## The meso-scale order structure of immiscible polymer blends

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Various nano-scale order structures formed by the micro phase separation of block copolymers are reported. On the other hand, the macro phase separation of immiscible polymer blends scarcely forms the order structure. We have reported the two dimensional hexagonally packed sphere structures in meso-scale based on the macro phase separation obtained by solvent casting from immiscible polymer blend solution <sup>1)</sup>.

Styrene butadiene rubber (SBR, Nihon Zeon Nipol 1502, styrene content ratio 23.5 %,  $Mw = 4.2 \times 10^5$ ) and acrylonitrile butadiene rubber (NBR, Nihon Zeon Nipol 1042 acrylonitrile content ratio 33.5 %,  $Mw = 4.5 \times 10^5$ ) were solved in Toluene and THF (3 wt %) with various blend contents. Within 3 days, the solution was separated to two phase. Subsequently, the solution was cast on Si wafer at room temperature. The obtained thin film was investigated by AFM (E-sweep, SII) and GISAXS (SPring-8, FSBL03XU)

Two dimensional hexagonally packed sphere structures were obtained by solvent casting from the SBR-rich layer of equilibrium phase separated NBR/SBR toluene solution. The diameter and the thickness of sphere domain was about  $1\sim3 \mu m$  and about  $40 \sim 100 nm$ , respectively. The thickness of thin film was about 7  $\mu m$ , thus the sphere domain was rather flat. The diameter of sphere and the distance between spheres depended on NBR fraction of NBR/SBR solution. From the AFM phase image analysis of the order structure, the spheres consisted of NBR shell and NBR rich core. Figure 1 show GISAXS profile of the thin film casting from equilibrium SBR rich phase in toluene solution. The sharp diffraction arc was

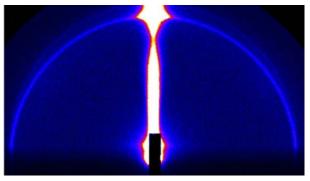


Fig. 1. 2D GISAXS image of NBR/SBR blend thin film

observed at  $q = 2.4 \text{ nm}^{-1}$ , which assigned to the order structure in acrylonitrile sequence of NBR. The azimuth profile of the diffraction at 2.4 nm<sup>-1</sup>, two maximums at 38 and 143° were observed. GISAXS profile indicated that the stacked structure of acrylonitrile sequence existed in the NBR shell of sphere. At the early stage of phase separation from NBR/SBR toluene solution, NBR aggregated on the interface of NBR rich phase, acrylonitrile sequences had an important role of meso-scale order structure.

[1] J. H. Jang, T. Inoue, M. Kawazoe and H. Yoshida, Polym. Preprt. Jp., 61, 1234 (2013).