Investigation of Morphological and Crystal Structural Change of Vinylidene fluoride-Trifluoroethylene Copolymers in Ferroelectric Phase Transition Process by Synchrotron DSC/WAXD/SAXS Simultaneous Measurements

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Introduction

Vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymers show the ferroelectric phase transition at a Curie transition temperature. For the sample with VDF contents higher than 80 mol %, the transition behavior is somewhat complicated compared the other copolymers, and the transition occurs between the polar crystalline forms I, II and the nonpolar high-temperature phase, where form I is the polar crystal of planar-zigzag chains, form II consists of molecular chains of TGTG* conformation, and HT phase consisting of conformationally-disordered chains of gauche type. It has been found that the structural change in crystal lattice affects not only the inside of the crystalline lamella but also the morphological change of stacked lamellae drastically[1)]. The morphological change and its relation with the crystal structural change have not yet been clarified at all. In this work, we will report the experimental data concerning the simultaneous measurements of DSC/WAXD/SAXS during the heating and cooling process of VDF 82% copolymer samples.

Experiments

VDF 82% sample consists of the form II was melted and quenched into liquid nitrogen vessel. Simultaneous measurements of DSC, WAXD and SAXS were carried out at BL40B2 of SPring-8. The wave length was 1.5Å. The sample was set in an aluminium pan with a thin bottom for the X-ray transmission. Afterward, the pan was installed into a DSC vessel, FP84 hot stage (Mettler-Toledo International Inc., U.S.A.) customized for measuring X-ray scattering at $2\theta < 28°$. The 2-dimensional WAXD pattern was taken with an imaging plate (IP) with a small hole in the center. Through this small hole, a scattered X-ray beam was collected with a R-AXIS IV++ IP System (Rigaku Co., Japan) at a distance of ca. 2m form the sample position. The simultaneous measurements of X-ray scattering patterns and DSC thermograms were performed for a sample for 30 sec at 5 min-intervals in the heating and cooling process at a rate of 1 °C/min.

Results and Discussion

As an example the transition behaviour of the heating process for melt-quenched sample is shown in Figure 1, where the starting sample was in the crystalline form II. The long period (d_l), and the mean lamellar thickness (<*d*>) were calculated by the one-dimensional electron density correlation function evaluated by the SAXS profile. The relative intensity of the reflection from the form II decreases and that from the HT phase increases instead in the temperature region from T_A to T_B indicated in the DSC thermogram. On the other hand, <*d*> and d_l increased largely and slightly due to thermal expansion, respectively. In the temperature region from T_B to T_C, the intensities of II form and HT phase drastically decreased, and the amorphous intensity increased. DSC/WAXD/SAXS data suggested that the phase transition form II to the HT phase enhanced lamellar thickening without large change in lamellar stacking distance, and then the HT phase melted with increasing the lamellae thickening distance.

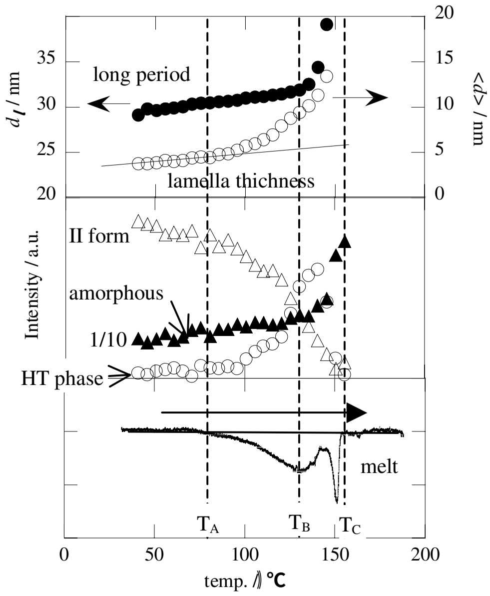

Figure 1. Temperature dependencies of, the mean lamellar thickness (○) and the long period (●), the X-ray (200, 110) intensities of the II form(△) and HT phases (•) and amorphous phases (△). (c): DSC thermogram measured for the melt-quenched sample.

References

1) Tashiro et. al., Preprints, Japan, 34 (1985).