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Pressure-Induced Microphase Separation of Block Copolymers in the Aqueous Solution

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従来、高分子水溶液系への圧力効果はホモポリマーの系を中心に研究が行われてきた [1]。本研究では、これまでにほとんど研究例のないブロックコポリマー水溶液の系を用いることで、マイクロ相分離に伴い出現する構造形成を利用して、圧力による構造の変化を定量的に議論することを目指している。SANS (小角中性子散乱) による測定の結果、高温 (45°C)、大気圧下でマイクロ相分離を起こし bcc 構造をとっている系に圧力を加えると、100MPa 近傍でマイクロ相分離構造が消失し、溶液中に分散することを確認した。ところが、さらに圧力を加えていくと、200MPa 近傍で再び構造形成がなされていく、という温度変化においては見られない、再起的な構造の変化を得ることができた。一方、低温 (28°C) で 300MPa まで加圧を行うと、散乱関数が Ornstein-Zernike 式に従いながら、相関長が連続的に増大していくことが観測された。ブロックコポリマーは、大気圧下での温度による相分離が 1 次転移的であることが知られているが、今回の実験の結果からは、低温での圧力変化が 2 次転移的な相分離を起こし、また、その相分離もマイクロ相分離ではなくマクロな相分離を起こす可能性が示唆された。

1 Introduction

In the past, pressure effects on the structure of polymer solutions have been mainly studied by using homopolymers. Only few reports about block copolymer solutions were published so far. It is known that block copolymers undergo microphase separation, which enable us qualitative analyses of structural changes by pressurizing. Thus, we investigated the pressure effects on the block copolymers in aqueous solutions by using small-angle neutron scattering (SANS) and dynamic light scattering (DLS).

2 Experiments

The sample we used was 15 %, pEOEOVE-b-pMOVE(poly(2-(2-ethoxy)ethoxyethyl vinyl ether)-block-poly(2-methoxyethyl vinyl ether)) [2] in D₂O. We constructed a pressure-temperature phase diagram (P :

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0.1–300MPa, T : 20–70°C) by DLS. Pressure-dependent SANS experiments were conducted with a high-pressure cell, PCI-400-SANS (Teramex, Co.Ltd., Kyoto, Japan).

3 Results and discussions

Figure 1 shows the SANS results obtained at various pressures at 45°C. At this temperature, under atmospheric pressure, the SANS curve suggested formation of bcc lattice structures with micelles composed of a central core of pEOEOVE. At 100MPa, the peak related to the bcc structure disappeared, meaning dissolution of block copolymers. However, by further pressurizing, another peak appeared at 250MPa. This peak indicated the microphase separation of block copolymers different from those observed under low pressures. This finding of re-entrant phase behavior is similar to those in earlier studies [1].

Figure 2 shows a trend of divergence of the correlation length, ξ , by pressurizing at 28°C. Here, ξ were obtained by fitting with the Ornstein-Zernike equation. The continuous increase of ξ at low temperatures implies that pressurizing of block copolymers in the aqueous solution induces a second-order macrophase separation in contrast to the fact that increasing of temperature causes a weak first-order transition. The evaluated critical exponent was 0.629 and was close to the value in the earlier study[1].

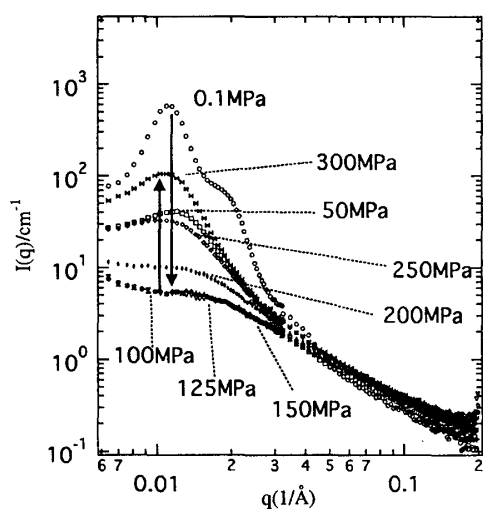


Figure 1: SANS intensity, $I(q)$, by pressurizing at 45°C

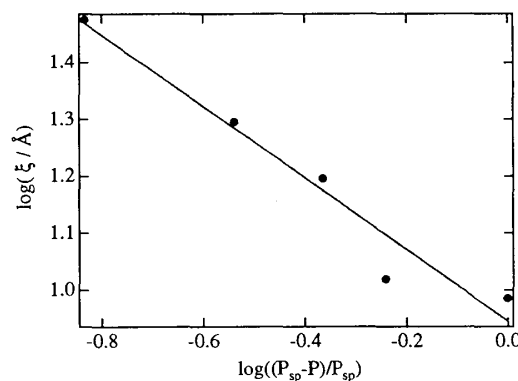


Figure 2: Correlation length by pressurizing at 28°C

References

- [1] M. Shibayama et al., *Macromolecules* **37** (2004), 2909.
- [2] S. Sugihara et al., *Macromolecules* **38** (2005), 1919.