Electronic Supplementary Material (ESI) for Soft Matter
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Supplementary Information

SEM measurement of frozen nanoporous structure. To observe swollen structure by ex-situ microscopy analysis, we prepared nanoporous structure template with swollen state by following process. α,α,α-trifluorotoluene (TFT, purchased from Aldrich) solution was cast on Si wafers, and dried in vacuum for 1 day to obtain thick films for CO_2 process. The sample was placed in a high-pressure vessel and pressurized in CO_2. The CO_2-swollen specimen was then thermally quenched to -10 ˚C isobarically to freeze the structure, and CO_2 was subsequently depressurized at a rate of 0.5 MPa/min. To remove topmost surface, nanoporous structure converted from swollen state was treated with reactive ion etching (SAMCO compact etcher FA-01) with a CF_4 flow rate of 2 ml/min, a pressure of 10 Pa, and power density of 0.1 W/cm^{-2} for 30 s. Under this condition, ca. 30 nm etching was performed, and the internal structure exposed by the etching was observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4880) after Osmium coating. An SEM image of PMMA-PFMA after the CO_2 treatment is shown in Fig. S1.

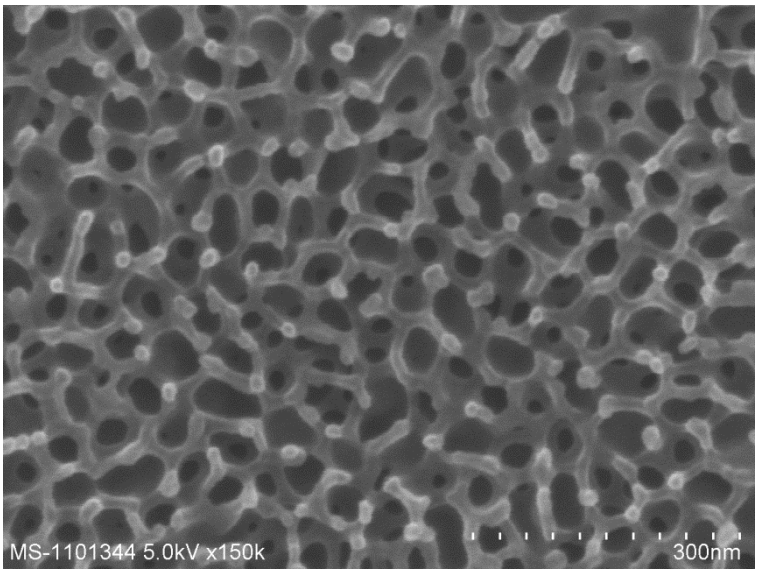

Fig. S1 An SEM image of PMMA-PFMA treated with CO_2 at 10 MPa and at 60 ˚C.

In situ SAXS measurement. To obtain a monolithic sample for SAXS experiment, PMMA-PFMA was dissolved into TFT, and was repeatedly cast into a mold. Before SAXS measurement, the sample was dried in vacuum for 1 day. The sample was then placed in a high-pressure vessel with diamond windows. The vessel was connected with high-performance liquid chromatography pump (JASCO PU-2080-CO2 plus) and backpressure regulator (JASCO SCF-Bpg). SAXS measurement was performed at Photon Factory BL-6A and 15A in KEK. An image intensifier accompanied with charge coupled device (CCD) camera was used as an X-ray detector. The SAXS patterns were calibrated by collagen from chicken tendon. Wavelength of X-ray was 1.5 Å, sample-to-detector

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distance was 2.0 m, and measurable q range was $0.01 < q < 0.14$ Å^{-1}.

Fig. S2 shows full width at half maximum (FWHM) of the SAXS profiles. Usually, scattering intensity and FWHM change discontinuously near ODT points. However in this study, scattering intensity is also affected by CO_2 swelling because selective swelling changes scattering contrast between domains. On the other hand, FWHM value of scattering pattern derived from fluctuation is several times larger than that from ordered phase. However, we did not observe such significant change of FWMH. The Bragg peaks suddenly disappear as the degree of swelling increases with CO2 density, which could be the character of swelling induced ODT. Therefore we define the point that the scattering peaks disappeared as ODT.

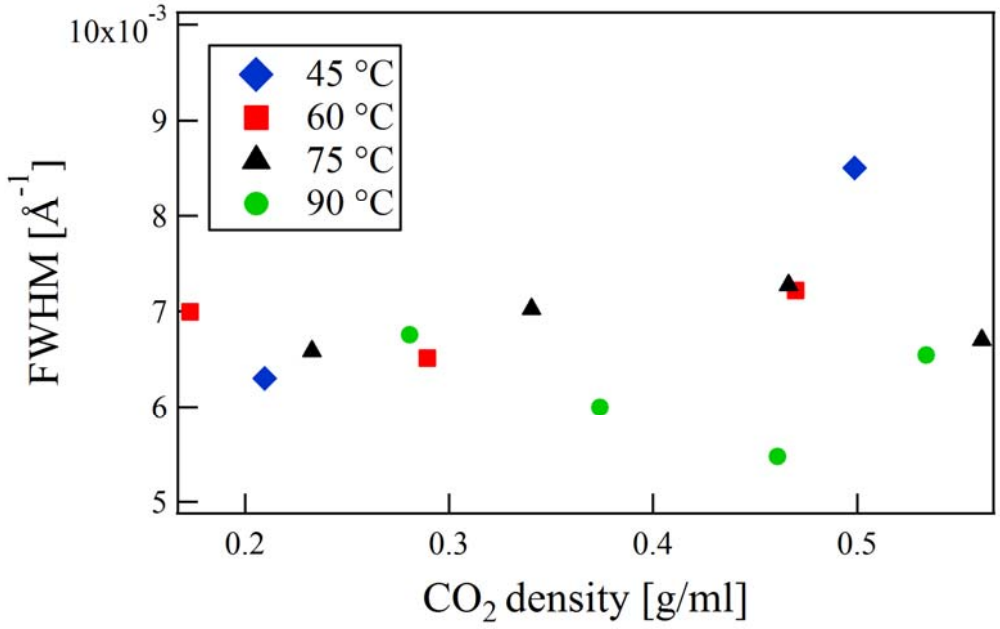

Fig. S2 Full width at half maximum of scattering profiles plotted against CO_2 density.

***In situ* swelling measurement**. To measure swelling ratio of polymers in CO_2, we developed *in situ* thickness monitor using spectroscopic reflectometer. PMMA-*b*-PFMA was spun-cast on a Si wafer from TFT solution, and placed in a custom-designed high-pressure vessel. The vessel was connected to a HPLC pump (JASCO PU-2086 plus) and a backpressure regulator (JASCO BP-2080 plus). Reflectivity of polymer thin film was measured through a sapphire window of the vessel, and film thickness was calculated by fitting the reflectivity. As a light source and a detector, MC-2530 and MCPD-3700 (Otsuka Electronics) were used, respectively. Swelling ratio was calculated from thickness change of the sample films assuming uniaxial swelling. Polymer concentration in the swollen specimen was calculated from initial thickness divided by swollen one. The reliability of this measurement will be discussed in a separated paper.