Topology-Transformable Block Copolymers Based on a Rotaxane Structure: Change in Microstructures and Bulk Properties with the Same Composition

Topology is essential in chemistry to describe the features of single molecules and molecular assemblies; thus, topological transformations have attracted great attention for their potential applications. Topology also dominates the characteristics of polymers, especially in multicomponent systems. However, the polymer topology is usually fixed during polymerization. In this study, topology-transformable block copolymers that are connected via rotaxane linkages were synthesized. We present systems in which the topology transformation of block copolymers changes their microphase-separated structures and macroscopic properties. In this highlight, we rationalize a topology-transformation-induced change in microphase-separated structures by simultaneous small-angle X-ray scattering and wide-angle X-ray diffraction measurements.

Topology is essential in chemistry to describe the features of not only single molecules, but also molecular assemblies. The topology of polymers affects their microscopic structure and macroscopic properties [1]. Therefore, polymers whose properties can be changed by inducing a transformation in their topology represent an attractive class of polymer systems. However, the polymer topology is usually fixed during polymerization. Hence, the synthesis of polymers that can undergo a topological change while keeping their composition remains challenging. In this study, the initial microphase-separated structure of block copolymers (BCPs) was converted by a polymer topology transformation via a movable rotaxane linkage at the junction point [2]. Two types of topology-transformable BCPs were prepared and characterized: i) rotaxane-linked ABC star-BCPs [Fig. 1(A)], which are designed to undergo a transition in their microphase-separated structure, and ii) A₈B₈ tetra-BCPs, which are designed to undergo a change in their properties upon topology transformation. We briefly present the results of i) rotaxane-linked ABC star-BCPs in this highlight.

The experimental details are shown in reference [2]. The morphologies of the ABC-type BCPs before (star-ABC) and after (linear-ABC) the topology transformation [Fig. 1(A)] were characterized using scanning transmission electron microscopy (STEM) and small-angle X-ray scattering (SAXS). The bright-field STEM image of star-ABC [Fig. 1(B)] shows a spherical structure in which the distance between neighboring spheres is approximately 24 nm, whereas that of linear-ABC [Fig. 1(C)] depicts a mixed structure of lamellar (d = 37 nm) and cylinder-like structures. The dark areas were assigned to the poly(dimethylsiloxane) microdomain, which was supported by sharpened and newly-appeared BEAMLINES

**REFERENCES**


**BEAMLINES**

BL-6A and BL-10C


**Figure 2:** Results of simultaneous (A) SAXS and (B) WAXD of star- and linear-ABCs at various temperatures.