

Structural Changes in Crystallization and Ferroelectric Phase Transition of Fluorine Polymers

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In a series of papers we have investigated the structural changes in isothermal crystallization of polyethylene through the time-resolved measurements of SAXS, WAXS, FTIR, WANS, and SANS [for example, *Polym. J.*, **31**, 677 (1999)]. The regularization to orthorhombic phase is found to occur not directly from the molten state but *via* the transient and conformationally-disordered hexagonal phase. The similar hexagonal phase can be seen also for vinylidene fluoride (VDF) copolymers [Ferroelectric Polymers: Chemistry, Physics, and Technology (H. S. Nalwa edt.), Marcel Dekker Inc., p.63 (1995)]. In these cases the molten phase crystallizes at first as the conformationally-disordered hexagonal phase or nonpolar paraelectric phase (high-temperature phase, HT) when the samples are cooled slowly from the melt, and this HT phase transforms to ferroelectric polar crystal phase (or low-temperature phase, LT) below the Curie transition temperature (Tc). When the sample is cooled suddenly to the temperature above Tc, the crystallization to the HT phase is predicted to occur. But, when the sample is cooled suddenly down below Tc, does the melt crystallize into the LT phase directly or *via* HT phase through the conformational ordering from disordered trans-gauche form to regular all-trans form? The latter idea is based on the so-called Ostwald principle: the transition between the two stable phases might occur passing through the thermodynamically-unstable intermediate phase(s). In order to check this principle we have measured the time-dependent structural changes in the crystallization

process of vinylidene fluoride-trifluoroethylene copolymer with VDF 73 mol% content (Tc = 80°C) by using a temperature jump equipment with rapid scanning SAXS (BL10C) and WAXS (BL15A) apparatuses.

As reported already, the temperature jump could be made at a rate of 600–1000°C/min, during which the WAXS and SAXS data were collected every 3–10 sec. When the temperature jump was made from the melt to the temperature region of HT phase (103°C), the crystallization of the HT phase could be observed clearly as judged from the evolution of the sharp (100) reflection. On the other hand, when the jump was made to 73°C below Tc, the appearance of the HT phase could not be detected but only the broad peak due to the LT phase and the amorphous phase could be observed, i.e., the crystallization was considered to occur directly from the melt to the LT phase not *via* the HT phase. This experimental result might indicate the breakdown of the Ostwald principle. But, the observation of LT phase might come from such a situation that the crystallization to the HT phase and the phase transition from the HT to LT phase are too fast to detect by the present experimental technique and these two phenomena might have already passed before the sample was dropped to the position of the X-ray beam during the temperature jump process. We are now refining the experimental conditions furthermore so as to confirm the above-mentioned results.