

In-situ small angle X-ray scattering study of order-disorder transition of semi-fluorinated block copolymer in supercritical carbon dioxide

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1 Introduction

Supercritical carbon dioxide (scCO₂) has been drawing a lot of attentions as a potential substitute for conventional organic solvents.[1] Recently, several studies have focused on scCO₂ as a medium to tune morphologies of block copolymers or polymer blends.[2] CO₂ can swell various polymers and enhance miscibility between different polymers. In general, swelling of block copolymers in CO₂ can affect phase behavior of block copolymers, which is similarly observed in conventional solvents. Such an effect depends on miscibility of each domain toward CO₂; when the domains are similarly swollen, CO₂ behaves like a neutral solvent to screen the interaction between the domains. For example, screening unfavourable interaction enhances miscibility of poly(styrene-*b*-isoprene) (PS-PI), and its upper order-disorder transition (UODT) temperature decreases in CO₂. [3] In contrast, when there is large difference in the degree of CO₂ swelling between the domains, CO₂ can promote phase separation, similar to conventional selective solvents. CO₂-induced depression of lower disorder-order transition (LDOT) temperature has been reported for block copolymers with polystyrene (less CO₂-philic) and *n*-alkyl methacrylates (more CO₂-philic), which similarly exhibit LDOT in their neat bulk.[4-6]

Our group has reported the swelling-induced OOT using poly(styrene-*b*-perfluorooctylmethyl methacrylate) (PS-PFMA).[7-9] In addition, regardless of swelling selectivity, CO₂ swelling drastically promotes re-organization of the microphase-separated structure of strongly-segregated block copolymers, which is kinetically trapped in vacuum due to extremely large χN .

2 Experiment

We investigated CO₂-induced order disorder transition of poly(methyl methacrylate-*b*-perfluorooctylmethyl methacrylate) (PMMA-PFMA) by *in situ* SAXS. PMMA-PFMA (18,300-10,100 g mol⁻¹) was synthesized via sequential living anionic polymerization. PMMA is more CO₂-philic than PS but still much less CO₂-philic than PFMA, so PMMA-PFMA has smaller swelling selectivity compared to previously reported PS-PFMA, which showed OOT with increasing pressure of CO₂.

In-situ SAXS experiments were performed at 6A beamline of Photon Factory in KEK. The bulk samples were placed in a stainless steel high-pressure vessel with diamond windows. The vessel was connected to a high-pressure liquid chromatography pump (JASCO PU-2080) and a back pressure regulator (JASCO SCF-Bpg). *In-situ* X-ray scattering analysis was performed through the

diamond windows at 60 degree C under pressure of CO₂. Scattering from the windows was negligible. An image intensifier accompanied with a charge coupled device (CCD) camera was used as an X-ray detector. The scattering images were calibrated by collagen from chicken tendon.

3 Results and Discussion

In situ SAXS was performed to measure the swollen structure. PMMA-PFMA was pressurized stepwise at 90 °C. Up to 20 MPa, each profile shows a single Bragg peak without higher order ones, indicating that the structure lacks long-range order. While $d = 2\pi/q_1$, where q_1 is the position of each first order Bragg peak, increased monotonically with CO₂ pressure, phase transition was not observed. However, the Bragg peak disappeared completely at 25 MPa, suggesting that ODT was induced. Here we define the poorly ordered bicontinuous structure with a single Bragg peak as "ordered" structure and the structure without even a first order Bragg peak as "disordered" structure. The lack of well-defined ordered structure has been often found in block copolymers with fluorinated domains due to its extremely large interaction parameter to conventional polymers, which do not allow block copolymer molecules to diffuse and rearrange into well-ordered domains. We interpreted that ODT was induced in the range 20-25 MPa. The summary of phase registration is shown in Fig.1.

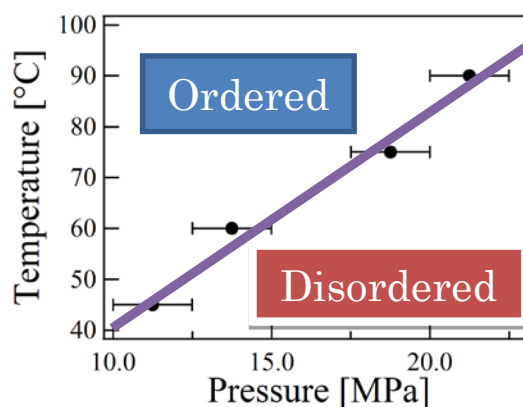


Fig.1 Phase diagram of PMMA-PFMA in CO₂. The line was drawn simply to guide the eye.

We found that χ parameter depresses so significantly by swelling in CO₂ that PMMA-PFMA is transformed into disordered phase. While PMMA-PFMA does not exhibit LDOT, PMMA-PFMA in CO₂ clearly shows LDOT behaviour, in which disordered phase appears at lower

temperature as shown in Fig.1. Appearing disordered phase at lower temperature is the signature of the effect of CO₂, which becomes denser and swell polymers more at lower temperature.

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