Ordered and Foam Structures of Semifluorinated Block Copolymers in Supercritical Carbon Dioxide

We conducted *in situ* small-angle X-ray scattering (*in situ* SAXS) in supercritical carbon dioxide ($scCO_2$) using a high-pressure cell with diamond window to reveal the order-order transition (OOT) of semi-fluorinated block copolymers induced by $scCO_2$. $ScCO_2$ preferentially swells fluorinated polymers, which apparently increases the volume fraction of the fluorinated domain in block copolymers. By *in situ* SAXS, we observed swelling-induced OOT from cylinders to lamellae, and a unique transition from lamellae to a "foam" structure. This unique transition was revealed by *in situ* SAXS with a specifically designed high-pressure cell and the use of intense X-rays at the Photon Factory.

Block copolymers self-assemble into various ordered structures with 10 nm-scale periodicity, such as body-centered cubic (BCC) spheres, hexagonally-packed cylinders, lamellae, and bicontinuous structures such as gyroid [1]. The self-assembly is called microphase-separation, and is desired for applications such as bottom-up nanolithography. The structure is determined by the volume fraction of one component (f) and by the product of the interaction parameter between different domains (χ) and the degree of polymerization (N). Therefore, one method to control the structure is to change χ by tuning the temperature. Meanwhile, f is fixed for a given block copolymer, but can apparently be changed by adding components with selective affinity for one domain (*e.g.* homopolymers and selective solvents).

As a unique selective solvent, our group has been employing $scCO_2$, which is realized at 31.1ºC and 7.4 MPa or above and successfully induced OOT in semi-fluorinated block copolymers [2]. Most polymers do not dissolve in $scCO_2$ but are swollen with $scCO_2$ as a function of temperature and pressure. Among various polymers, fluoropolymers are the most CO_2-philic. Consequently, fluorinated domains in block copolymers are selectively swollen in $scCO_2$, which increases the apparent volume fraction (f_{eff}) of the fluorinated domain. In this method, f_{eff} depends on the temperature and pressure of CO_2, and so we can tune f_{eff} continuously and reversibly. In addition, CO_2 can be removed without destroying the swollen structure by freezing and gradual depressurization. During the depressurization process, the space occupied by CO_2 turns into nanopores, and hence a nanoporous structure can be obtained from the block copolymer template.

Recently we reported *in situ* analysis of CO_2-induced OOT [3]. While we have observed the frozen nanoporous structure, the swollen structure in CO_2 had not been investigated previously. Therefore, we conducted *in situ* SAXS, to reveal the swollen morphology and OOT. We used a semifluorinated block copolymer, poly(styrene-*b*-perfluorooctylethyl methacrylate) (PS-PFMA, M_n = 17,700 - 6,230 kg/mol). A custom-designed high-pressure vessel was connected with a pump and a backpressure regulator. Samples in the vessel were irradiated with X-rays through the diamond windows of the vessel. SAXS experiments were performed at BL-6A in the Photon Factory. SAXS profiles were calibrated with collagen from chicken tendon. We also prepared a frozen nanoporous sample by swelling a sample in CO_2 for 2 h at 60ºC, freezing the sample to –10ºC, and depressurizing CO_2 at a rate of 0.5 MPa/min.

Figure 1 shows SAXS profiles of PS-PFMA in CO_2 as a function of pressure. The as-cast sample showed several Bragg peaks with a peak ratio of 1 : $(3)^{1/2}$: 2, indicating a hexagonally-aligned structure. From this profile and composition ratio of PS-PFMA, we concluded that hexagonal cylinders with PFMA cores are formed in the as-cast specimen. The sample was then pressurized in CO_2 at 60ºC. At 10 MPa, the peak ratio changed to 1 : 2: 3, indicating that PFMA was preferentially swollen in CO_2 and OOT from cylinders to lamellae (a more PFMA-rich structure) was induced.

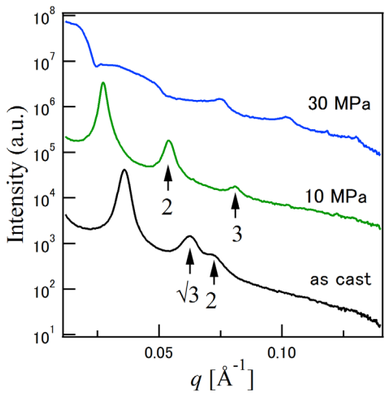

Figure 1: SAXS profiles of PS-PFMA as a function of CO_2 pressure at 60ºC. Data were taken from Ref. [3] (reproduced by permission of The Royal Society of Chemistry).

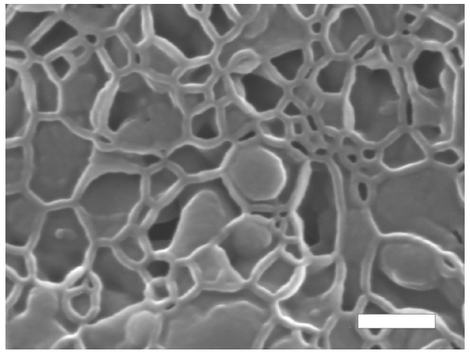

Figure 2: An SEM image of PS-PFMA treated with CO_2 at 30 MPa and at 60ºC. The horizontal scale bar indicates 200 nm.

We raised the CO_2 pressure further, and observed that the Bragg peaks dissipated and other scattering in low-q emerged above 20 MPa. This indicates that lamellae were further transformed into another structure. From the fringe position of the new scattering pattern, we speculated that a sheet-shaped structure was formed. To confirm the structure, we prepared a nanoporous sample by freezing the swollen structure. By scanning electron microscope (SEM) measurements, we observed a "foam" structure, where PS-PFMA composes a bilayer membrane and 100 nm-scale cells are surrounded by a membrane (Fig. 2).

From SAXS experiments, we observed an intriguing pressure response of the foam. When we raised the pressure from 25 to 30 MPa stepwise, the form factor weakened temporarily and recovered gradually (see Fig. 3). This indicates that the foam structure was pressed by static pressure and returned to lamellae, and then gradually transformed into the foam again.

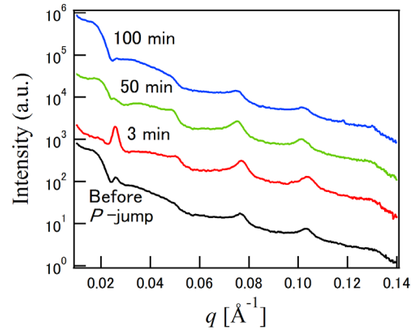

Figure 3: SAXS profiles as a function of time after pressurization from 25 to 30 MPa. 0 min denotes the time immediately before pressurization. This figure was taken from Ref. [3] (reproduced by permission of The Royal Society of Chemistry).

By time-resolved SAXS with synchrotron radiation, we were able to observe not only the swollen structure, but also the unique relaxation process of the structure, such as the expansion of foam-like structures with increasing pressure.

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