論文内容の要旨

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The crystallization behavior and higher-order structure formation in multicomponent polymer systems containing crystalline components are governed by the following contributing factors: the dilution effect on the crystallization by the amorphous component, the competition between the crystallization and molecular diffusion, and the interplay between the crystallization and liquid-liquid phase separation (LLPS). In this study, based on these factors, the crystallization kinetics and the lamellar structure formation in crystalline polymer blends were revealed, using small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) techniques, differential scanning calorimetry (DSC) and polarized and phase-contrast optical microscopies.

In Chapter 1, the crystallization behavior and the higher-order structure formation in the miscible crystalline/amorphous blend composed of poly(vinylidene fluoride) (PVDF) and isotactic-poly(methyl methacrylate) (*i*-PMMA) were investigated, where *i*-PMMA, which is crystallizable, was in an amorphous state during the crystallization of PVDF because of its extremely slower crystallization. As is expected for a typical miscible crystalline/amorphous blend, PVDF exhibited depressions of both the overall crystallization rate and the melting temperature depending on the blend composition. In the formation of the crystalline lamella, the amorphous *i*-PMMA component was included between the PVDF crystalline lamellae and increased the spacing in the PVDF-rich blends. However, the inclusion of *i*-PMMA into the interlamellar region was limited in the PVDF-poor blends, i.e., a part of *i*-PMMA was excluded from the region. These results were attributed to the competition between the crystallization of PVDF and the molecular diffusion of *i*-PMMA; the crystallization rate of PVDF becomes lowered relative to the diffusion rate of *i*-PMMA, as the content of PVDF decreases.

In Chapter 2, the subsequent crystallization of *i*-PMMA after completion of the crystallization of PVDF was investigated, that is the crystallization under the pre-formed higher-order structure of PVDF. The overall crystallization rate of the subsequent crystallization of *i*-PMMA was enhanced, in which the induction period for the nucleation of *i*-PMMA in the blends was remarkably shortened compared to that in the neat *i*-PMMA. It was concluded that this shortened induction period arose from the role of the pre-existing PVDF crystals as a nucleating agent. The morphological parameters such as the long period, crystalline lamellar thickness and interlamellar spacing estimated from the SAXS experiments indicated that *i*-PMMA was crystallized between the PVDF crystalline lamellae and further expanded that spacing. In the blend that contains relatively less *i*-PMMA content, a confined crystallization of *i*-PMMA was suggested by the depression of the Avrami index, the lower crystallinity of *i*-PMMA and the limited space of the crystallizable region (interlamellar region of the pre-formed PVDF crystal).

In Chapter 3, the crystallization occurring simultaneously with LLPS was presented, using a partly-miscible crystalline/amorphous blend system composed of poly(ethylene glycol) and *i*-PMMA, which has an upper critical solution temperature (UCST)-type LLPS phase diagram. In this system, *i*-PMMA was again dealt with as an amorphous component. When the crystallization of PEG occurs simultaneously with the spinodal decomposition, the overall crystallization rate was more enhanced at higher crystallization temperatures T_c. This unique behavior is different from the result deduced from the usual crystallization mechanism that the crystallization is slower at higher T_c. Therefore, it was concluded that this enhancement could be explained by the fluctuation-assisted secondary nucleation based on the Mitra-Muthukumar theory that the smaller quench depth from the spinodal temperature contributes to faster nucleation. In the crystalline lamellar formation, it was indicated that *i*-PMMA component was excluded from the interlamellar region during the crystallization of PEG.

In Chapter 4, the spherulite growth of poly(ε-caprolactone) (PCL) in blends with styrene-oligomer (SO) was evaluated mainly using the time-resolved phase-contrast and polarized microscopies. As some researchers reported, the PCL spherulite growth accompanied by the exclusion of SO component from the spherulite was observed, in which the droplet-like SO domains were observed at the spherulite growth front in the blend composition of LLPS. The SO droplets interfere with the spherulite growth for a while, and then these were disappeared in the matrix at the late stage of crystallization. With the disappearance of the SO droplets, the spherulite growth was recovered.

In Chapter 5, finally, the crystallization behavior and higher-order structure of a polymer with a specific molecular shape, the star-like polymer and its blends with the linear polymer, were investigated using well-characterized poly(tetrahydrofuran) (PTHF). In the crystallization of the neat star PTHF, higher nucleation density and lower spherulite growth were observed by comparing to those in the linear PTHF. These results were attributed to the higher chain density and lower molecular mobility of the star PTHF, respectively. In the blends of the linear and star PTHFs, generating nuclei in the star-rich blends was as many as in the neat star PTHF. On the other hand, the spherulite growth rate varied linearly with the blend composition. From these results, it was concluded that the nucleation is governed by a major component polymer in the blends, whereas the spherulite growth progresses cooperatively without distinction between the linear and star polymers.