

## Small-angle neutron scattering study of block copolymers in supercritical carbon dioxide

M. Itoh, H. Yokoyama, K. Mayumi, K. Ito, N. Osaka, H. Endo, M. Shibayama  
*University of Tokyo*

Depending on volume fraction of each block, degree of polymerization and interaction between blocks, several microphase-separated morphologies are observed in diblock copolymers. These morphologies are kinds of micro-phase separation of each blocks: Examples are spheres, cylinders and lamellae ordering in long-ranged periodic structures, such as cubic lattice of spheres and hexagonal lattice of cylinders. In addition to those classic morphologies, 3D continuous networking structures, which are called bicontinuous structures, have been reported. We have succeeded in inducing multiple order-to-order phase transitions by swelling selectively CO<sub>2</sub>-philic blocks with supercritical CO<sub>2</sub> and changing pseudo-volume fraction. This morphology change was anticipated by ex-situ analysis of the samples frozen and removed from supercritical CO<sub>2</sub>. However, in-situ measurement of selectively swollen block copolymers in supercritical CO<sub>2</sub> has never been conducted. Thus this time we performed in-situ measurement of swollen block copolymers in CO<sub>2</sub> by neutron scattering analysis.

We analyzed the morphologies of Poly(styrene-*b*-perfluorooctylethyl methacrylate)s (PS-PFMAs), using small angle neutron scattering measurement system SANS-U, at JRR-3. PFMA is CO<sub>2</sub>-philic and highly swollen in CO<sub>2</sub>. We prepared three samples differing with the ratio of PS to PFMA and total degree of polymerization, of which molecular weights and weight fraction of PFMA are 18,600 and 20 % (S1), 17,400 and 48% (S2), and 23,000 and 28 wt% (L), respectively. Samples for SANS were made by casting from trifluorotoluene solutions. Then the samples were placed into high-pressure cell with CO<sub>2</sub> pressure and temperature

controls. This time, temperature was fixed at 60 degree C and pressure was varied from atmospheric pressure to 30MPa.

Fig.1 shows the pressure dependence of SANS profiles. Profiles in each graph are seriated in increasing order of pressure. Fig.1a is scattering patterns of S1. At 0.1MPa the peak positions of  $q$  (1:1.73), corresponding to Hex lattice of PFMA Cylinders is found. Similarly, the profile at 15MPa agrees with lamellar peak pattern. At 10 MPa, at which the effective volume fraction is between cylindrical and lamellar morphologies, unknown peak pattern appeared. Because the first and second order peaks were not well separated due to limited resolution, we cannot assign the morphologies at this point, but the peak ratio is inconsistent with either cylinder or lamellar. Pressurizing from 15MPa to 20MPa we observed sudden change of the first peak position followed by BCC/SC lattice of spheres at 25MPa and 30MPa(1:1.44). The sudden change of the first order peak position can be interpreted as evidence of exchange of the matrix. Scattering profiles of S2 with higher PFMA fraction (48%) is shown in Fig.1b. In as cast state, peaks appear at 1, 1.99, 2.97 relative to the first order, which is lamella. In pressurizing process at 15 MPa, peak ratio 1:1.74:1.86 was observed. This pressure and hence the effective volume fraction is in bicontinuous regime, but identifying this structure requires additional experiments. As pressurizing continuously, the polymer structure changed to Hex of cylinder at 25MPa and finally the structure factor vanished at 30MPa.

Fig.1c shows the scattering function of L with the higher mass. From peak ratios of as cast specimen and at the pressure upto 20MPa, the morphology is always Lamella.

At a pressure over 25MPa peak becomes weak, and at 30MPa structure factor completely disappears.

As can be seen from these three samples, we observed multiple order-to-order transitions. We are continuing in-situ measurement with SANS on new additional samples with different ratio of PFMA and the degree of polymerization.

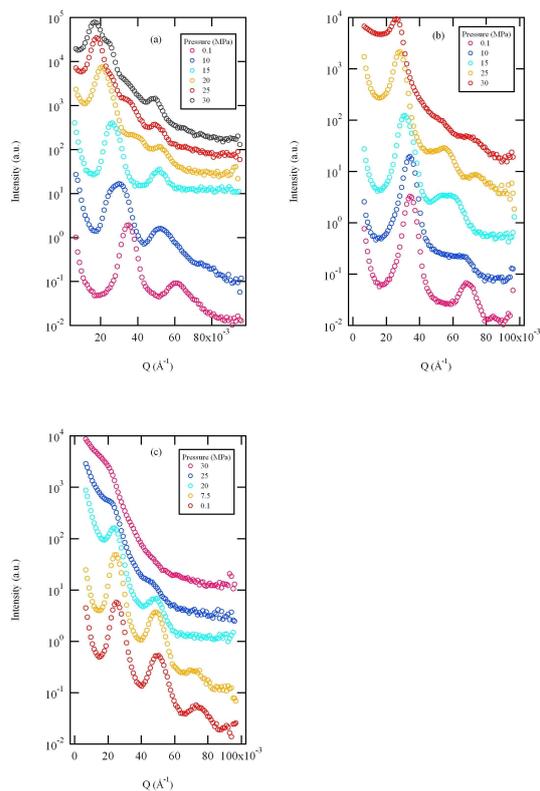


Fig. 1. Fig. 1. Small angle neutron scattering patterns of PS-PFMA with different molecular weight and fractions at several different CO<sub>2</sub> pressures: (a)  $M_n = 18,600$  and PFMA wt% = 20; (b) 17,400 and 48%; (c)  $M_n = 23,000$  and PFMA = 28 wt%.