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Thermoreversible Morphology Transition from Block-Type Supramacromolecules via Hydrogen Bonding in an Ionic Liquid

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Block copolymers have been extensively studied for four decades, focused on their nanophase-separated structures[1−5] since the structures have been expected for various applications.[6−8] As an alternative way to produce high-performance and high-functional materials, the introduction of supramolecular concepts into macromolecular systems has been actively employed,[5,9−11] especially with expectation of attaining dynamic molecular self-assembly.[12−16]

As was reported previously, we have investigated the combination of self-assembling nature of block copolymers and supramolecular concepts, i.e., a "block-type supramacromolecule"[17,18] composed of end-modified component polymers which we call macromolecular building blocks. The term "supramacromolecule"[15,17−19] used here denotes supramolecular assembly composed of macromolecules. (Note the term "block-type supramacromolecule" is used throughout this paper instead of "supramolecular diblock copolymer" which is also used to denote another supramolecular complex. See refs 20 and 21.) Our works have clarified that block-type supramacromolecules consisting of different macromolecular building blocks represent nanophase-separated structures as common block copolymers, which has been also reported by others including the pioneering work by Russell et al.[22−29] These block-type supramacromolecules are also expected to dissociate into macromolecular building blocks and exhibit phase separation between two phases in a macroscopic length scale under certain external stimulus such as mechanical force or temperature;[30−32] however, dynamic transition between nanophase separation and macrophase separation originated from noncovalent bonding was not reported in these works. There are a few experimental reports on detecting thermoreversible transition between nanophase separation and macrophase separation,[33,34] where macromolecular building blocks with comparatively low glass transition temperatures (T_gs)[35,36] and comparatively small molecular weights ($M_n \sim 10\,000$) were used to avoid lowering the molecular mobility by chain entanglement.[37,38] Hence, there are still factors limiting the molecular mobility, that is, T_g and/or entanglement, in case we examine rapid thermoreversible responses from block-type supramacromolecules with high molecular weights.

In this Communication, we propose a new strategy to produce thermoreversible block-type supramacromolecules which provide dynamic transition of their morphology derived from hydrogen bonding as schematically shown in Figure 1. To attain the molecular mobility under better control, we use a nonvolatile and thermally stable solvent, i.e., an ionic liquid,[39−43] which could remove the effects of T_gs of polymers by plasticizing polymers as a solvent but with a large liquidus temperature range. The ionic liquid used in the present work is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMITFSI),[44] which is also hydrophobic. Two macromolecular building blocks were designed to form a block-type supramacromolecule: one is a poly(3,4,5-trimethoxystyrene)[45] with a small linker of poly(4-hydroxystyrene) on the end as a hydrogen-bonding proton donor (actually, a block copolymer of poly(3,4,5-trimethoxystyrene)-*b*-poly(4-hydroxystyrene), $\mathrm{PTS}_{-\mathrm{PHS}}$), and the other is a poly(*n*-butyl acrylate) with a small linker of poly(2-vinylpyridine) on the end as a hydrogen-bonding proton acceptor (a block copolymer of poly(*n*-butyl acrylate)-*b*-poly(2-vinylpyridine), $\mathrm{PBA}_{-\mathrm{P2VP}}$), both of which are soluble or at least dispersible in the ionic liquid. Phenol units in poly(4-hydroxystyrene) should be hydrogen-bonded with pyridine units in poly(2-vinylpyridine)[10,46−48] even in an ionic liquid.[15,19]

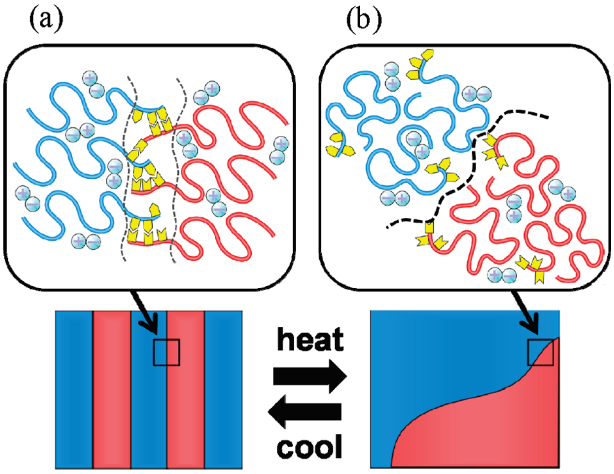

Figure 1. Schematic illustration of thermoreversible morphology transition between nanophase separation and macrophase separation from block-type supramacromolecules with multiple hydrogen bonds in nanoscopic length scale and molecular level: (a) at a low temperature; (b) at a high temperature. Note the complete macrophase separation will be achieved at high temperatures enough to neglect hydrogen-bonding interaction.

