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Influence of the third monomer component on the X-ray-analyzed crystal structure of ethylene–tetrafluoroethylene copolymer

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ABSTRACT

Influence of the third monomer component on the crystal structure of the low-temperature phase of ethylene (E)–tetrafluoroethylene (TFE) alternating copolymer —$(CH_2CH_2CF_2CF_2)_n$— was investigated by the measurement of 2-dimensional wide-angle X-ray diffraction (WAXD) diagrams. Nonafluoro-1-hexene (NFH) and hexafluoropropylene were chosen as the third monomer component (termonomer) with the side chains of —C_4F_9 (ET-C4F9) and —CF_3 (ET-CF3), respectively. Although the termonomer content was low, 1.5 and 2.7 mol%, respectively, the third monomer component has been found to affect more or less the crystal structure of the original 2-component ET copolymer. The crystal structure of these three types of ET copolymer is commonly of the triclinic type. In the case of ET-C4F9 terpolymer, the unit cell size and the setting angle of the planar-zigzag chains in the unit cell are almost the same as those of the 2-component ET copolymer. On the other hand, in the case of ET-CF3 terpolymer, the unit cell becomes larger and the chain setting angle is appreciably different from the 2-component ET copolymer's case. As reported in the previous paper (*Macromolecules*, 44, 1540 (2011)), the long C_4F_9 side chains are not included in the crystal lattice but they are excluded on the lamellar surfaces, not giving significant effect on the inner structure of the unit cell. The short CF_3 groups are included in the crystal lattice and expand the unit cell, resulting in the significant modification of the chain setting angle. These copolymers are known to show the phase transition between the low-temperature-phase and high-temperature phase in a certain temperature region. The transition region is not very different between the 2-component copolymer and ET-C_4F_9 terpolymer, while ET-CF_3 terpolymer shows the transition in an appreciably low temperature region below the room temperature. The difference in such a characteristic phase transition behavior originates from the above-mentioned different situation of the long and short side groups.

1. Introduction

Ethylene (E)–tetrafluoroethylene (TFE) alternating copolymer (ETFE) is one of the melt-processable fluororesins. Because of the excellent thermal and chemical durability and electric properties, ETFE is used for such various industrial applications as chemical equipment materials, wire coating insulations, etc. [1,2]. 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.

This copolymer exhibits the reversible phase transition at around 100 °C between the low- and high-temperature phases [3–15]. Recently we performed successfully the detailed crystal structure analysis of the low-temperature phase of ETFE copolymer with E/TFE = 50/50 M ratio

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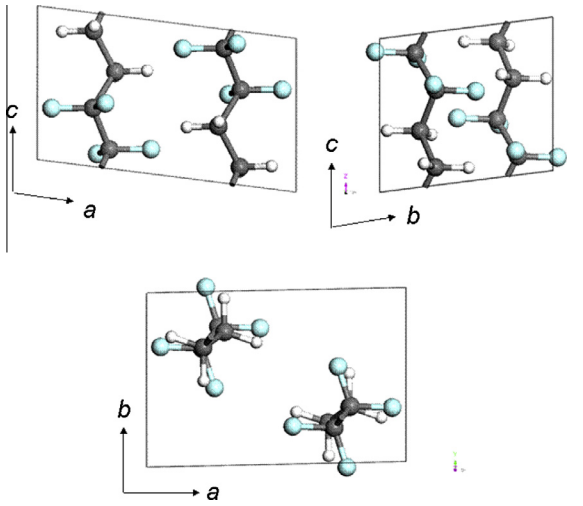

Fig. 1. Basic crystal structure of 2-component ETFE copolymer analyzed using the X-ray diffraction diagram shown in Fig. 4 [17].

[13,16,17], as shown in Fig. 1. The unit cell is of a triclinic type with $a = 8.46$ Å, $b = 5.67$ Å, c (fiber axis) = 5.00 Å, $\alpha = 83.0°$, $\beta = 97.0°$ and $\gamma = 89.7°$ and the space group $P\bar{1}$ [17]. The two chains of slightly-deflected but essentially planar-zigzag conformation are packed in the unit cell with the zigzag plane parallel to the $1\bar{1}0$ direction. These two chains are connected by a point of symmetry and packed upward and downward along the chain axis. The crystal structure model shown in Fig. 1 was proposed so that the observed Bragg's reflections were reproduced as reasonably as possible. More strictly speaking, however, the structure contains some degree of disorderliness about the relative height of the chains. In fact, as will be mentioned again in a later section, the observed $00l$ reflection profile was reproduced well by assuming the existence of small domains of regular chain packing structure and the random aggregation of small domains with the translational disorder along the c-axial direction [17].

