Morphology Transition of Double Zwitterionic Block Copolymers Based on Aggregation Characteristics of Zwitterions

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Abstract

Phase diagrams of double zwitterionic diblock copolymers composed of a poly(carboxybetaine methacrylate) (PCB) and a poly(sulfobetaine methacrylate) (PSB) chains (PCB-*b*-PSB) in water was unraveled using small angle X-ray scattering. PCB-*b*-PSBs with long PSB chain produced ordered periodic structure and the morphology transformed depending on the polymer concentration through the selective PCB phase volume expansion, whereas those with short PSB chain were disordered. The molecular weight dependent phase separation and preferential distribution of water to the PCB phase were rationalized by the unique aggregation behavior of PSB chains.

1. Introduction

Block copolymers show lyotropic ordered nanostructure transition due to the volume fraction and interaction parameter variations[1)]. Nowadays, phase separation and ordered nanostructure transition of double hydrophilic block copolymers (DHBC) were reported, but the combination of DHBC is limited to conventional non-ionic synthetic polymers including polyethylene oxide and polyoxazolines and/or biopolymers including carbohydrates[2)]. We discovered a lyotropic morphology transition of a new class of DHBC composed of a poly(carboxybetaine methacrylate) (PCB) and a poly(sulfobetaine methacrylate) (PSB) chains (PCB-*b*-PSB)[3)]. In this study, we addressed phase behavior of the PCB-*b*-PSBs in water associating with the molecular weight and polymer concentration (**Fig. 1**).

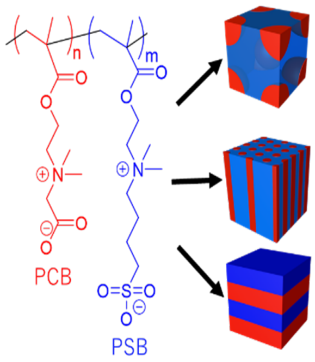

Fig. 1 Schematic of lyotropic ordered structure transition in PCB-*b*-PSB block copolymer solutions.

2. Experiment

PCB-*b*-PSB diblock copolymers with a variety of molecular weight and volume fraction were prepared by sequential reversible addition fragmentation chain transfer polymerization. The molecular weight and the distribution were determined by gel permeation chromatography. The ordered morphologies of the concentrated PCB-*b*-PSB aqueous solutions were verified employing small angle X-ray scattering (SAXS). The diblock copolymers were abbreviated as PCB_{LM}-*b*-PSB[n] (n = 41, 56, 71, 83, 94) and PCB_{HM}-*b*-PSB[n] (n = 23, 46, 55, 64, 78), where the n is volume fraction of the PSB chains (f_{PSB}) in the block copolymers calculated by the molecular weight. The PCB_{LM}-*b*-PSB[n] series and PCB_{HM}-*b*-PSB[n] series consist of PCB block with molecular weight range of 9,500 to 9,800 and 24,400 to 27,600, respectively.

3. Results and discussion

Both the 40 wt% PCB_{LM}-*b*-PSB[n] and PCB_{HM}-*b*-PSB[n] aqueous solutions exhibited multi-scattering peaks derived from the structure factor in the SAXS profiles at specific f_{PSB} range (**Fig. 2**). The PCB_{HM}-*b*-PSB[n] series produced ordered morphology in the wide f_{PSB} range in comparison with the PCB_{LM}-*b*-PSB[n] series, and the morphology transformed from from hexagonally packed columnar (HEX) to lamellar (LAM) to inverse HEX with PSB cylinders with decreasing polymer concentration due to the PCB phase volume expansion. To address the insight of f_{PSB} dependent morphology transition, hydrodynamic radius of gyration of the PSB homopolymers was verified by dynamic light scattering measurement. While the short PSB chains existed as isolated single chain in water, the long PSB chains aggregated. Thus, the aggregation efficiency of PSB chains significantly depends on the molecular weight. Since the aggregation of PSB chains induces the phase separation of PCB and PSB chains, the PCB-*b*-PSBs with long PSB chain achieve the phase separation. Besides, the PSB phases with pseudo network by sulfobetaine couples shows limited capacity of water, morphology transition was induced by the preferential distribution of water molecules into PCB phases because of the osmotic demands.

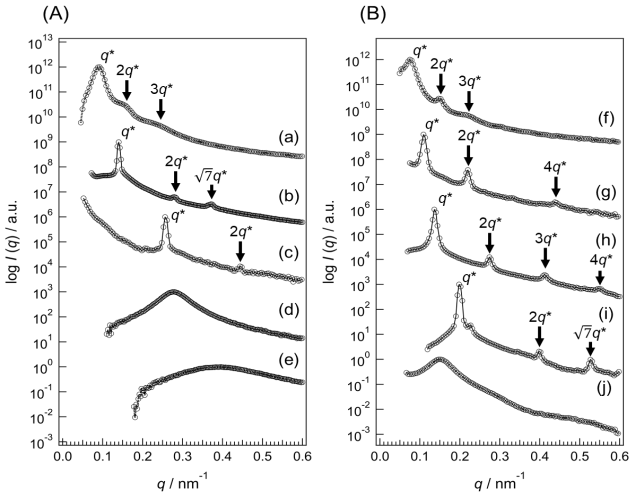

Fig. 2 SAXS intensity profiles of the 40 wt% PCB-*b*-PSB aqueous solutions; (A) PCB_{LM} series; (a) PCB_{LM}-*b*-PSB[94], (b) PCB_{LM}-*b*-PSB[83], (c) PCB_{LM}-*b*-PSB[71], (d) PCB_{LM}-*b*-PSB[56], (e) PCB_{LM}-*b*-PSB[41], (B) PCB_{HM} series; (f) PCB_{HM}-*b*-PSB[78], (g) PCB_{HM}-*b*-PSB[64], (h) PCB_{HM}-*b*-PSB[55], (i) PCB_{HM}-*b*-PSB[46], (j) PCB_{HM}-*b*-PSB[23].

4. Conclusions

Double zwitterionic PCB-*b*-PSB diblock copolymers with long PSB chain produced ordered morphology and exhibited lyotropic morphology transition due to phase separation triggered by molecular weight dependent aggregation of PSB chains. The precise ordered mesophase control of highly biopassive block copolymers is valid for design of biocompatible stimuli-responsive molecular systems.

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References

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