

Order-Order Transition of Block Copolymers Swollen with Supercritical Carbon Dioxide

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In diblock copolymers (BCP), a variety of microphase separated morphologies in a scale of tens of nanometer have been observed depending on the volume fraction of blocks, degree of polymerization and interaction parameter between blocks. Similar morphologies have been found in different class of softmatters: for example, surfactant/solvent and BCP/solvent systems form similar morphologies, which resulted from its amphiphilicity and solvent selectivity. By using additional degree of freedom by using a solvent, the morphologies becomes a function of concentration, which can be easily changed. We have succeeded in inducing order-to-order phase transitions (OOT) by swelling selectively CO₂-philic blocks of BCP by changing the pressure of supercritical CO₂, which controls apparent volume fraction of CO₂-philic blocks.[1-4] The CO₂ pressure induced morphology changes were anticipated by ex-situ analysis of the samples that was frozen and removed from supercritical CO₂. However, the OOT mechanism by selective swelling hasn't clearly understood. Thus this time we performed in-situ measurement of swollen BCP in CO₂ by neutron scattering analysis. We analyzed the morphologies of Poly(styrene-*b*-perfluorooctylethyl methacrylate)s (PS-PFMAs), using small angle neutron scattering, SANS-U at JRR-3, Tokai, Japan. PFMA is CO₂-philic and is expected to be highly swollen in CO₂. We prepared six block copolymers differing in the ratio of PS to PFMA and total degree of polymerization, of which molecular weights are in the range from 10,000 to 25,000 and of which morphologies are Sphere, Cylinder and Lamellar. Then the samples were placed into a high-pressure cell with pres-

sure and temperature controls. We observed multiple OOT as a function of CO₂ pressure on the pressure dependence of SANS scattering patterns. Depending on the initial morphology, which is the one at atmospheric pressure, multiple phase transitions starting from the hexagonal packed PFMA cylinders to the inversed body centered cubic lattice of PS were observed; however, the sample with spherical PFMA domains as the initial morphology maintains its spherical morphology irrespective of pressure while the lattice constant increases with pressure.

[1] H. Yokoyama, L. Li, C. Dutriez, Y. Iwakura, K. Sugiyama, H. Masunaga, S. Sasaki, H. Okuda, *Macromolecules* 41, 8626-8631, (2008). [2] H. Yokoyama, C. Dutriez, L. Li, T. Nemoto, K. Sugiyama, S. Sasaki, H. Masunaga, M. Takata, and H. Okuda *J. Chem. Phys.*, Vol. 127, 014904-1 - 014904-9 (2007). [3] L. Li, H. Yokoyama, *Angew. Chem. Int. Ed.* 45, 6338-6341 (2006). [4] H. Yokoyama, L. Li, K. Sugiyama, T. Nemoto, *Adv. Mater.*, 16, 1542-1546 (2004).