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SCFT simulation and SANS study on spatial distribution of solvents in microphase separation induced by a differentiating non-solvent in a semi-dilute solution of an ultra-high-molecular-weight block copolymer

K Ando^{1,2}, T Yamanaka^{1,2}, S Okamoto^{*1,2}, N Sakamoto³, D Yamaguchi⁴,
S Koizumi⁴, H Hasegawa⁵ and N Koshikawa⁶

¹ Department of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, JAPAN

² ISS Advanced materials research and Application Center, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, JAPAN

³ Analysis and Simulation Center, AsahiKASEI Corp., 2-1 Samejima, Fuji, 416-8501, JAPAN

⁴ Advanced Science Research Center, Japan Atomic Energy Agency, Tokai, Ibaraki 319-1195, JAPAN

⁵ Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura A3-014, Nishikyo-ku, Kyoto 615-8530, JAPAN

⁶ Space Environment Utilization Center, Tsukuba Space Center, Japan Aerospace Exploration Agency, 2-1-1 Sengen, Tsukuba-shi, Ibaraki 305-8505, JAPAN

E-mail: okamoto.shigeru@nitech.ac.jp

Abstract. Lyotropic order-disorder transition (ODT) in a semi-dilute solution of an ultra-high-molecular-weight block copolymer using a neutral solvent and a differentiating non-solvent was investigated. The role of the differentiating non-solvent in the ODT was revealed by the spatial distribution of the solvents simulated theoretically by the self-consistent field (SCF) theory approach and demonstrated experimentally by small-angle neutron scattering (SANS). The solutions of polystyrene-*block*-poly (*tert*-butyl methacrylate) (PS-*b*-PtBuMA) with an ultra-high-molecular-weight (UHMW) in a mixture of tetrahydrofuran (THF)/ water as a good and neutral solvent and a differentiating non-solvent, respectively, were used. The contrast variation method by SANS experimentally demonstrated that THF and water collectively move into the PtBuMA phase and that the volume fraction ratios of water to THF in both phases are almost equivalent to each other. This means that the solvent mixture of THF and water behaves as a single and strongly selective solvent. The collective movement of the solvents was well reproduced by the simulation. Interestingly, it was also suggested that THF gather in the vicinity of styrene-(*tert*-butyl methacrylate) interface to shield the unfavorable strong interaction between the PS and the PtBuMA phases and that water gather in the center of the PtBuMA phase to decrease the unfavorable contact with the PS phase.

* To whom any correspondence should be addressed.

1. Introduction

The most interesting feature of block copolymers (BCPs) is that they spontaneously form various microdomain structures with periodicity on the order of the molecular size, such as spheres, cylinders, lamellae and gyroids by the change of volume fraction of the constituent blocks. Many researches have been extensively conducted on microdomain structures in bulk [1-3] or solutions of neutral solvents [4-8]. Selective solvents provide richer phase behavior with thermotropic and lyotropic order-disorder transition (ODT) and order-order transition (OOT) and also expand the reachable morphologies [9-12]. These characteristics enable us to apply BCPs to functional materials. BCPs with ultra-high molecular weight (UHMW), for example, have the potentials to form promising photonic crystals since the periodicities are on the order of visible light [13-15]. However, it is difficult to obtain highly ordered structures of UHMW BCPs in bulk or concentrated solutions because of their high viscosity. Lodge et al. reported a strongly selective solvent enhances the segregation power between constituent block chains [11, 12]. Thus we prepared semi-dilute solutions of BCPs using strongly selective solvent mixtures. This low concentration sufficiently decreased the viscosity while the segregation power was kept high enough to induce microphase separation. As a result, we obtained highly ordered photonic copolymers and succeeded in fabrication of non-linear optical materials [16]. Fuse et al. first reported a microphase separation induced by solvent mixture of a good and selective solvent in a low concentration solution [17]. We also found that the addition of “differentiating non-solvent” to a semi-dilute BCP solution of a neutral solvent induces microphase separation. Here we define “a differentiating non-solvent” as a solvent that is miscible with a neutral solvent and immiscible with either constituent blocks but that has slight affinity to one of the blocks. Interestingly, the solvent mixture showed high selectivity to one component. To our knowledge, a systematic investigation on ODTs and OOTs induced by a strongly selective solvent in a semi-dilute solution has not been conducted. In this paper, we employ a semi-dilute solution of polystyrene-*b*-poly(*t*-butyl methacrylate) using tetrahydrofuran and water as a neutral and a differentiating non-solvent, respectively. Water has slight affinity for *tert*-butyl methacrylate because of the polarity of the carbonyl groups. This system shows lyotropic ODT, OOTs and macrophase separation, which will be described elsewhere. Here we investigate the role of the differentiating non-solvent in the mechanism of the microphase separation. Especially, we focus on the spatial distribution of the differentiating non-solvent and that of the neutral or common solvent under the influence of the differentiating non-solvent, which will be revealed by using computer simulation on the basis of the self-consistent field (SCF) theory and the contrast variation method by small angle neutron scattering (SANS) with the combination of deuterated and protonated solvents.

