Polymer 49 (2008) 5497–5503

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

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

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ARTICLE INFO

*Article history:*
Received 14 June 2008
Received in revised form 6 October 2008
Accepted 14 October 2008
Available online 18 October 2008

*Keywords:*
Ethylene–tetrafluoroethylene copolymer
Third component
Crystal phase transition

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.