Double Hydrophilic Nano-Scale Compartment Produced by Microphase Separation of Zwitterionic Block Copolymers

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Block copolymer solutions yield ordered lattice structures through microphase separation. The morphology depends on the volume fraction of the two phases which is modulated by the polymer concentration and selectivity of the solvents. We reported a lyotropic microphase separation in concentrated aqueous solutions of a double zwitterionic diblock copolymer (PCB2-*b*-PSB4), which is composed of a poly(carboxybetaine methacrylate) (PCB2) and a poly(sulfobetaine methacrylate) (PSB4) (**Figure 1**).[1)] The morphology depended on the polymer concentration due to the limited water capacity of the PSB4 phase. This copolymer can be regarded as a new type of molecular compartment that is valid for biomedical platforms. In this paper, the phase behavior of the double zwitterionic PCB2$_n$-*b*-PSB4$_m$ diblock copolymer aqueous solutions was mapped out to address the insights into the unique microphase separation due to the specific interactions of zwitterions.

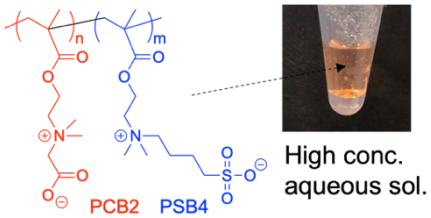

Figure 1. Chemical structure of PCB2$_n$-*b*-PSB4$_m$ and the aqueous solution.

The phase assignment and determination of the lattice structure geometry were conducted by small angle X-ray scattering (SAXS). The SAXS profiles of the PCB2$_n$-*b*-PSBX$_m$ aqueous solutions exhibits multiple peaks, and the scattering vector of peaks depended on the polymer concentration (f) and volume fraction of PSB4 chain (f_{PSB}). The lattice structure transformed from periodic two phase lamellar to hexagonal packed columnar due to the volume expansion of PCB2 phase. The f vs f_{PSB} phase diagram showed order-order transition boundaries with vertical above f = 0.44 while with negative slope below indicating that water exhibited polymer concentration-dependent selectivity, which is neutral above threshold polymer concentration but selective towards PCB2 below the threshold (**Figure 2**). This work advanced our understanding of the microphase separation of zwitterionic block copolymers and it was valid for novel molecular design of aqueous functional materials.

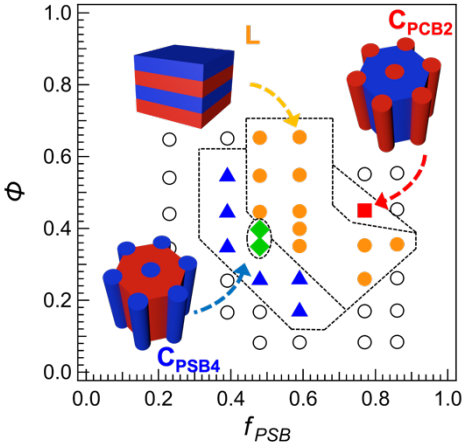

Figure 2. Polymer concentration, ϕ, vs volume fraction of PSB4 in the block copolymers, f_{PSB4}, phase diagrams for (A) PCB2$_n$-*b*-PSB4$_m$ diblock copolymer aqueous solutions at 25°C.

References:

1) M. Takahashi, Y. Higaki *et al.*, *Macromol. Chem. Phys.* **222**, 2000377 (2021).
2) Y. Higaki *et al.*, *Macromol. Chem. Phys.* **224**, 2200416 (2023).

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