2. Experimental

2.1. Materials.

A polystyrene-*block*-poly (*tert*-butyl methacrylate) (PS-*b*-PtBuMA) diblock copolymer with an UHMW was synthesized by the anionic living polymerization procedures under high vacuum. Prior to polymerization, styrene and *tert*-butyl methacrylate monomers were purified from commercial product by *tert*-butyl magnesium chloride and triethyl aluminium, respectively. Tetrahydrofuran (THF), the polymerization solvent, was also purified under vacuum by sodium. Polystyrene was polymerized first using *sec*-BuLi as the initiator in THF at -50 °C for 2 hours. Then *tert*-butyl methacrylate was added to form PS-*b*-PtBuMA diblock copolymer and allowed to proceed for 24 h, followed by the termination with methanol. The molecular weight and the polydispersity of PS-*b*-PtBuMA were characterized by gel permeation chromatography (GPC). The weight-averaged molecular weight, M_w , and PDI were estimated to be 8.2×10^5 g/mol and 1.2, respectively. The volume fraction of polystyrene, f_{PS} was evaluated to be 0.43 by $^1\text{H-NMR}$. Hence the degrees of polymerization of PS and PtBuMA were 2910 and 2970, respectively.

2.2. Small-angle neutron scattering (SANS).

Small-angle neutron scattering measurements with a SANS-J-II spectrometer were performed at JRR-3 (Japan Research Reactor-3) in the JAEA (Japan Atomic Energy Agency, Tokai, Japan). The wavelength (λ) was 0.665 nm. The scattering intensity was detected by a 5 inch size cross-wired position-sensitive photomultiplier tube (R3239, provided by Hamamatsu Photonics Co. Ltd.) with a thin sheet of ZnS/6LiF scintillator (0.2 mm thickness) [18]. The camerallength between a sample and the detector was 3.5 m. The scattering vector is defined by $q = (4\pi\sin\theta)/\lambda$, where 2θ is the scattering angle. All the samples were filled in a quartz cell with the sample thickness of 2mm thickness. Exposure time was 1800 sec. The observed two-dimensional scattering intensities were azimuthally averaged and corrected for transmission, sample thickness, electric background, empty cell contributions and incoherent scattering. They were scaled to absolute intensity by using Al as a secondary standard. BCP solutions were prepared using tetrahydrofuran (THF) as a neutral solvent and water as a differentiating non-solvent. Four combinations of deuterated/protonated THF (d-THF and h-THF) and deuterated/protonated water (D₂O and H₂O) were prepared with the ratios of d-THF/h-THF/ D₂O/ H₂O = 1/0/1/0, 1/0/0/1, 0/1/1/0 and 0/1/0/1 by volume, for the contrast variation measurements. For the other experiments, deuterated THF and D₂O were used. Polymer concentration was kept constant at 9.7 vol % for all the solutions.

