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In-situ small-angle X-ray scattering measurements to reveal nano-structure formation during solvent evaporation from a block copolymer solution

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Block copolymers undergo microphase separation in a few tens of nanometres, because of strong segregation between constituent block chains comprising different chemical species. This stems in molecular origins where dimension of block chains is of tens of nanometers. Depending on composition, the morphology of such a nano-structure can be altered as spheres, cylinders, double gyroid or lamellae. It is well known that physical properties of block copolymers strongly depend on the morphology. Not only the morphology, but the orientation of the nano-structures are key factors to be taken into account in order to control materials properties more efficiently, such as imparting anisotropy of properties. Controlling of orientation of the nano-structures is therefore one of the fundamental ways to novel specialty materials.

Generally speaking, manipulation of microdomain orientation is performed by applying external fields such as flow, shear, electric field, magnetic field, and so forth. On the other hand, it is also known that spontaneous orientation takes place in some sophisticated experiments. One of the examples is parallel orientation induced by substrate such that for instance lamellar microdomains tend to orient parallel to the substrate after complete evaporation of the solvents when the block copolymer solution is subjected to the solution cast. Nevertheless, when such spontaneous orientation is originated and how it proceeds are unknown. This may be ascribed to the experimental difficulty in conducting in-situ observation (for the sake of structural analyses) during the solvent evaporation. Recently, high brilliant synchrotron radiation becomes available and this is useful for such in-situ observation. In this study, we have conducted in-situ small-angle X-ray scattering (SAXS) measurements using high brilliant synchrotron radiation to detect the origination of the spontaneous orientation during solvent evaporation.

The block copolymer sample used is polystyrene-*block*-polybutadiene-*block*- polystyrene (SBS) triblock copolymer with the number-average molecular weight M_n = 6.31×10^4 and the polydispersity index M_w/M_n = 1.15. The volume fraction of polystyrene (PS) moiety is 0.56. Although this SBS neat sample forms lamellar microdomains, a blend of this SBS and PS homopolymer was used for the study of ordering of spherical microdomains. For this purpose, the total PS content was adjusted at 0.84. Methyl ethyl ketone, which is a selective solvent for SBS (selectively good for PS but selectively poor for polybutadiene), was used for solution casting. The in-situ SAXS measurements were carried out at room temperature at BL40B2 beamline in the synchrotron radiation facility, SPring-8 (Hyogo, Japan), which provides us high brilliance and highly parallel synchrotron X-rays. A home-made container, which will be described later, was put on an electric balance, to check the temporal change in the solution weight. The electric balance was then placed in the sample position for the SAXS measurements. The initial polymer concentration was 20wt%.

To conduct the in-situ measurements without imposing any perturbation on the casting solution undergoing the microphase separation (microdomain formation), we have to design a special container of the solution, of which side wall can let the X-ray beam go through without absorption. For this purpose, we have prepared an ark made of an aluminum foil with approximately 6 micrometer thickness (by applying the Origami method). A piece of the slide glass was glued at the bottom of the Al ark.

Positioning precisely the incident X-ray beam just at the solution in contact with the substrate was able to be performed as follows; we controlled the height of the sample stage which was pulse motor driven so as to detect the transmitted beam intensity being half of the one for the beam without being blocked by the substrate.

In conclusion, we have established the in-situ SAXS measurement technique by designing the special container made of Al foil at the synchrotron facility. It is expected that this technique uncovers many kinds of the process of structure formation in solutions such as orientation of the microdomain structures.

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