By the way, a commercial ETFE sample is not a simple 2-component copolymer, but it contains some amount of the third comonomer unit (terpolymer). An introduction of the third monomer component had solved such a serious problem as the low thermal stress resistance of the 2-component ETFE copolymer [18]. The thermal stress phenomenon is encountered when the ETFE 2-component sample is strongly constrained at both of the ends. The sample is broken relatively easily when it is heated up to the high temperature region near the melting point. An introduction of the third monomer component with relatively long side groups was proposed to increase the so-called taut tie chains connecting the neighboring lamellae, making the sample more mechanically tough [18]. The existence of the third monomer units possessing the side groups affects more or less the crystallinity, crystallite size, phase transition behavior and physical properties of the original ETFE copolymer, as already reported in our previous papers [19,20]. For example, in the case of the terpolymer containing long side chains (—C_4F_9), the phase transition temperature was not very much affected by the existence of the side chains. On the other hand, the crystal phase transition temperature is drastically shifted to a low temperature side by an introduction of termonomer units with short CF_3 side chains, as shown in Fig. 2. These phase transition behaviors are reasonably interpreted by assuming that the long side groups are excluded out of a crystal lattice, whereas the short chain groups are included in the lattice (see Fig. 3).

If the role of the side chains is different as shown in Fig. 3 depending on the length of the side chain group, it may be also expected that the inner structure of the unit cell is affected also differently. It is easy to imagine the change of chain packing structure for the copolymer containing the short CF_3 side groups since the CF_3 groups are included in the lattice and expand the unit cell size more or less. In the case of long C_4F_9 side groups, we may have two possibilities. Since these groups are not included in the crystal lattice, the influence on the chain packing structure might be quite small and the crystal structure may be essentially the same as that of the 2-component ETFE copolymer. Another possibility is that the existence of C_4F_9 side groups on the lamellar surfaces modifies the surface structure and so the surface energy is changed correspondingly, resulting in the change of the inner chain packing structure since the lamellar thickness is not very large to ignore the surface effect. The similar discussion had been made for the linear low-density polyethylene (LLDPE) samples with the different types of side chains [21–25]. Some kinds of side chains (for example, the methyl and ethyl groups)

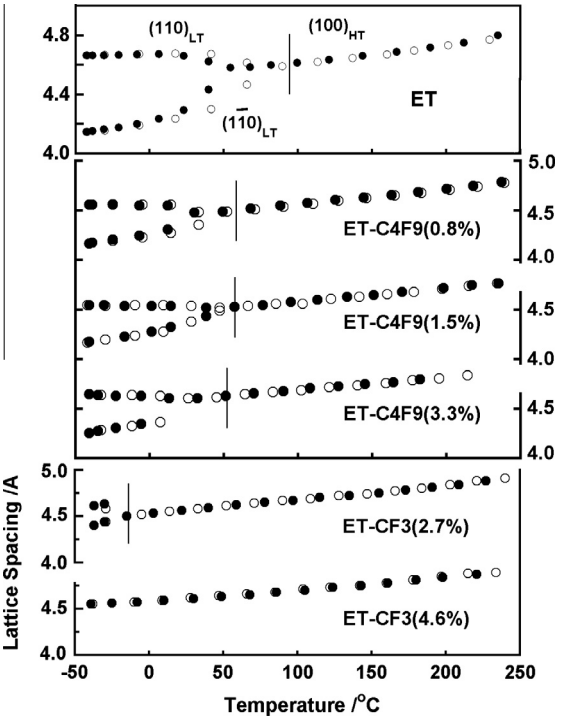

Fig. 2. Phase transition behaviors revealed for a series of ETFE copolymers with and without the third monomer component. The transition temperature between the low-temperature (LT) and high-temperature (HT) phases is shifted to the lower temperature side depending on the type and content of the third monomeric unit. The open and solid circles indicate the heating and cooling processes, respectively [20].