2.3.1 Theory.

We used computer simulation software, SUSHI, based on the self-consistent field (SCF) theory in the OCTA system [19] to calculate equilibrium concentration distribution ϕ of K-type segments taking the chain conformation into account using the path integral formalism. To calculate the statistical distribution of the chain conformation, they focused on a single chain in a system composed of mutually interacting many chains, and approximate this tagged chain by a single ideal chain in a mean field. For that reason, this mean field is called self-consistent field. Here we briefly summarise the theory described by Honda et al. [19]. The self-consistent field is a potentials field determined by the interaction between segments and the incompressible conditions and is given by

$$V_K(r) = W_K(r) + \gamma(r), \quad (1)$$

where $\gamma(r)$ is a potential decided by incompressibility condition and $W_K(r)$ is the mean field resulting from the interaction between segments, and is given by

$$W_K(r) = \sum_{K'} \chi_{KK'} \phi_{K'}(r). \quad (2)$$

The subchain is independent statistically and the statistical weight can be described by

$$\frac{\partial}{\partial i} Q_K(i', \vec{r}; i, \vec{r}) = \left[\frac{b^2}{6} \nabla^2 - \beta V_K(\vec{r}) \right] Q_K(i', \vec{r}; i, \vec{r}). \quad (3)$$

By solving equation 3, path integral is determined and the concentration distribution ϕ of K-type segments can be calculated by

$$\phi_K(r) = M_K \frac{\int_0^N ds \int dr_0 \int dr_N Q_K(0, r_0; s, r) Q_K(s, r; N, r_N)}{\int dr_0 \int dr_N Q_K(0, r_0; N, r_N)}. \quad (4)$$

the self-consistent field $V_K(r)$ depends on the segment concentration $\phi_K(r)$. Then, $\phi_K(r)$ is calculated from the path integral $Q_K(i, r)$ through equation 4. Finally, the path integral $Q_K(i, r)$ is obtained by solving equation 3 that contain the self-consistent field $V_K(r)$. Therefore, $V_K(r)$, $\phi_K(r)$ and $Q_K(i, r)$ define themselves in a recursive manner or self-consistently. In our case, the volume fraction of the components $\phi_\alpha(r)$ (α = PS, PtBuMA, THF, water) are functions for which the total free energy attains a minimum.

2.3.2 Simulation condition.

We performed one-dimensional simulation on the basis of SCF theory as described above. The polymer concentration, ϕ_p , was fixed at 9.7vol %. The order-disorder transition and the order-order

Table 1. Interaction parameter χ between A and B.

	PS	PrBuMA	THF	water
PS	0	1.46	0	4.07
PrBuMA		0	0	0.01
THF			0	0
Water				0

transition between lamellar and gyroid and cylinder occurred with increase of ϕ_w at this polymer concentration, which will be described in detail elsewhere. Below $\phi_w=3.6$ vol %, the system was in the disordered state by using UV-vis spectrometer. SAXS measurements revealed lamellar structure were formed at $\phi_w = 3.6$ vol % and cylinder structure were formed at $\phi_w = 6.4 - 9.1$ vol %. The spectroscopic measurements also revealed that gyroid structure were formed $\phi_w = 5$ and 5.4 vol %. Rigorously speaking, a comparison between the free energies of all the different possible morphologies is needed to determine the most stable one. However, we neglected these comparisons for the simplicity of discussion in this study: We concentrated on the strong effect of differentiating non-solvent on the drastic selectivity increase of the solvent mixture, the resulting phase separation phenomenon and the solvent distribution in the phases. We employed the system size optimization method that minimizes the free energy density of the system by optimizing the length of the one-dimensional simulation space on which reflection boundary condition is satisfied [20]: The system size, X , is automatically optimized around $X=256$. The degrees of polymerization was set $N_{PS}:N_{PrBuMA}:N_{THF}:N_{Water} = 29:39:1:1$. Note that $N_{PS}:N_{PrBuMA} = 29 : 39$ is employed in order that the ratio of the values reflect the volume fraction determined by 1H -NMR, i.e., $f_{PS} = 0.43 \approx 29 / (29 + 39)$, even though the actual degrees of polymerization of the synthesized copolymer is 2910 and 2970, respectively. The Flory-Huggins interaction parameters, χ_s , between the components are shown in table 1. For simplicity, the value of χ_s between THF and the other was set at 0, because THF mixes freely with water and is very good solvent for PS and PrBuMA. The other values of χ_s were determined to match the calculated phase diagram with the experimental phase diagram.

