Pressure-Induced Phase Separation of Block Copolymers in Aqueous Solution

N. Osaka\textsuperscript{A}, T. Karino\textsuperscript{A}, S. Okabe\textsuperscript{A}, M. Nagao\textsuperscript{A}, M. Shibayama\textsuperscript{A}, A. Sasai\textsuperscript{B}, S. Aoshima\textsuperscript{B}

\textsuperscript{A}ISSP-NSL Univ. Tokyo, \textsuperscript{B}Osaka Univ.

Recently, pressure effects on polymer aqueous solutions have attracted attention in the fields of industrial applications. On the other hand, little work was done in basic polymer science, though pressure is an important variable as one of the thermodynamic parameters. Therefore, we focus on the phase behaviors and structural change of polymers in D\textsubscript{2}O by varying pressure and temperature.

Block-copolymers, we used, are thermosensitive polymers, showing LCST (Lower Critical Solution Temperature) at about 40\degree C in D\textsubscript{2}O. In the former study\cite{1}, phase behaviors at various pressures and temperatures were intensively studied with a concentrated polymer solution (15wt\%). However, in that case, complex interactions between micelles prevented detailed and microscopic analyses of the polymers and the hydrated water. Therefore, to understand the pressure effect more quantitatively, dilute polymer solutions (0.5wt\%) where the micellar interaction can be ignored was used in this study.

Pressure dependent SANS experiments were conducted with a pressure chamber, PCI-400-SANS, Teramex, Co. Ltd. Kyoto, Japan. The applied pressure was transmitted via a rubber diaphragm connected to the inner cell made of aluminum with quartz and sapphire windows. The outer chamber was filled with D\textsubscript{2}O and the pressure was controlled by pressurizing D\textsubscript{2}O by a double-cylinder hand pump. The SANS measurements were done at $T$: 28, 40, 50\degree C and $P$: 0.1-400MPa. The SANS experiments were done according to the $P$-$T$ phase diagram obtained by dynamic light scattering (DLS) experiments.

Micellization temperatures (MT) were detected by DLS by increasing temperature at fixed pressures. By increasing temperature, a new peak was observed, which is ascribed to the micellar diffusive mode. Obtained $P$-$T$ phase diagram was a upward-convex curve, which behavior is very similar with the former concentrated solution\cite{1}.

SANS experiments were done by pressurizing at fixed temperatures. At 28\degree C below MT, the block copolymers underwent micellization at high pressure. At 40 and 50\degree C, which were close to and above MT, respectively, the micelles were formed at ambient pressure. By pressurizing, the micelles were destroyed at near 100MPa and the block copolymers were dispersed. However, further pressurizing induced reentrant micellization at near 200MPa. Fig. 1 shows the schematic pictures of the same core-size-micelles at 50\degree C at low pressure (left) and high pressure (right) obtained by fitting the scattering curves with the use of Pedersen’s micellar model\cite{2}. The water volume fraction in the micellar core was larger at the high pressure than at the low pressure. This result indicates that hydrophobic interaction important to form micelles was weak at high pressures and another competing interaction might be dominant at high pressures.

References
Fig. 1. Schematic picture of the same-core-size micelles at 50°C. (left) at low pressure and (right) at high pressure.