process.

X-ray coherent domain size due to the enhanced thermal motion of the molecular chains. The second layer line becomes diffuse at higher temperature as shown in Figure 4, indicating the generation of some disorder in the relative height of the thermally-activated chains.

To investigate the thermal motion of polymer chain more concretely, the temperature dependent Raman spectral measurement was carried out. Figure 6 shows the Raman spectra measured for the uniaxially-drawn ETFE α form at the various temperatures. The whole profile of the spectra is almost unchanged, but the half-width of the bands is found to change clearly in the transition temperature region. For example, Figure 6 (b) shows the half-width estimated for the 1444 cm^{-1} CH_2 bending band, the 836 cm^{-1} CF_2 stretching band, and 328 cm^{-1} CF_2 bending band.[7] An increase of half-width reflects the shortening of the relaxation time of the molecular motion. Therefore, the deflection point detected in Figure 6 (b) indicates the enhanced activation of the thermal motion, probably the rotational motion of the chains around the chain axis. In addition, the generation of Raman bands corresponding to the skeletal gauche bonds is detected above 100 °C.[8] For example, the broad bands at 820 and 628 cm^{-1} correspond to the trans-gauche sequence as seen in the spectra of poly(vinylidene fluoride) forms II and III.[6] In Figure 6 (b) is plotted also the relative intensity of gauche bands against temperature. In this way, in the orthorhombic-to-hexagonal phase transition of ETFE α form, the thermal motion of chains is activated with some gauche bands generated in the skeletal linkages.

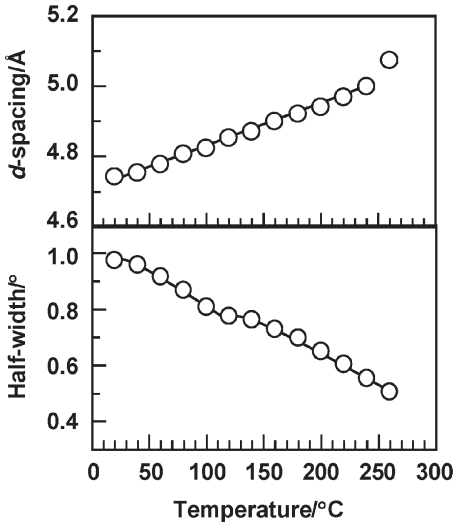

Figure 5.
Temperature dependence of lattice spacing and half-width of the innermost equatorial reflection of the α form.

Phase Transition of the β Form

Although the indexing of the X-ray reflections observed for the β form has not yet been made exactly, the temperature dependence of the lattice spacings was estimated for some equatorial-line reflections. As shown in Figure 7, the three reflections merge into one above the transition region to the hexagonal phase. It should be noticed here that the tilting phenomenon, detected as a shift of reflection positions, is kept even

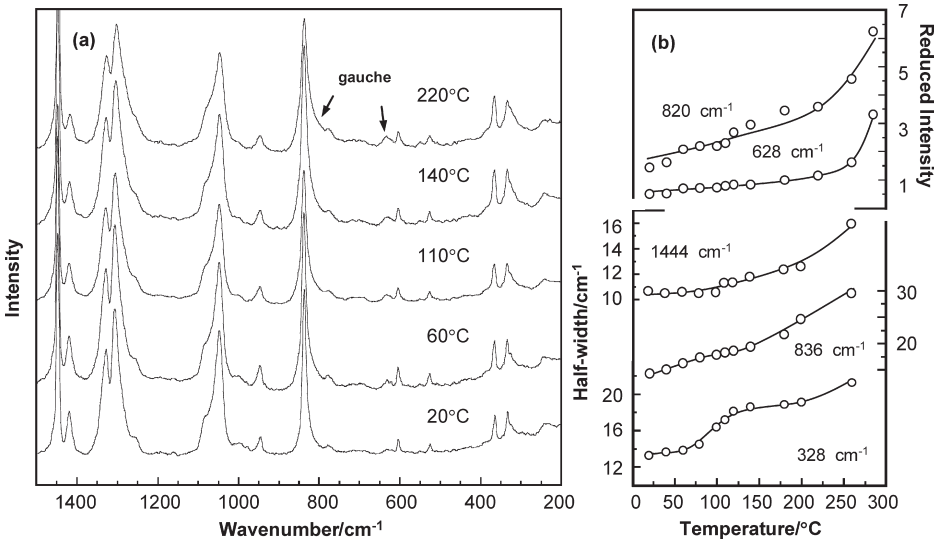

Figure 6.
(a) Raman spectra taken at various temperatures. (b) Temperature dependence of Raman intensities at 820 and 628 cm^{-1} and half-width of the Raman bands at 1444, 836, and 328 cm^{-1}.

after the transition, suggesting the reservation of the tilted crystallite geometry.

