Materials Science

15A/2008G701

Morphological Changes in a Diblock Copolymer upon Chemical Modification

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Introduction

In general, segregation power of diblock copolymers is expressed as χN, where χ is the Flory-Huggins interaction parameter and N is the degree of polymerization. When a value of χN increases, a diblock copolymer transitions from a disordered state to an ordered one and it forms microphase-separated structures such as sphere, cylinder, gyroid and lamella *etc*. However, the effects of χ and N on the morphology and the domain spacing have not been distinguished so far. We studied the changes in microphase-separated structures of a series of diblock copolymers composed of poly(4-*tert*-butylstyrene) (B) and poly(4-*tert*-butoxystyrene) (O) upon hydrolysis reaction where O can be tuned to poly(4-hydroxystyrene) (H) through the reaction.

Experiments

A BO block copolymer was synthesized by a sequential anionic polymerization. The number-average molecular weight, M_n, was evaluated to be 67k by membrane osmometry and the volume fraction was determined to be 0.45 by ^{1}H NMR. Hydrolysis reaction of the BO copolymer was conducted by heating in 1,4-dioxane with excess amount of hydrochloric acid. H conversion, f_H, was controlled by solution concentration, reaction time and temperature. Mechanism of hydrolysis reaction of O was separately characterized by ^{1}H- and ^{13}C- NMR and MALDI-TOF mass spectroscopy. Microphase-separated structures were evaluated by transmission electron microscopy (TEM) and small-angle x-ray scattering (SAXS). SAXS measurements were conducted at the beamline 15A in Photon Factory, KEK, Japan.

Results and Discussion

Figure 1 shows TEM images and SAXS patterns for the BO samples with various f_H values. The non-hydrolyzed BO sample shows correlation hole scattering. On the other hand, all the hydrolyzed samples gave several scattering peaks that originated from microphase-separated structures. This implies that the segregation between blocks become stronger with an increase of f_H. Integer order peaks corresponding to alternating lamellar structure appear from 0.16 and above. Peaks representing another structure were also seen from 0.40-0.79. This result indicates that morphological transition occurs when the BO undergoes hydrolysis reaction. Lamellar domain spacing, D, abruptly increases when the f_H value reaches 0.40 and it remains constant from 0.40 onwards. This result shows that the chains stretched perpendicular to lamellar interface as the segregation between blocks becomes stronger with an increase of f_H and a maximum segregation is attained at 0.40.

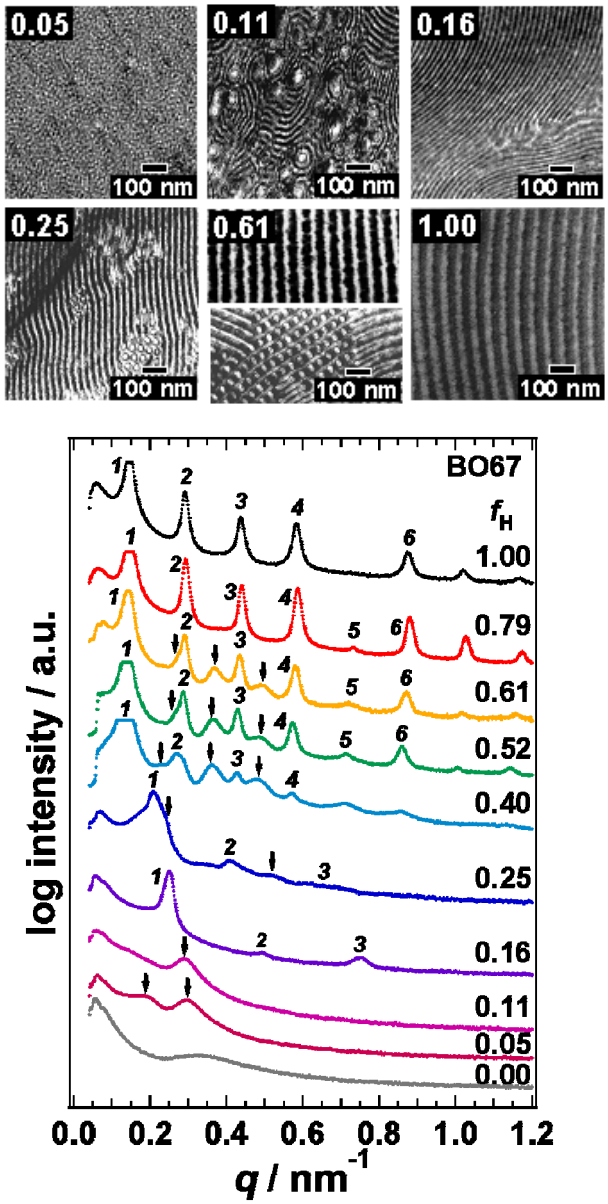

Figure 1. TEM images and SAXS patterns for BO samples with various f_H.

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