It is often difficult to observe nano-scale structures of polymeric materials using conventional TEM because of its weak scattering contrast. As one of methods to produce image-contrast without any artificial staining, LAADF-STEM was applied in this study, and examined on its quantitative feature for observation of fine structures in a block copolymer. Since LAADF-STEM provides a kind of dark-field image like HAADF-STEM, the contrast can be improved drastically from conventional bright-field imaging. Moreover, LAADF-STEM is powerful not only to produce a contrast but also to utilize more scattered electrons than the case of HAADF-STEM, indicating that the LAADF-STEM could be more practically usable for radiation-sensitive materials.

Actually, it is expected to visualize micro-phase-separated morphology of block copolymers with sufficient contrasts by LAADF-STEM, corresponding quantitatively to the mass-thickness difference among micro-separated phases. LAADF-STEM was applied for observation of a diblock copolymer of poly(vinyl phenol)-block-polystyrene (PVPh-b-PS), in which a low detection angle (β=19–50 mrad in JEM-2200FS) was adopted for creating a contrast without artificial staining. FIG. 1 shows well-ordered lamellae morphology observed in cross-sections of the copolymer prepared by sequential living anion polymerization and subsequent hydrolytic deprotection. The bright domain corresponds to high density layer of PVPh, and the dark to low density layer of PS. Firstly, the density difference between PVPh (ρ_{PVPh}) and PS (ρ_{PS}) domains was evaluated from an intensity profile in FIG.1, resulting into ρ_{PVPh}/ρ_{PS} = 1.09±0.03. This ratio is reasonable although it is slightly smaller than 1.12 estimated from the reported densities of both homopolymers. On the base of the quantitative contrast, it is possible to examine quantitatively the morphology of phase separation, the local distribution of micro-domains and the interfaces in separation of phase domains. As shown in FIG. 2, for instance, one may see at glance that the mechanical cleaving is happened only at the high density domain of PVPh with bright contrast, presumably owing to its brittleness. As a further application, the temperature dependence of image contrast showed a kink at 90 °C, relating obviously to a glass-transition of PS (FIG. 3), which allows us to estimate the Tg and difference in thermal expansion coefficients of rubbery and glassy states of PS. These observations demonstrate that LAADF-STEM is an effective tool to image quantitatively nano-scale domains of polymers.

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Fig. 1: LAADF-STEM image of PVPh-b-PS with lamellae structure of bright PVPh and dark PS layers with a regular spacing of 40 nm. Intensity profile was measured along the blue box in the figure to estimate the density ratio of both layers.

Fig. 2: LAADF-STEM image of cleaved part in PVPh-b-PS thin section. The outer layer after cleaving is always the bright PVPh layer, presumably owing to its high brittleness.

Fig. 3: LAADF-STEM intensity change against temperature around Tg of PS. A kink is observed around 90 °C, indicating the change in thermal expansion coefficient of PS layer against that of the glassy PVPh at the glass transition.