3. Result and Discussion

3.1 Result of simulation.

In figure 1, we show the calculated composition profiles of the four components, PS, PrBuMA, THF and water, at $\phi_p = 9.7$ vol % and $\phi_w = 1.8$ vol %. The left axis indicates the concentrations of PS, PrBuMA and water (designated as ϕ_{PS} , ϕ_{PrBuMA} and ϕ_w , respectively) and the right axis indicates the concentration of THF (designated as ϕ_{THF}) and the bottom axis indicates the spatial axis, x . The red,

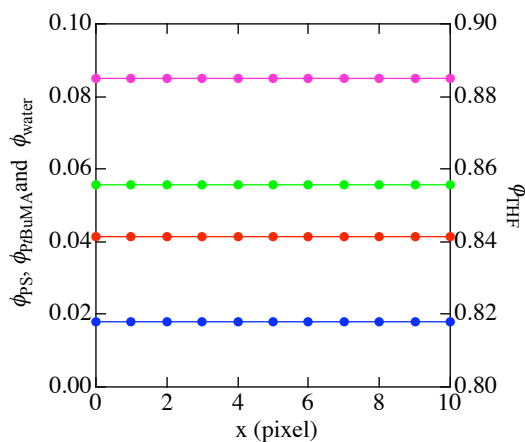


Figure 1. Spatial distribution of all the components at $\phi_w = 1.8$ vol %.

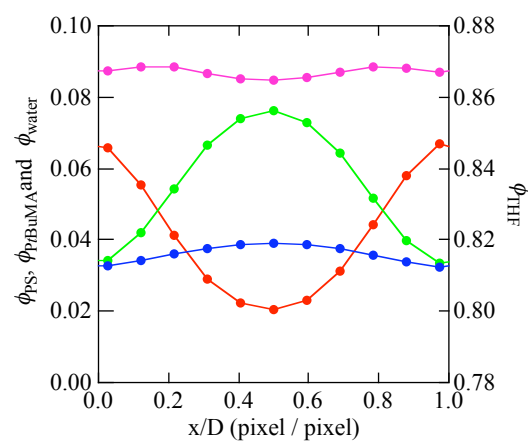


Figure 2. Spatial distribution of all the components at $\phi_w = 3.6$ vol %.

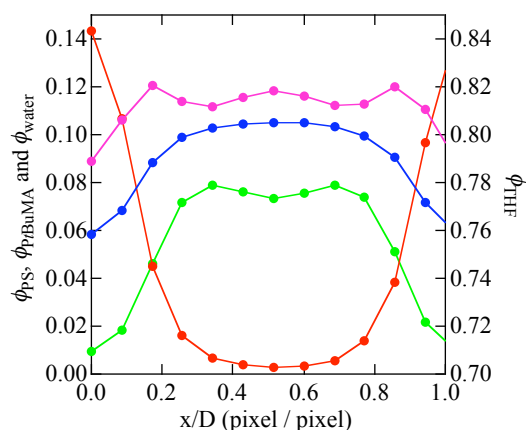


Figure 3. Spatial distribution of all the components at $\phi_w = 9.1$ vol %.

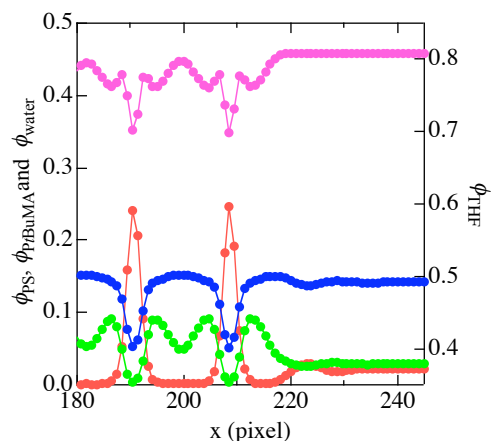


Figure 4. Spatial distribution of all the components at $\phi_w = 13$ vol %.