The temperature dependence of the Raman spectra of the β form is shown in Figure 8. In higher temperature region, the bands become broader corresponding to the increase in the thermal mobility in the hexagonal phase as seen in Figure 8 (b). Similarly to the case of α form, the generation of broad gauche bands is detected as seen in Figure 8 (a) and (b). Therefore, we may say the same situation as the α form: the thermally-activated thermal motion starts to occur above 110 °C attendant with the conformational disordering through partial trans-to-gauche change.

Conclusion

The phase transitional behavior and the thermal motion of molecular chains have been investigated for the ETFE α and β crystalline forms by measuring the X-ray

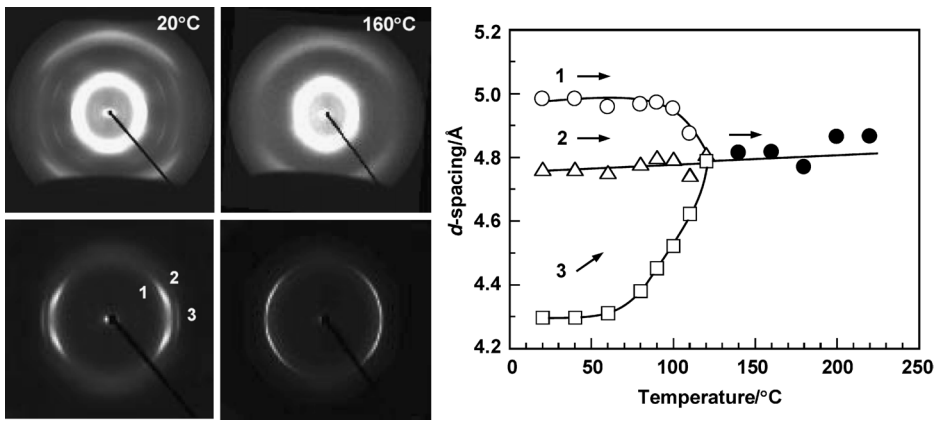

Figure 7.
Temperature dependence of lattice spacings of three innermost equatorial reflections of the β form.

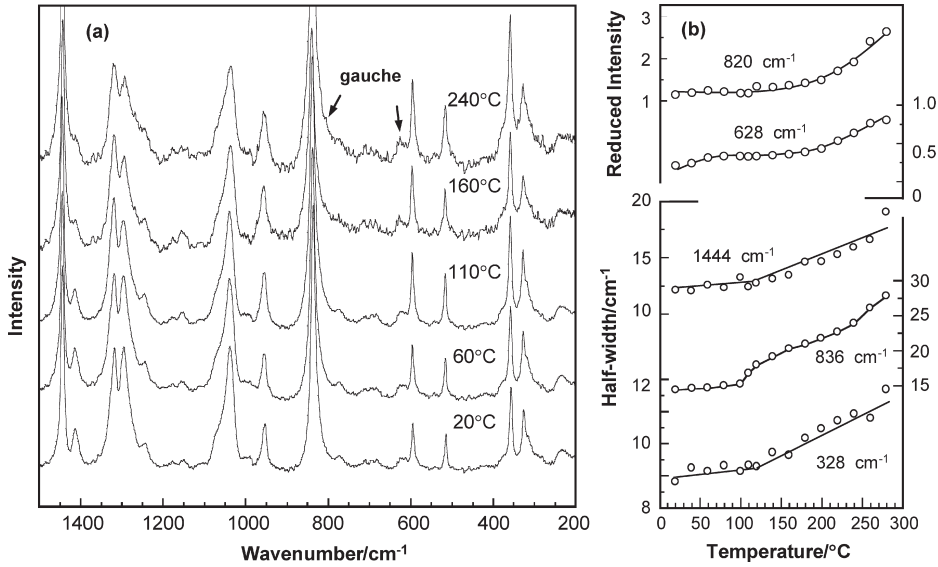

Figure 8.
(a) Raman spectra of the β form taken at different temperatures. (b) Temperature dependence of Raman intensities at 820 and 628 cm^{-1} and half-width estimated for the several Raman bands.

fiber diagrams and the polarized IR and Raman spectra in the course of heating process. The β form has been characterized by its tilting phenomenon of the crystallites. Both of the α and β forms were found to transform into the hexagonal phase above 110 °C, where the rotational motions of the conformationally disordered chains were found to be activated remarkably. We are now analysing the crystal structure of the α and β forms in detail including their temperature dependence.

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