Structure and Dynamics of Crystalline Soft Materials Revealed by Diffraction and Scattering Techniques

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Soft materials spontaneously form hierarchical microstructures ranging from subnanometers to micrometers by phase transitions such as crystallization and phase separation. In particular, crystallization has a significant effect on the structure formation of crystalline soft materials such as semicrystalline polymers, producing a variety of microstructures and properties. Wide-angle X-ray diffraction (WAXD)/small-angle X-ray scattering (SAXS) methods (SWAXS) are powerful techniques to study the hierarchical structure of materials and its dynamics. The author and collaborators have performed SWAXS on various crystalline soft materials and studied their structures and dynamics [1-7]. In this talk, some of the results will be presented.

Laboratory-scale SWAXS measuremsents were conducted by a NANO-Viewer (Rigaku) operating at 45 kV and 60 mA with Cu Kα radiation (λ = 0.1542 nm). An imaging plate BAS-IP SR 127 (Fujifilm) was used as a detector. Synchrotron SWAXS measurements were performed at BL-6A (λ = 0.1500 nm) and BL-10C (λ = 0.1488 or 0.1500 nm) in Photon Factory of KEK (Tsukuba, Japan). Various PILATUS detectors (Dectris) were used. Temperature-controlled sample stages were used: self-built or FP84HT TA Microscopy Cell (Mettler).

Bioplastics, polymers with low environmental impact, were targeted as homopolymers. The hierarchical structure and crystal polymorphism of novel bioplastics were clarified [3, 4, 7]. We also focused on the specially structured polymers—cyclic and cage-shaped polymers. The relationship between topology and hierarchical structure was studied [2]. In addition, the hexagonally packed structure of filamentous viruses and its orientation were analyzed and their effects on thermal diffusivity were evaluated [5].

In crystalline-crystalline diblock copolymers, it was revealed that crystal polymorphism can control the crystallization mode—simultaneous or sequential crystallization of two blocks—and the resultant morphology [6]. We also focused on ternary block copolymers that can be topologically converted from a star to a linear chain by introducing a rotaxane structure. The change in microphase-separated structure induced by topology transformation was clarified [1]. Crystallization/melting of crystalline blocks as well as glass transition of amorphous blocks had a great effect on the temperature dependence of the microphase-separated structure.

In addition to the above results, future prospective will be presented.

References

[1] Sato, H., Aoki, D., Marubayashi, H. *et al. Nat. Commun.* **12**, 6175 (2021).
[2] Mato, Y., Sudo, M., Marubayashi, H. *et al. Macromolecules* **54**, 9079–9090 (2021).
[3] Marubayashi, H., Ushio, T. & Nojima, S. *Macromolecules* **52**, 4624–4633 (2019).
[4] Marubayashi, H., Mizukami, R., Hamada, Y. *et al. Polym. Degrad. Stab.* **153**, 318–324 (2018).
[5] Sawada, T., Murata, Y., Marubayashi, H. *et al. Sci. Rep.* **8**, 5412 (2018).
[6] Osawa, S., Hijikawa, R., Marubayashi, H. & Nojima, S. *Polymer* **122**, 249–257 (2017).
[7] Marubayashi, H. *Sen'i Gakkaishi* **73**, 312–315 (2017).

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