green, purple and blue colors indicate the components of St, tBuMA, THF and water, respectively. As can be seen, the distributions of all the components are uniform over the whole system, i.e., the system is in the disordered state, which is in good agreement with the experimental data observed by UV-vis spectrometer. Next, the composition profiles were calculated for $\phi_w = 3.6$ vol % as exhibited in figure 2. For the simplicity, the profiles were shown over one period with the x-axis normalized by the domain periodicity, D. Here the value of D was 10.8 pixels. All the components periodically fluctuate around their average compositions, i.e., the system went into the ordered state by the increase of the solvent selectivity prompted by the addition of enough amount of water. Here it is worthy noting that the neutral solvent, THF, gathers in the vicinity of the phase boundary between PS and PtBuMA. This shield the unfavorable contact between the two components at the interface, as first reported by Lodge et al. [21]. It should be also noted that the water molecules locate in the middle of the PtBuMA, i.e., away from the interface, which also decreases the unfavorable contact [21]. We defined PS and PtBuMA phases as the regions where the concentrations are higher than their average values, from which the volume fractions of the phases were measured and will be discussed later in the next section. Figure 3 shows the calculated composition profile for $\phi_w = 9.1$ vol %. Here the profiles were plotted over one period with the x-axis normalized by the value of $D = 13.1$ pixels. The fluctuations of all the components were enhanced. Surprisingly, the spatial fluctuation of the neutral solvent, THF, was also enhanced to the same extent as the others, i.e., THF behaved as a selective solvent in the presence of water. The major amount of THF and water locate in the PtBuMA phase. This is qualitatively rationalized as follows; if THF uniformly distributes over the whole system while water is selectively introduced into the PtBuMA phase, the macrophase separation between THF and water should take place. This segregation brings about a huge entropy loss because the majority of the components (90.7 vol.% by volume or over 99 mol% by the numbers) consists of the small molecules, THF and water. Thus the segregation is energetically unfavorable. Figure 4 indicate the calculated composition profile for $\phi_w = 13$ vol %. The amount of water added to the system exceeded the upper limit of solubility in PtBuMA phase, so that the macrophase separation between solvents and BCP occurred. Indeed, two types of the composition fluctuation were observed: in the region at $0 \leq X \leq 210$, all the components periodically fluctuate around their average composition (microphase separation), while at $X \geq 210$, the space were mostly filled with solvents. Note that the typical profiles of the domain structures over two periods in the polymer-rich phase and those of an appropriate size in the solvent-rich phase were shown for the simplicity.

3.2 Small-angle neutron scattering (SANS).

As Takenaka et al. and Endo et al. reported, the contrast variation method by the SANS is a useful

Table 2. The scattering length density of polymers and solvents.

(cm^{-2})	ρ_{PS}	ρ_{PtBuMA}	$\rho_{\text{h-THF}}$	$\rho_{\text{d-THF}}$	$\rho_{\text{H}_2\text{O}}$	$\rho_{\text{D}_2\text{O}}$
$\rho_{\beta} \times 10^{10} \text{ }^a$	1.34	0.537	0.183	6.39	-0.560	6.34

^a β = PS, PtBuMA, h-THF, d-THF, H₂O and D₂O

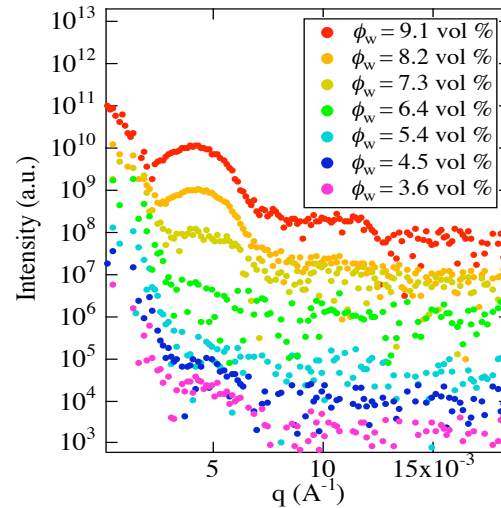


Figure 5. 1-D scattering profiles for the solution of deuterated THF and D₂O at the polymer concentration of 9.7 vol % with increase of ϕ_w .

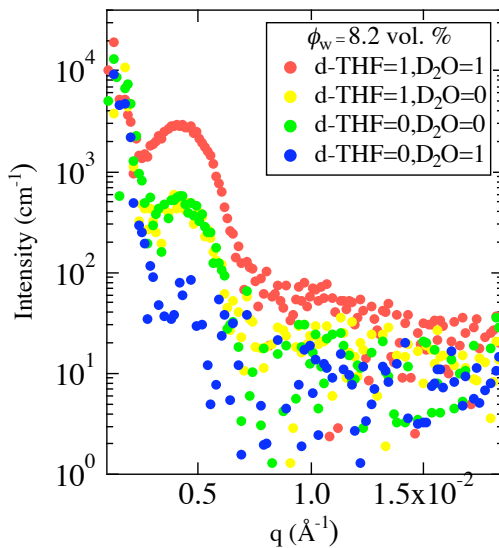


Figure 6. 1-D scattering profiles at $\phi_w = 8.2$ vol %.

