Photon Factory Activity Report 2012 #30 (2013) **B**

BL-15A/2007G204

Thermally-Induced Structural Change in Block Copolymer Thin Films

Naoya Torikai[1,*], Norifumi L. Yamada[1], and Daisuke Kawaguchi[2]
[1]Neutron Science Laboratory, KEK, Tsukuba 305-0801, Japan
[2]Department of Applied Chemistry, Nagoya University, Nagoya 464-8603, Japan

1 Introduction

A block copolymer with incompatible components exhibits rather complicated phase-separation behavior in a thin film due to the effects of spatial confinement and interfacial interaction with air or a substrate. So far, there have been many studies on the phase-separated structures of block copolymers in their thermodynamically equilibrium state. The detailed interfacial structure and segment distribution in a lamellar microdomain were examined by static neutron reflectivity measurement. In this study, the ordering process of block copolymers in spin-coated thin films above their glass transition temperature, T_g, was investigated by *in-situ* grazing-incidence small-angle X-ray scattering (GISAXS) measurement using a home-made evacuable high-temperature cell.

2 Experiment

The samples used in this study are AB diblock and ABA triblock copolymers with polystyrene, PS (=B), and poly(2-vinylpyridine), P2VP (=A). The total molecular weight and the volume fraction of PS block chain were 151×10^3 and 0.79, and 135×10^3 and 0.82 for the di- and tri-block copolymers, respectively. It was confirmed that both the block copolymers form spherical microdomains in the bulk. The thin film specimens were prepared by spin-coating their dilute solutions in *p*-dioxane on silicon wafers.

The time-resolved *in-situ* GISAXS measurement was performed on small-angle X-ray diffractometer at BL-15A of the Photon Factory, KEK, Tsukuba. The wavelength of X-ray was 0.15 nm. A two-dimensional charge-coupled device (CCD) detector with 9inches image intensifier was used. All the data were collected for 1 second, after temperature was jumped to 200°C.

3 Results

Fig. 1 compares time evolution of GISAXS patterns for the di- and tri-block copolymer thin films during the thermal annealing at 200°C. Even for the as-prepared film the di-block copolymer exhibited two diffraction spots symmetrically relative to the beam center in the lateral direction implying the existence of spatial correlation due to phase-separation, while the tri-block did not. The two diffraction spots in the lateral direction became intense for both the block copolymers with increasing the annealing time. After the annealing, the diffraction spots remained at R.T.

Acknowledgement

We are very thankful to Prof. A. Takano and Prof. Y. Matsushita of Nagoya University for their kind offer to use their block copolymers in this study. We are also deeply indebted to Prof. H. Okuda of Kyoto University for his kind support of GISAXS experiment.

*Current address: Department of Chemistry for Materials, Mie University, 1577 Kurimamachiya, Tsu, Mie 514-8507, Japan. ntorikai@chem.mie-u.ac.jp

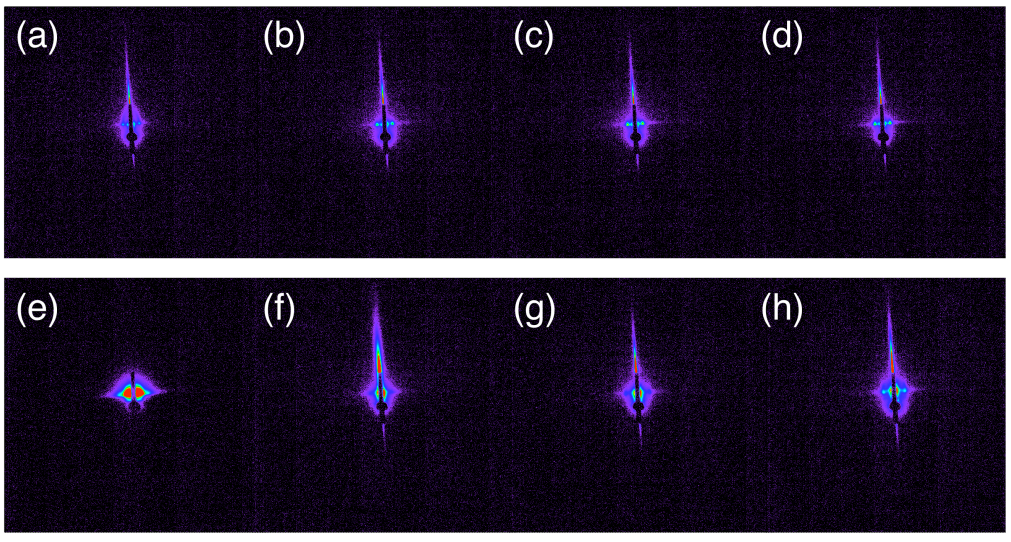

Fig.1: The time-evolution of GISAXS patterns for (a-d) di- and (e-h) tri-block copolymer thin films. (a) and (e), and (d) and (h) were taken at R.T. before and after the annealing, respectively.