Synthesis of two polymers mentioned above has been carried out precisely via reversible addition−fragmentation chain transfer (RAFT) polymerization.[15,18,49,50] The molecular weights of both polymers were designed as ca. 50 000, but the degrees of polymerization of the small linkers were designed to be 15 so as to have appropriate hydrogen-bonding association strength, referring to the previous work.[15] Details in synthetic procedure are shown in Scheme 1. (See also Supporting Information.) Polydispersity of polymers and its precursors was measured by size exclusion chromatography (SEC) with three TSKgel G4000H_{HR} columns (Tosoh Corp.). Molecular weights were determined precisely by ^{1}H NMR (Varian Unity Inova 500 MHz).[51] For $\mathrm{PTS}_{-\mathrm{PHS}}$, a total number-average molecular weight (M_n), a polydispersity index (PDI), and degrees of polymerization (DPs) were 53 000, 1.09, and 264/13 (PTS/PHS), while those for $\mathrm{PBA}_{-\mathrm{P2VP}}$ were determined to be 54 000, 1.45, and 412/15 (PBA/P2VP), respectively. Note that PDIs of these polymers are small enough for the following experiments.[52,53] These two polymers were blended in the IL, EMITFSI. The weight ratio of $\mathrm{PTS}_{-\mathrm{PHS}}$:$\mathrm{PBA}_{-\mathrm{P2VP}}$:IL for preparation was set as 20:20:60 and we call "solution A". To prepare the blend sample homogeneously, cosolvent procedure[54] was used which is advantageous for preparation of homogeneous ionic liquid solutions.

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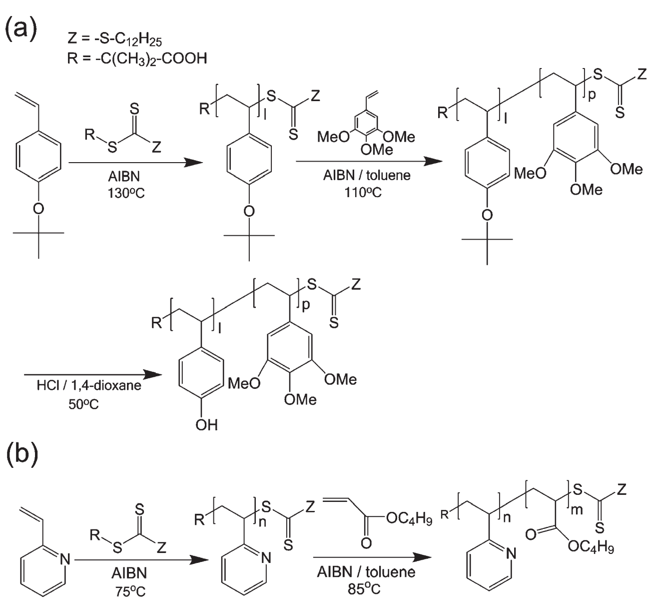
Scheme 1. Synthesis of Macromolecular Building Blocks: (a) PTS$_{-\mathrm{PHS}}$; (b) PBA$_{-\mathrm{P2VP}}$



Tetrahydrofuran (THF) was used as a volatile cosolvent, and it was removed *in vacuo* at 110 °C for 1 h. To compare the association/dissociation behavior of a block-type supramacromolecule with the structural behavior of a common block copolymer in an IL, we also prepared an IL solution (solution B) with 40 wt % of a poly(3,4,5-trimethoxystyrene)-*b*-poly(*n*-butyl acrylate) (PTS−PBA) (see Scheme S1 in the Supporting Information). M_n, PDI, and degrees of polymerization for PTS-PBA are 80 000, 1.18, and 212/305 (PTS/PBA), respectively. T_gs of polymers do not matter in this study because T_gs are lowered below room temperature by the added ionic liquid with a T_g of around −90 °C (see the DSC section in the Supporting Information). Small-angle X-ray scattering (SAXS) measurements for these solutions were conducted to observe morphology of the polymer solutions at the beamline 15 A in the Photon Factory, Tsukuba, Japan. Approximately 20 min was taken to attain each set temperature, and measurements were carried out 5 min after the thermometer attained the set temperature. Other measurement conditions are in the Supporting Information.