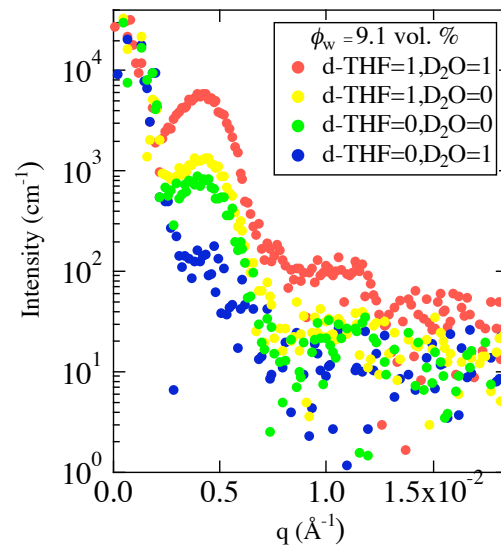


Figure 7. 1-D scattering profiles at $\phi_w = 9.1$ vol %.

measurement for evaluation of the distribution of a specific component in complex system [22, 23]. Lodge et al., for example, experimentally demonstrated the distribution of solvent to the interface between different phases in BCP solutions near order-disorder transitions by the SANS contrast variation method as described above [21]. Here, we performed SANS contrast variation measurements in order to investigate the distribution of the BCP and the solvent molecules in the semi-dilute solution. Figure 5 shows 1-D SANS from the BCP dissolved in deuterated THF and deuterated water at the constant polymer concentration of 9.7 vol % with varying the water concentration at $\phi_w = 3.6 - 9.1$

vol %. The peak position gradually shifted toward the lower q -region with increasing the amount of water. The scattering length densities of the polymer chains and deuterated and protonated solvents are shown in table 2. The value of the scattering length density of PS ($\rho_{\text{h-PS}} = 1.34 \times 10^{10} \text{ cm}^{-2}$) is higher than that of PtBuMA ($\rho_{\text{h-PtBuMA}} = 0.537 \times 10^{10} \text{ cm}^{-2}$). At $\phi_w = 3.6$ and 4.5 vol %, the system was in the weak segregation regime and thus the scattering peak was very weak. Subsequently peaks disappeared at $\phi_w = 5.4$ and 6.4 vol % because water selectively went into the PtBuMA phase as was described by the computer simulation in the previous section, thus the scattering length density of the PtBuMA phase increased and eventually the scattering length density matched between the two phases at these water concentrations. Above $\phi_w = 7.3$ vol %, the scattering length density difference reversed and became larger and the system went into the stronger segregation state, so that the scattering intensity became strong. The red profile at $\phi_w = 9.1$ vol % in figure 5 showed the multiple scattering maxima, indicating that well-ordered microdomain structures were formed under these conditions. At $\phi_w = 8.2$ vol % and 9.1 vol % where the relatively strong intensity was observed, a contrast variation experiment by SANS were performed using deuterated and protonated THF and water. This method allows us to determine the concentrations of the components in each phase by changing scattering contrast with combinations of the protonated and deuterated solvents. Figures 6 and 7 show the scattering intensity profile of the solutions at $\phi_w = 8.2$ vol % and $\phi_w = 9.1$ vol %. The scattering profiles of the red, yellow, green and blue colors indicate that the solvent mixture consists of deuterated THF and D₂O (designated as “d-THF = 1 and D₂O = 1”), deuterated THF and H₂O (d-THF = 1 and D₂O = 0), protonated THF and D₂O (d-THF = 0 and D₂O = 1), and protonated THF and H₂O (d-THF = 0 and D₂O = 0), respectively. The red scattering profiles for “d-THF = 1 and D₂O = 1” in figures 6 and 7 showed the multiple scattering maxima, which also indicate well-ordered microdomain structures were formed. The scattering intensity, $I(q)$, is proportional to the square of scattering length density difference, $\Delta\rho$, between the PS and the PtBuMA phases, the lattice factor, $Z(q)$, and the form factor, $P(q)$, respectively.

