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Time-resolved WAXS and SAXS measurements for structural study of crystallization and ferroelectric phase transition of fluorine polymers

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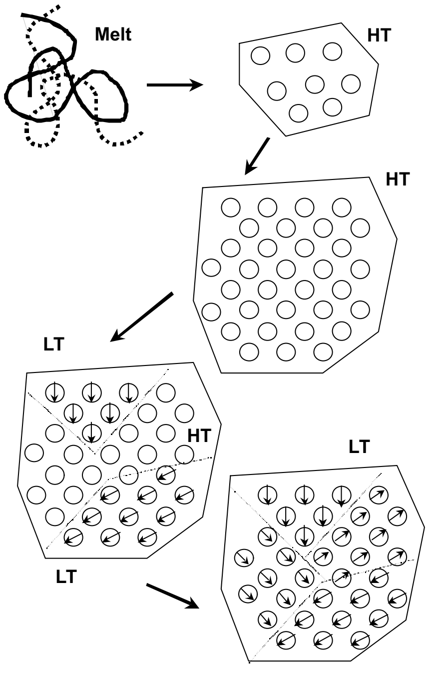
Vinylidene fluoride - trifluoroethylene (VDF-TrFE) copolymers exhibit the ferroelectric phase transition between polar low-temperature (LT) phase and nonpolar high-temperature (HT) phase at a Curie transition temperature (Tc). The structural change has been investigated in detail by combining various kinds of techniques [Ferroelectric Polymers: Chemistry, Physics, and Technology (H. S. Nalwa edt.), Marcel Dekker Inc., p.63 (1995)]. But, in order to clarify the transition mechanism in more detail, we need to investigate the kinetics of this phase transition. Then we have carried out the time-resolved measurements of wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) in the course of crystallization and ferroelectric phase transition though the temperature jump from the molten state.

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, the crystallization of the HT phase could be observed clearly as judged from the evolution of the sharp (100) reflection. Half width of the reflection was wide in the earliest stage of crystallization but decreased gradually with a passage of time. At the same time the peak position was found to shift to higher angle direction. On the other hand, when the jump was made to the region of LT phase below Tc, it was confirmed that the reflection of the HT phase appeared at first and then was replaced by the reflection of LT phase. The behavior of the HT reflection was essentially the same with the case of above-mentioned jump to the HT phase, but the reflection of the LT phase was found to be almost constant and quite broad compared with the width of the HT phase reflection. These observations allowed us to speculate the structural change shown in Figure. At first the HT phase is crystallized from the melt, but the crystallite size is small and chain packing is not tight. As the passage of time the crystallite size becomes larger and the chain packing becomes tighter. In this crystallite the phase transition from HT to LT phase occurs, just when the LT phase forms small domains with parallel dipole arrays, giving broad reflection of the LT phase. The number of these small domains increases gradually and the whole crystallite becomes an aggregation of domains of different dipole arrays or forms the so-called multi-domain structure.



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