

# Spontaneous perpendicular orientation of lamellar microdomains and subsequent kink formation during solvent evaporation from block copolymer solution

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## 1 Introduction

In recent years, a new material strengthening phenomenon as "kink strengthening phenomenon" has been discovered in the field of the metallic (Mg) alloy. Kink is a region where crystals are sharply bent. We consider the possibility of applying this concept to polymeric materials and are focusing on block copolymers that form lamellar microdomains consisting of hard and soft components. Previous investigations in our laboratory have used non-oriented lamellar microdomains, and the kink was introduced by uniaxial stretching, a method that destroys the internal structure of the material. Therefore, material strengthening through introduction of kinks has not been achieved to date. In this study, we focused on the effects of selective solvent and its evaporation, and examined the possibility of introducing kinks without conducting uniaxial stretching.

## 2 Experiment

The specimen used for this study is a polystyrene-block-polybutadiene-block-polystyrene triblock copolymer and the selective solvents were mixtures of n-heptane and dichloromethane, which are selectively good solvents for PB (polybutadiene) and PS (polystyrene), respectively. Note that the mixtures of n-heptane and dichloromethane were used for more precise control of the degree of selectivity. To analyze the nano structures in the as-cast and annealed specimens, transmission electron microscopy observation and two-dimensional small-angle X-ray scattering (2d-SAXS) measurements were conducted at room temperature at the BL-10C beamline at the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. A collagene was used as the standard sample to calibrate the magnitude of the scattering vector,  $q$ , as defined by  $q = (4\pi/\lambda) \sin(\theta/2)$ , with  $\lambda$  and  $\theta$  being the wavelength of X-ray and the scattering angle, respectively.

## 3 Results and Discussion

As a result, the edge-view 2d-SAXS pattern relevant to the kinking was obtained for the as-cast specimens by using the 25/75 mixture of n-heptane and dichloromethane. On the contrary, the spontaneous lamellar orientation (small-sized lamellae), perpendicular to the surface of the as-cast specimen, was found in the as-cast specimens of the SBS by using pure n-heptane and the mixtures in which the dichloromethane content is lower than 50%. This indicates that the selective solvent (selectively poor for the hard PS) can induce the spontaneous orientation of lamellae, although the detailed mechanism is unknown. To explain the mechanism of the spontaneous kinking of the lamellae, the spontaneous perpendicular orientation of lamellae may take place first and then successively kinking occurs during the further solvent evaporation. It is speculated that naïve balance of the solvent mixture enables the spontaneous kinking in the 25/75 mixture of n-heptane and dichloromethane. Since the evaporation speed of those solvents are very much different, the unbalanced evaporation speed can sensitively control the mixing ratio of the solvents. This means that the solvent selectivity to the PS and PB is changing during the solvent evaporation, while the viscosity of the cast solution also increases (or more rigorously the vitrification timing of the hard PS-rich domains can be modified). Such a complicated situation for the case of the 25/75 mixture became suited accidentally for the spontaneous kinking of the SBS lamellae. The perpendicular orientation of the SBS lamellae was found to proceed more with increasing the size of lamellae by the thermal annealing at 150°C for 3 hours.

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