$$I(q) \approx \Delta\rho^2 Z(q)P(q) \quad (5)$$

The SANS profiles in figures 6 and 7 have the primary intensity maxima at ca. 4.32×10^{-3} and ca. $4.19 \times 10^{-3} \text{ \AA}^{-1}$, respectively. The peak position and the shape of the profiles remained unchanged while the peak intensity altered with the contrast variation. Therefore, we consider that the product, $Z(q)P(q)$, was constant throughout all the contrast. The equation 5 is simplified as follows;

$$I(q) \approx \Delta\rho^2$$

$$= \left[\phi_{\text{PS_PS}} \times \rho_{\text{PS}} + \phi_{\text{w_PS}} \times \rho_{\text{water}} + \phi_{\text{THF_PS}} \times \rho_{\text{THF}} - \left(\phi_{\text{PtBuMA_PtBuMA}} \times \rho_{\text{PtBuMA}} + \phi_{\text{w_PtBuMA}} \times \rho_{\text{water}} + \phi_{\text{THF_PtBuMA}} \times \rho_{\text{THF}} \right) \right]^2 \quad (6)$$

where ϕ_{i_PS} ($i = \text{PS, water and THF}$) and ϕ_{j_PtBuMA} ($j = \text{PtBuMA, water and THF}$) are volume fractions of i -th and j -th species in the PS and the PtBuMA phases, respectively. The values of ρ_{water} and ρ_{THF} indicate the scattering length densities of water and THF: $\rho_{\text{water}} = \rho_{\text{H}_2\text{O}}$ or $\rho_{\text{D}_2\text{O}}$ and $\rho_{\text{THF}} = \rho_{\text{h-THF}}$ or $\rho_{\text{d-THF}}$. Note that we should consider the four combinations of deuterated/protonated water (D₂O and H₂O) and deuterated/protonated THF (d-THF and h-THF) for equation 6. The scattering intensity from the solution with the ratio of d-THF/h-THF/ D₂O/ H₂O = 1/0/1/0 is designated as $I_{dd}(q)$. In the same way, $I_{dh}(q)$, $I_{hd}(q)$, $I_{hh}(q)$ are used. The ratios of the scattering intensities $I_{dd}(q) / I_{dd}(q)$, $I_{dh}(q) / I_{dd}(q)$, $I_{hd}(q) / I_{dd}(q)$, $I_{hh}(q) / I_{dd}(q)$ were calculated. Table 3 shows comparison of the ratios of the experimental and calculated scattering intensities. All the experimental ratios were consistent with the calculated ratios except for I_{hd} / I_{dd} at $\phi_w = 8.2$ vol %. We consider this slight error occurred due to the statistical precision because $I_{hd}(q)$ was very weak. Table 4 shows the composition of each component in each phase determined from the values in table 3. The values of $\phi_{\text{water_PtBuMA}}$ and $\phi_{\text{THF_PtBuMA}}$ at $\phi_w = 8.2$ vol % are 9.80 and 84.8 vol %, respectively, and greater than the average values (8.2 and 82.1 vol %, respectively), while $\phi_{\text{water_PS}}$ and $\phi_{\text{THF_PS}}$ are smaller than the averages. Thus $\phi_{\text{PS_PS}}$ is greater than the

Table 3. Ratio of experimental and calculated peak intensities at $\phi_w = 8.2$ and $\phi_w = 9.1$ vol %.

	$\phi_w = 8.2$ vol %		$\phi_w = 9.1$ vol %	
	experimental	calculated	experimental	calculated
I_{dd}/I_{dd}	1	1	1	1
I_{dh}/I_{dd}	0.18	0.18	0.23	0.23
I_{hd}/I_{dd}	0	0.02	0.02	0.02
I_{hh}/I_{dd}	0.18	0.18	0.14	0.14

Table 4. Composition of each component in each phase.

