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 characteristic features 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) A_2B_2 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 ($d \approx 37$ nm) and cylinder-like structures. The dark

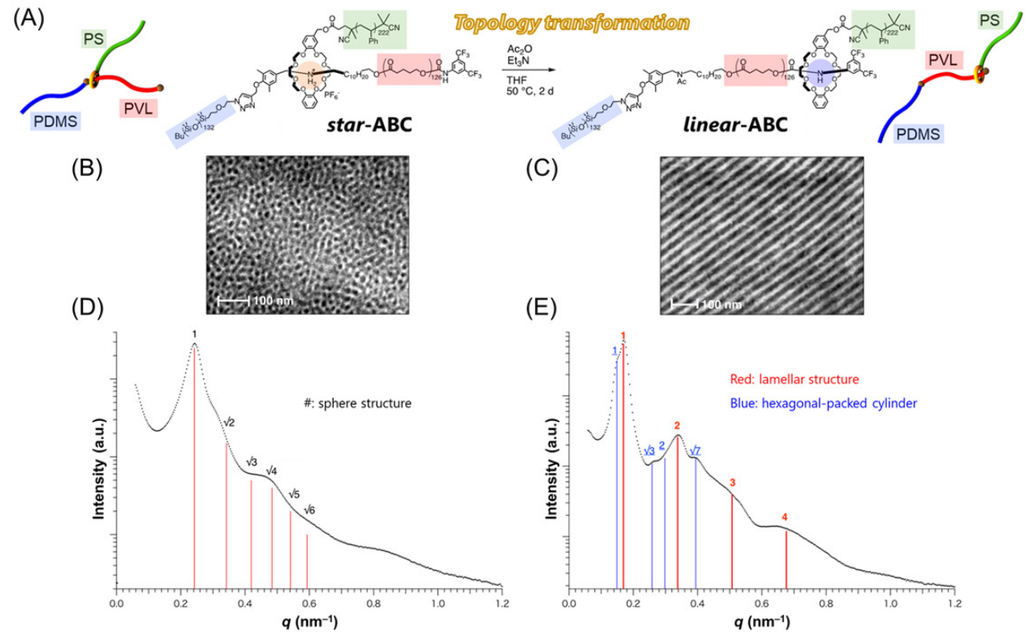

Figure 1: (A) A rotaxane-linked ABC *star*-BCP designed to undergo a change in its microphase-separated structure. **(B)** Bright-field STEM images of *star*-ABC and **(C)** *linear*-ABC. **(D)** SAXS profiles of *star*-ABC and **(E)** *linear*-ABC.

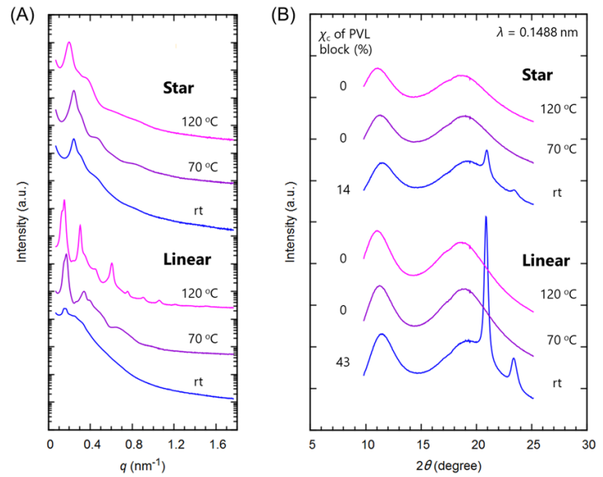

Figure 2: Results of simultaneous **(A)** SAXS and **(B)** WAXD of *star*- and *linear*-ABCs at various temperatures.

areas were assigned to the poly(dimethylsiloxane) microdomains, which was supported by energy dispersive X-ray spectroscopy. The SAXS profiles before and after the topology transformation are shown in **Fig. 1(D)** and **1(E)**, respectively. The SAXS measurements were performed at room temperature, 70°C [> melting temperature (T_m) of poly(valerolactone) (PVL) block], and 120°C [> glass-transition temperature (T_g) of polystyrene (PS) block]. The profiles at 70°C are shown as representative. The spacings of the primary peaks (26 nm for *star*-ABC; 37 nm for lamellar structure in *linear*-ABC) agree well with those obtained from STEM images. Thus, the spherical microdomains formed by *star*-ABC were transformed into a mixed structure of lamellar and cylinder-like structures in *linear*-ABC by the topology transformation.

Next, the temperature-dependent changes in morphologies of two BCPs are discussed based on simultaneous SAXS and wide-angle X-ray diffraction (WAXD) [**Fig. 2(A)** and **(B)**], respectively]. SAXS profiles of *star*-ABC are clearly different from those of *linear*-ABC irrespective of temperature. SAXS profiles of *linear*-ABC show a drastic change with increasing temperature, unlike *star*-ABC. This difference would be attributed to a large difference in the WAXD crystallinity of PVL blocks ($\chi_{c,\,PVL}$). In the case of *star*-ABC, only a small amount of PVL blocks can crystallize, and so the microdomain structure should be less affected by the crystallization of PVL blocks. On the contrary, highly crystalline PVL blocks in *linear*-ABC should deform the microdomain structure [3]. The drastic increase in SAXS peak intensity of *linear*-ABC with increasing temperature to 70°C indicates the ordering of distorted microdomain structure by melting of PVL crystals. With further increase of temperature to 120°C, the system of *linear*-ABC would become closer to the equilibrium ordered morphology, which is supported by sharpened and newly-appeared higher-order SAXS peaks. In addition, the increase in domain spacings was observed at 120°C in both BCPs, which can be explained by the ordering of microphase-separated structure and thermal expansion of PS domains.

The microphase-separated structure of *linear*-ABC can be interpreted by two models: (i) Because the interaction between urethane linkage/crown ether in *linear*-ABC is not so strong as *sec*-ammonium/crown ether interaction in *star*-ABC, the wheel component might move as temperature increases. In most cases, the wheel component should be loosely fixed at the end of the PVL chain, but probably some of it is not located at the chain end. A mixture of polymers with different topologies might lead to a mixture of morphologies. (ii) Another structural model is a single ordered morphology, a hexagonally perforated layer morphology, in which lamellar and cylinder structures are observed depending on the viewing direction [4]. When some grains with different orientations are adjacent, both morphologies are observed at the same time. However, STEM images are not clear enough to identify the morphology; the detailed structural model of *linear*-ABC remains an open question.

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BEAMLINES

BL-6A and BL-10C

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