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Thermoreversible Block-Type Supramacromolecules in an Ionic Liquid

Hajime YAMAGISHI, Atsushi NORO*, Yushu MATSUSHITA
Department of Applied Chemistry, Nagoya University
Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Introduction

Block copolymers have been extensively studied for four decades in polymer science, focused on their nanophase-separated structures [1] because the structures have been expected for various applications. As an alternative way to produce high-performance and high-functional materials, the introduction of supramolecular concepts into macromolecular systems has been actively employed, especially with expectation of attaining dynamic molecular self-assembly. Here we provide a new strategy to produce thermoreversible block-type supramacromolecules [2,3] which give dynamic transition of their morphology derived from hydrogen bonding as schematically shown in Figure 1. To attain the molecular mobility under better control, we used a nonvolatile and thermally stable solvent, *i.e.*, an ionic liquid.

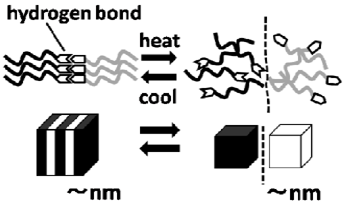

Figure 1. A cartoon of block-type supramacromolecules.

Experimental Section

The ionic liquid used in the present work is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMITFSI). Two component polymers were synthesized to build up a block-type supramacromolecule: one is a poly(3,4,5-trimethoxystyrene) with a small linker of poly(4-hydroxystyrene) as a hydrogen bonding proton donor ($\text{PTS}_{\text{-PHS}}$, M_n = 53,000) and the other is a poly(*n*-butyl acrylate) with a small linker of poly(2-vinylpyridine) as a hydrogen bonding proton acceptor ($\text{PBA}_{\text{-P2VP}}$, M_n = 54,000), both of which are solube in the ionic liquid. These two polymers were blended at a weight ratio of 1:1 in the IL. Phenol units in poly(4-hydroxystyrene) should be hydrogen-bonded with pyridine units in poly(2-vinylpyridine) even in an ionic liquid. Small angle X-ray scattering (SAXS) measurements for the solution were conducted at 25 °C, 70 °C, and 115 °C to observe morphology transition of the solution at the beamline 15 A in the Photon Factory, Tsukuba, Japan.

Results and Discussion

Figure 2 compares SAXS profiles at 25 °C, 70 °C, and 115 °C for the solution. A vertical axis is arbitrary intensity in logarithmic scale, while a horizontal axis shows the magnitude of the scattering vector, q (= $4\pi\sin\theta/\lambda$), where λ (= 0.15 nm) and 2θ are the wavelength of X-ray and scattering angle, respectively. There are two integer order peaks at the relative q values of 1 and 3 on the profile at 25 °C, where even number order peaks are suppressed, indicating an alternating lamellar nanophase-separated structure with almost the same domain thickness. Domain spacing, D, was evaluated to be 57 nm from the simple relationship, $q_1 = 2\pi/D$, where q_1 denotes the magnitude of scattering vector at the 1st order peak, 0.11 nm^{-1}. When a temperature was raised to 70 °C, the peaks became broader, suggesting the deterioration of orientation. As a temperature goes up higher to 115 °C, all the peaks finally disappeared.

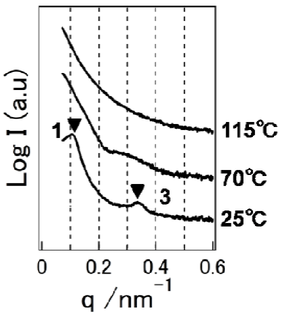

Figure 2. SAXS profiles of the solution.

In our molecular design shown in Figure 1, hydrogen bonding should be formed between phenol units in $\text{PTS}_{\text{-PHS}}$ and pyridine units in $\text{PBA}_{\text{-P2VP}}$, forming diblock-type or star-type supramacromolecules. As a result, a lamellar nanophase-separated structure was clearly observed by SAXS at a low temperature as 25 °C; however, hydrogen bonding interaction could be weakened by temperature increase. Eventually, complete dissociation between macromolecular building blocks at higher temperatures might cause macrophase separation. This is consistent with peak disappearance on the profile at a high temperature as 115 °C.

References

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[2] A. Noro et al., Biomacromolecules 7, 1696 (2006).
[3] A. Noro et al., Macromolecules 41, 9277 (2008).

* noro@apchem.nagoya-u.ac.jp