	$\phi_w = 8.2$ vol %		$\phi_w = 9.1$ vol %	
	PS phase	PtBuMA phase	PS phase	PtBuMA phase
PS	16.3	0	19.0	0
PtBuMA	0	5.40	0	4.40
THF	78.0	84.8	75.2	84.6
water	5.70	9.8	5.80	11.0

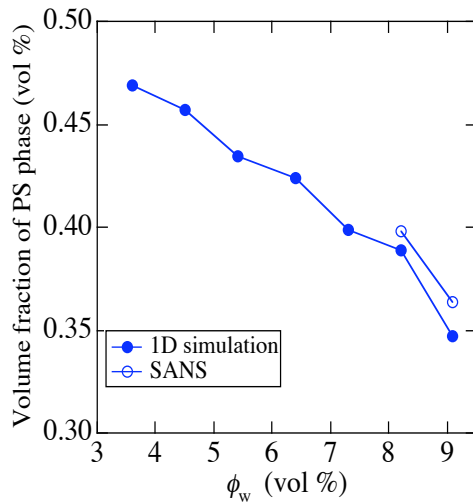


Figure 8. The change of volume fraction of PS phase as a function of ϕ_w .

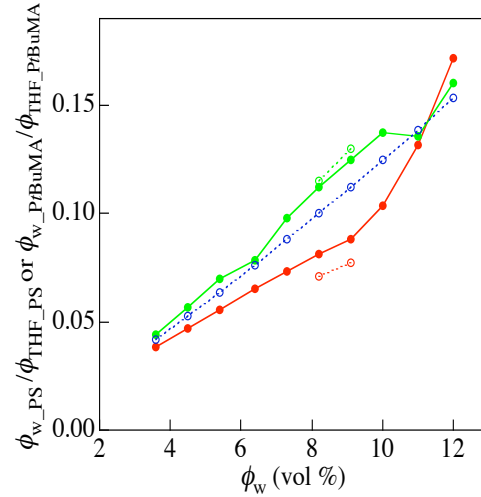


Figure 9. The volume fraction ratios between water and THF in both phases as a function of ϕ_w .

average (9.7 vol %) and ϕ_{PtBuMA_PtBuMA} is smaller than that (9.7 vol %). Note that both of ϕ_{PS_PS} and ϕ_{PtBuMA_PtBuMA} should be 9.7 vol % if the solvents uniformly distribute over the whole system. These tendencies are enhanced at $\phi_w = 9.1$ vol % as shown in table 4. The volume fraction of the PS phase at $\phi_w = 8.2$ and 9.1 vol % are shown by the open circles as a function of ϕ_w in figure 8, where the calculated values obtained by SUSHI are also plotted by the closed circles. Both of the experimental and the theoretical values decreased with the increase of ϕ_w . In other words, the PS phase was deswelled while the PtBuMA phase was swelled. This means that the solvents moved from the PS phase into the PtBuMA phase progressively as ϕ_w increased. Here it is interesting to investigate the ratio of the water content to the THF content in each phase. The values of $\phi_{water_PS} / \phi_{THF_PS}$ and $\phi_{water_PtBuMA} / \phi_{THF_PtBuMA}$ are shown by the red and the green open circles, respectively, as a function of ϕ_w in figure 9. The theoretical values obtained by SUSHI are also plotted by the red and the green closed circles. The experimental values are in good agreement with the theoretical ones and approximately close to those averaged over the whole system shown by the blue open circles. These results of figures 8 and 9 means that the ratio of the water content to the THF one was kept almost constant while both of water and THF moves from the PS phase into the PtBuMA phase by the addition of water. Therefore we consider that water and THF distribute together as a single solvent.

4. Conclusion

The mechanism of the lyotropic microphase separation induced by the differentiating non-solvent in the semi-dilute solution of an UHMW PS-*b*-PtBuMA was studied by simulation on the basis of SCFT and SANS. The composition of each component in each phase was evaluated by the SANS contrast variation method. It was found that at higher ϕ_w , major amount of water and THF selectively located in the PtBuMA phase than in the PS phase. The two solvents, THF and water, collectively moved from the PS phase to the PtBuMA phase by the addition of water in order to avoid unfavourable entropy loss by the separation of the solvents. In other words, de-swelling of PS and swelling of PtBuMA occurred. Additionally, the ratios of the amounts of the solvents in both of the phases are close to each other. This means that the solvent mixture behaved as a strongly selective single solvent and enhanced the segregation power between the PS and the PtBuMA phases. These tendencies were well reproduced by the simulation based on the SCF theory. Two- and three-dimensional simulations of this semi-dilute solution system are still under investigation in order to reproduce the lyotropic OOT and will be reported in future.

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