Figure 2 compares SAXS profiles at various temperatures for the solution A. Temperature was varied from 30 to 110 °C. Measurements were taken every 20 °C from lower to higher temperatures and vice versa. A vertical axis is arbitrary intensities in logarithmic scale, while a horizontal axis shows the magnitude of the scattering vector, q ($= 4\pi \sin \theta/\lambda$), where λ and 2θ are the wavelength of X-rays and scattering angle, respectively. The profiles were displayed in the following order from bottom to top: 30, 50, 70, 90, 110, 90, 70, 50, and 30 °C. The bottom-side profiles were measured upon heating, whereas the top-side profiles were upon cooling. There are four integer order peaks at 0.1, 0.21, 0.31, and 0.42 nm^{-1} on the profile of 30 °C, where even number order peaks are suppressed, indicating alternating lamellar nanophase-separated structure with uniform domain thickness. Domain spacing, D, was evaluated to be 61 nm from the simple relationship $q_1 = 2\pi/D$, where q_1 denotes the magnitude of scattering vector at the first-order peak, 0.1 nm^{-1}, and D satisfies with Bragg's condition, $2D \sin \theta = \lambda$. When a temperature increased to 50 °C, the peak position shifts to lower angle and the peaks became broader, suggesting domain expansion and deterioration of ordering. As temperature goes up higher, the peaks become broader and broader, and finally all peaks disappeared at 90 °C and also 110 °C.

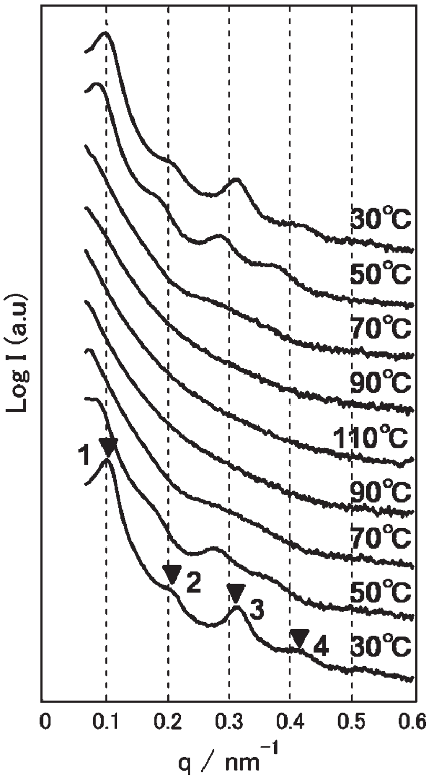


Figure 2. SAXS profiles of block-type supramacromolecules (PTS$_{-\mathrm{PHS}}$/PBA$_{-\mathrm{P2VP}}$) in an IL at various temperatures. The temperature increased from the bottom one (30 °C) to the middle one (110 °C) and decreased from the middle to the top (30 °C).

In our molecular design shown in Figure 1, hydrogen bonding should be formed between phenol units in PTS$_{-\mathrm{PHS}}$ and pyridine units in PBA$_{-\mathrm{P2VP}}$, which was confirmed for a similar system in an IL by FT-IR,[15] forming diblock-type or star-type supramacromolecules. These block-type supramacromolecules could possess a mixed phase as a huge junction, i.e., the third intermediate phase of P2VP/PHS, in which several PHS and P2VP linkers are included, forming "Janus micelles"[55,56] with coronas of PTS/PBA phases. Because of the strong repulsive force between PTS and PBA (see Figure 3 and the discussion), the coronas of PTS/PBA should phase-separate between the PTS phase and the PBA phase with a junction core of P2VP/PHS mixed phase in nanoscopic length scale.[46] As a result, the lamellar nanophase-separated structure was clearly observed by SAXS at a low temperature of 30 °C; however, hydrogen-bonding interaction could be weakened by temperature increase. At elevated temperatures of 50 or 70 °C, dissociation of hydrogen bonding could occur and the supramacromolecules are dissociated into macromolecular building blocks, where poor ordering of nanophase-separated structures arises and some dissociated building blocks might induce domain spacing expansion.[57] Eventually, complete dissociation between macromolecular building blocks might cause macrophase separation at higher temperatures. This is consistent with peak disappearance on the profile at high temperatures of 90 and 110 °C.

When the solution A is cooled down from high temperatures, hydrogen bonds between PTS$_{-\mathrm{PHS}}$ and PBA$_{-\mathrm{P2VP}}$ regenerate with decrease of temperature. It also reconstructs hydrogen bonded block-type supramacromolecules, forming essentially the same nanophase-separated structure as the initial one at 30 °C, which corresponds to the top profile in Figure 2.

