Structural Evolution in Crystallization Process of Polyoxymethylene

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Crystallization mechanism of polymer materials is quite complicated. In a series of papers we have carried out the measurements of X-ray scattering and vibrational spectra in the crystallization process of various kinds of polymers. The combination of X-ray and infrared/Raman techniques should give us many useful information about the structural evolution viewed from the various points. In the present study we have performed the wide-angle (WAXS) and small-angle X-ray scattering (SAXS) measurements in the crystallization process of polyoxymethylene [POM, -(CH2O)n-] during the cooling process from the melt. The thus-obtained data were combined with the separately measured infrared spectral data in order to clarify the structural evolution from the microscopic point of view.

The measurement of infrared spectra in the cooling process of POM revealed that the folded chain crystal (FCC) grew in the temperature region just below the crystallization temperature, which was followed by the formation of extended chain crystal (ECC) in a little lower temperature region [H. Hama and K. Tashiro, Polymer, in press]. The SAXS measurement made in the cooling process from the melt clarified that the lamellar stacking structure was formed below the crystallization temperature and that new lamellae were generated from the amorphous regions sandwiched in between the initially-created lamellae. This new lamellar formation was found to occur in the same temperature region as that of the observation of ECC bands in the infrared spectral measurement. The SAXS data were analyzed quantitatively on the basis of one-dimensional lamellar stacking structure model with the insertion of new lamellae taken into account.

The structural evolution process derived from all these data is illustrated in Figure 1. When the POM sample is cooled from the melt, the stacked lamellar structure of FCC morphology is formed with a long period of ca. 17 nm (temperature region I). As the temperature is lowered furthermore (region II), the new lamellae are crystallized in between the original lamella and the long period changes finally to 6 nm. This new lamellar insertion occurs at a probability of 30%. That is to say, the lamellar stacking structure is not perfect but disordered due to the coexistence of original and inserted lamellae. Some molecular chains passing through the neighboring lamellae are considered to be extended during the formation of the inserted new lamellae, resulting in the local formation of ECC morphology, as revealed by the infrared spectral data (region III).

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![Figure 1. Structural evolution process of POM in the cooling process from the melt.](image_url)