We discuss further the power law exponent of the intensity profiles at the low angle in Figure 2. At the complete macrophase separation state which is a two-phase structure with sharp phase

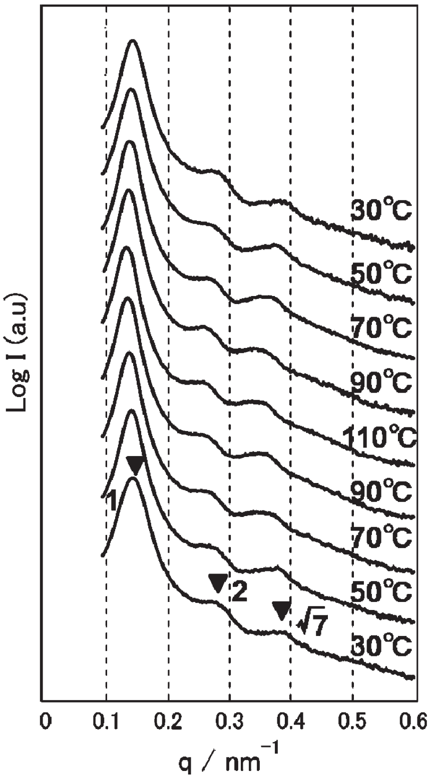


Figure 3. SAXS profiles of a block copolymer (PTS−PBA) in an IL at various temperatures. The temperature increased from the bottom one (30 °C) to the middle one (110 °C) and decreased from the middle to the top (30 °C).

boundaries, SAXS intensities (I) are known to show a characteristic power law exponent at the lower angle against scattering vector, i.e., $I \sim q^{-4}$ (or log $I \sim -4$ log q) according to Porod's law.[58] Although all the peaks disappeared on the profiles at 90 and 110 °C in Figure 2, the profiles still show smaller power low exponent of approximately −1.6. This indicates that samples at 90 and 110 °C do not reach complete macrophase separation or do not have a sharp interface. This is reasonable if we refer to the Arrhenius equation,[15,19] $K \sim \exp(E_a/RT)$, where K is an association constant, E_a is an activation energy, R is the gas constant, and T is an absolute temperature. When the temperature increases, the association constant of this hydrogen-bonded system is reduced gradually according to the Arrhenius equation, not abruptly, This indicates the fact that hydrogen bonding is still active in the system even at 110 °C, although the strength of hydrogen bonding is not enough to form nanophase-separated structure from block-type supramacromolecules. In any event, the fact that the power law exponent does not obey the q^{-4} law in Figure 2 is also consistent with the above speculation.

As a control experiment, SAXS was measured for the solution B composed of PTS−PBA/IL at the same temperatures adopted for the solution A. Figure 3 displays those SAXS profiles. The difference in temperature dependence between Figures 2 and 3 is evident. The most important aspect of Figure 3 is that the solution B gives the very similar scattering results with peaks at relative q values of 1, 2, and $7^{1/2}$ at various temperatures, indicating cylindrical nanophase structure in an IL is quite stable and irrespective of temperatures employed. This is because the present diblock copolymer is composed of two different polymers with a covalent bonding connection, whereas a block-type supramacromolecule is hydrogen-bonded, so that the morphology transition of the solution A system from PTS$_{-\mathrm{PHS}}$/PBA$_{-\mathrm{P2VP}}$ is thermoreversible. The phase separation of the solution B at 90 and 110 °C also guarantees the immiscibility between PBA and PTS in an IL; i.e., the repulsion force between these two components is strong enough to phase-separate even at high temperatures. Therefore, thermosensitivity of the solution A is attributed to hydrogen bonding.

In this Communication, we have demonstrated thermoreversible morphological transition from block-type supramacromolecules in an ionic liquid induced by hydrogen-bonding association−dissociation. SAXS was used to reveal the thermoreversible morphological transition by changing temperature. The ionic liquid solution of PTS$_{-\mathrm{PHS}}$/PBA$_{-\mathrm{P2VP}}$ displayed nanophase-separated lamellar structure at 30 °C, due to forming block-type supramacromolecules via hydrogen bonding in an ionic liquid. As temperature increases, hydrogen-bonding interaction is weakened, and SAXS profiles finally displayed no scattering peaks at 90 and 110 °C, where the sample is causing macrophase separation between PTS$_{-\mathrm{PHS}}$ and PBA$_{-\mathrm{P2VP}}$. In addition, it has been found that nanophase-separated structures appeared again upon cooling; i.e., thermoreversible phenomenon was observed in this work. The solution of a block copolymer with one covalent bond as a junction point did not show this distinctive and dynamic morphological behavior. Thus, this type of thermoreversible morphology transition in nanometer length scale could be achieved in similar systems if appropriate molecular design is performed. This could also be a useful guide to buildup of a new high-functional and high-performance nanostructured materials.

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Supporting Information Available: Details of synthesis, characterization of polymers, and additional SAXS information. This material is available free of charge via the Internet at http://pubs.acs.org.

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